Our latest work on pyranopterin molybdenum enzymes focuses on (1) understanding how molybdenum is incorporated into the enzymes, (2) electronic structure contributions to substrate oxidation and reduction, and (3) how the Mo center is coupled into long-range superexchange pathways for electron transfer regeneration of the active site. First, we present our work on molybdate binding to the unique pyranopterin dithiolene (PDT) ligand. The PDT is comprised of a dithiolene and a heterocyclic pterin ring system that are fused together by a pyran ring. When bound to Mo, this ensemble is known as the molybdenum cofactor (Moco). Next, we will detail studies directed toward understanding the mechanism of Moco sulfuration and molybdenum hydroxylase activity. Finally, we will discuss our current understanding of how the PDT functions in catalysis. We will focus on the ability of the PDT to serves as an electronic conduit in order to couple the Mo ion with other electron transfer centers in the protein, and will discuss our latest spectroscopic and bonding studies that show how the PDT is involved in electron transfer reactivity. This includes a remarkable study that shows the redox state of the pyranopterin affects its ability to display either “wire-like” or “diode” behavior, supporting a complex and flexible electronic structure of the PDT that underscores its critical role in enzyme function.