

Think, Pair, Share: Insight into Electronic Structure from Single Crystal Structures of Redox-Active Ligands

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Metal ligand cooperativity is an essential strategy for both synthetic and biological systems, and it has the potential to enhance and extend the reactivity and properties of transition metals. We have developed a series of cobalt complexes with a non-innocent, tert-butyl dihydrazonopyrrole ligand scaffold, and within these have been able to show the ability of these complexes to enable metal-ligand cooperative hydrogenation reactivity as well as stabilize unusual oxidation states and electronic structures. Further investigation has also suggested the possibility of modulating the metal-ligand oxidation states and magnetic properties of these complexes via the addition or removal of simple neutral ligands as well as by exchanging the anionic substituents (also investigated by XAS and XPS techniques). Additionally, we have developed a series of tetrathiafulvalene-based molecular complexes, with a diagnostic internal C-C bond that offers regular insight into ligand spin state, and also potentially with interesting ligand-metal geometric relationships, that also modulate the properties of the isolable complexes. We find that single crystal x-ray diffraction at different temperatures is an ideal technique for establishing structure-function relationships for a variety of spin and electronic structures within a family of redox-active metal-ligand complexes.