Spectroscopic studies of the molybdenum centers of enzymes and related model compounds

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Molybdenum enzymes play vital roles in all forms of life. Sulfite oxidizing enzymes occur in animals, plants and bacteria. Their oxidized active sites exhibit square pyramidal five-coordinate geometry with equatorial and axial oxo groups and three equatorial thiolate sulfur atoms – two from the ene-dithiolate fragment of the pyranopterin unit present in all molybdenum and tungsten enzymes and one from a cysteinyl side chain. During catalysis these enzymes pass through the Mo(V) state which can be studied in detail by electron spin echo envelope modulation (ESEEM) and pulsed electron nuclear double resonance (ENDOR) spectroscopy. Pulsed EPR investigations as a function of pH, anions in the media, and mutations of the protein will be presented for the animal, plant and bacterial enzymes and related to molecular structure and proposed reaction mechanisms. Pulsed EPR data for the high pH form of chicken sulfite oxidase enriched in ^{17}O (I = 5/2) have provided the first evidence for exchange of axial oxo ligands in these enzymes. The validity of the assignment has been confirmed by ESEEM examination of $[Mo^{17}O(SPh)_4]^-$. The possible roles of the ene-dithiolate unit in molybdenum enzymes is being probed by gas-phase photoelectron spectroscopy and density functional theory of well-defined model compounds.