

Hush theory in a copper mixed valence bioinorganic model generated photochemically

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In the present study a copper mixed valence (MV) compound has been generated photochemically from the $(\text{CH}_3\text{COO})_2\text{Cu}(\text{II})\text{Cu}(\text{II})(\text{OOCCH}_3)_2$ dimeric species in 95/5% (vol./vol.) methanol/acetic acid mixture as solvent. The MV species shows two intervalence (IT) bands at 19.6 and 10.4 kK and seven complex lines in the EPR spectra at room temperature. Although the two bands are IT bands in character, only the second (960 nm) could be related through the Hush and Hopfield theories to a thermal electron transfer process between the copper centers with kinetic parameters $\Delta G^\ddagger = 21.6 \text{ kJ mol}^{-1}$ and $k_{\text{th}} = 1.2 \times 10^9 \text{ s}^{-1}$ (Hush) or $4.0 \times 10^{11} \text{ s}^{-1}$ (Hopfield) at 298 K and related to the change from $(d_{x^2-y^2})_2\text{Cu}(\text{I})(d_{x^2-y^2})\text{Cu}(\text{II})$ to $(d_{x^2-y^2})_1\text{Cu}(\text{II})(d_{x^2-y^2})_2\text{Cu}(\text{I})$ electronic configuration (D_{4h} symmetry for each copper center). The electronic assignment of the more energetic band is also discussed. The value obtained for k_{th} is in the range measured by EPR spectroscopy for other $\text{Cu}(\text{II})\text{Cu}(\text{I})$ dimeric systems and provides