

Electronic Studies of Metallocene–dithiolate Ring Folding: Implications for Molybdenum and Tungsten Enzymes

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Gas-phase photoelectron spectroscopy and density functional theory have been used to study the electronic structure of bent metallocene–dithiolate molecules as minimum molecular models of the active site features of pyranopterin Mo/W enzymes. The compounds $\text{Cp}_2\text{M}(\text{S-S})$ $\text{Cp}_2\text{M}(\text{S-S})$ {where $\text{M}=\text{Ti}$, V and Mo , (S-S) is 1,2-ethenedithiolate, 1,2-benzenedithiolate or 1,3-propanedithiolate and Cp is cyclopentadienyl} provide access to formally d^0 , d^1 and d^2 electronic configurations of the metal - those of the active site metal during catalysis. A "dithiolate-folding-effect" involving an interaction of metal and sulfur orbitals is demonstrated in metallocene complexes with arene- and ene-dithiolate ligands. These results show that the amount of folding is dependent on the electron configuration of the metal and that the unsaturated carbon-carbon bond is necessary to poise the energy-level of the filled symmetric S_π^+ orbital for participation in dithiolate ring folding. It is proposed that this interaction facilitates the buffering of electron density at the metal center, and is a factor in the electron transfer reactions that regenerate the active sites of Mo/W enzymes.

