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Charge-Transfer Spectra of Model Cu(II) Chromophores

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Electronic 'tuning' of copper proteins for specific O_2-transport, redox, and oxygenase functions is determined by the number, nature and geometrical arrangements of the protein side-chain donor ligands which bind the copper ion(s) at the active site(s). The resulting energies and orientation of the upper occupied Cu(II) orbitals and d-vacancy in the oxidized proteins generally can be inferred from the ESR and ligand field (LF) spectra. At higher energies than those of LF absorptions, Cu(II) chromophores exhibit ligand to metal charge-transfer (LMCT) absorptions. These absorptions reflect a potentially important yet little studied aspect of electronic structure: the relative overlaps of the σ- and π-symmetry ligand donor orbitals with the Cu(II) d-vacancy. We review recent studies of the LMCT spectra exhibited by structurally unambiguous model Cu(II) chromophores containing ligation such as thiolate, thioether, imidazole, and imidazolate [1]. These results facilitate the understanding of corresponding LMCT absorptions exhibited by various copper proteins. Replacement of the Cu(II) in the model complexes and proteins by the less oxidizing Ni(II) and Co(II) ions results in characteristic blue-shifts of these LMCT absorptions, and supports an LMCT rather than MLCT assignment. Owing to the LF-dependency of the metal ion d-vacancy energy, the LMCT absorptions of planar Cu(II) and Ni(II) chromophores are blue-shifted relative to their approximately tetrahedral analogs.

Cu(II)–imidazole complexes exhibit LMCT absorptions originating from the ligand nitrogen lone pair and from two ring π orbitals, one having primarily carbon 2p character (π_1, HOMO) and the other having primarily nitrogen 2p character (π_2). The calculated (INDO/S method) orbital energy increases induced by successive ring methylations are correlated with red shifts of imidazole → Cu(II) LMCT exhibited by this series of complexes [2]. Spectroscopic effects associated with the orientation of the imidazole rings relative to the Cu(II) d-vacancy also are discussed. Imidazolate ligation results in a characteristic additional LMCT absorption at relatively low energy. The intense ($\epsilon > 1000$) near UV LMCT absorption associated with equatorial Cu(II)–thioether bonding disappears when, as for plastocyanin, the Cu(II)–thioether bond becomes elongated (apical) and is oriented normal to the d-vacancy. The syntheses and LMCT spectra of model M(II)–thiolate complexes (M = Cu, Co, Ni) are described briefly.

1 H. J. Schugar, 'Ligand to Metal Charge-Transfer Spectra of Cu(II) Chromophores'. In 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives', K. D. Karlin and J. Zubieta (eds.), Adenine Press, New York (1983).
2 E. E. Bernarducci, P. K. Bharadwaj, K. Krogh-Jespersen, J. A. Potenza and H. J. Schugar, submitted to *J. Am. Chem. Soc.*.

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Insights into Blue Copper Proteins Using Spectroscopic Methods

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By controlling the structure of the binding site, a protein can profoundly influence the properties of a metal center including its chemical potential, its kinetic reactivity and its binding constant. For example, it is evident from small molecule studies that electron transfer is much more facile in copper systems when minimal structural reorganization is required. To fill in some of the gaps in our knowledge about structural aspects of blue copper proteins, as summarized below, we have carried out a variety of physical studies on the proteins themselves as well as appropriate derivatives and relevant small molecules.

The nickel(II) derivative of azurin, Ni(II)Az, has been prepared and shown to contain two unpaired electrons which virtually rules out the possibility of a planar nickel site. This is despite the pronounced tendency of nickel(II) to prefer planar binding of an N_2S_2 donor set involving thiolate sulfurs [1]. The paramagnetism and the fact that d–d bands are found in the near infra-red argue for a pseudotetrahedral binding geometry and suggest that the metal binding