

Ruthenium and Osmium Complexes with Ligands Capable of Proton Coupled Electron Transfer



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In many reactions of biological and chemical interest, electron transfer events are accompanied by changes in proton content. Our lab is interested in synthesizing metal complexes with ligands that have proton transfer capabilities, enabling us to study how the protonation state affects the electronic structure of these complexes. We have synthesized a series of metal complexes containing hydroxy-substituted-polypyridyl ligands, most notably $[\text{Ru}(\text{bpy})_2(4\text{bpy}(\text{OH})_2)]^{2+}$ and $[\text{Ru}(4\text{bpy}(\text{OH})_2)_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine, $4\text{bpy}(\text{OH})_2 = 4,4'$ -dihydroxy-2,2'-bipyridine). These complexes have been studied by x-ray crystallography, UV/visible spectroscopy, luminescence spectroscopy, and electrochemistry. Most notably, the deprotonated form of $[\text{Ru}(\text{bpy})_2(4\text{bpy}(\text{OH})_2)]^{2+}$ has significant electronic differences from the more highly symmetrical deprotonated form of $[\text{Ru}(4\text{bpy}(\text{OH})_2)_3]^{2+}$. This is the result of significant molecular orbital mixing between the ruthenium d orbitals and deprotonated ligand in $[\text{Ru}(\text{bpy})_2(4\text{bpy}(\text{O}^-)_2)]$ that do not mix in the more highly symmetrical complex when deprotonated. These results are apparent in the spectroscopy as well as the electrochemistry in these complexes.

