

A Case Of UV-Induced Proton-Coupled Electron Transfer in Copper-Doped Zinc Creatinine Sulfate: An EPR, DFT, And Crystallographic Investigation

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Single crystal Electron Paramagnetic Resonance (EPR) spectroscopic, X-ray diffraction experiments, and DFT calculations were carried out to determine the crystal structure of zinc creatinine sulfate, to identify the doped Cu(II) binding site, and to investigate the mechanism behind proton-coupled electron transfer observed in UV exposed crystals. Similar to the cadmium-creatinine complex, the metal is not in coordination with the creatininium cation, but forms a hexahydrate which is buffered from the creatininium by an intervening sulfate ion. Both the EPR measured g (2.44, 2.13, 2.08) and copper hyperfine (325, 77, 0 MHz) tensors and structure are consistent with doped copper replacing zinc in the hexahydrate complex. The room temperature EPR tensors are similar to those previously observed for copper hexahydrate in other doped crystal systems, for example in doped Tutton salts, but only those measured at very low temperatures. In these other systems, vibration couplings stemming from dynamic Jahn-Teller effects cause tensor averaging at temperatures up to room temperature. The reasons why this does not happen in the cadmium and current zinc host structure is an area of recent study. Progress towards analyzing and correlating the unpaired Cu(II) and creatininium radical wavefunctions, the crystal structure and the proton-coupled electron transfer will be presented.