Systematic Approach to Geometric Determinants of XANES

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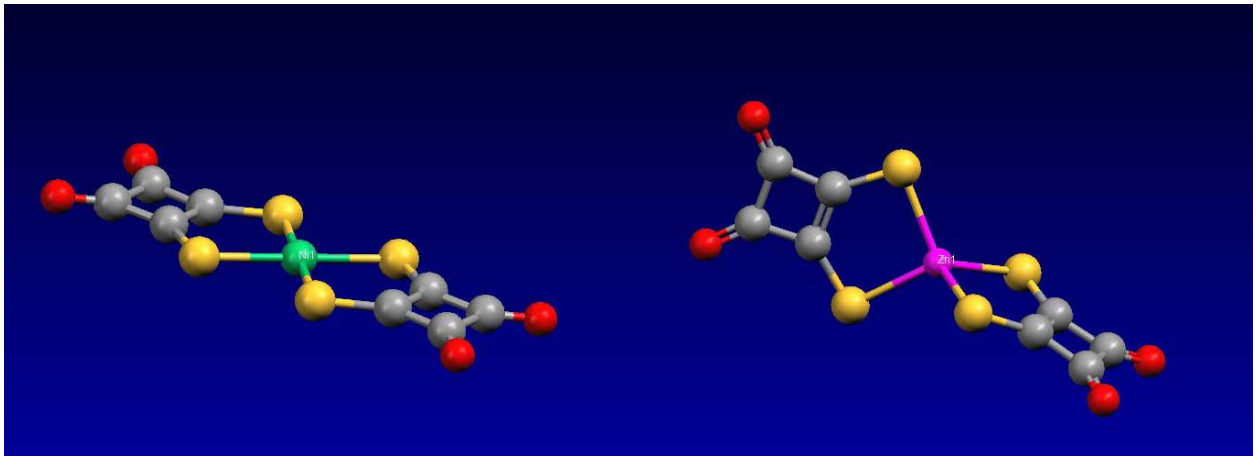
X-ray Absorption Near Edge Structure (XANES) is known to be sensitive to the local geometry of the absorbing atom, and thus to provide an important complement to Extended X-ray Absorption Fine Structure (EXAFS) which is most sensitive to radially averaged structure. We are using EXAFS and XANES to investigate the structure and function of Zn-containing alkyl-transfer enzymes. In the course of this work, we have encountered several examples of Zn sites that have identical EXAFS but distinct XANES features, presumably due to changes in the geometry of the Zn site. In an effort to understand the geometrical determinants of these changes in Zn XANES, we have undertaken a systematic investigation of the XANES spectra MCl_4^{2-} and ML_2^{2-} [L=1,2-cyclobutenedione-3,4-dithiolate] sites. Models (metal, counter-ion, etc.) were chosen to permit systematic exploration of metal-site geometry from tetrahedral to square planar. The dependence of spectra on geometry, and preliminary theoretical interpretation of these spectra will be presented.



$Zn(Dts)_2^{2-}$ $Ni(Dts)_2^{2-}$