

Blue Copper Proteins Model Complexes with Hydrotris(pyrazolyl)borate

Kiyoshi Fujisawa, Yuki Matsunaga, Nagina Amir, Yoshitaro Miyashita, Ken-ichi Okamoto
Department of Chemistry, University of Tsukuba 305-8571, Japan

Blue copper proteins work as electron transfer in biological systems. Because of their unusual spectral features including UV-Vis and EPR spectra, the active site structures of this class of proteins have received considerable attention for a long time. Based on X-ray analysis, these unusual characteristic spectral features were suggested to be due to the distorted tetrahedral coordination geometry, which is rare for copper(II) ion, with a covalently bound thiolate group. In order to probe these hypothesis using small molecule model compounds, we have synthesized and characterized four-coordinate and five-coordinate thiolato copper(II) complexes with hydrotris(3,5-diisopropyl-1-pyrazolyl)borate monoanion (L). Four-coordinate thiolato copper(II) complexes were prepared by the reaction of bis- μ -hydroxo complex $[\{CuL\}_2(\mu-OH)_2]$ with C_6F_5SH and Ph_3CSH at low temperature. Their structures were characterized by X-ray crystallography. Both four-coordinate thiolato copper(II) complexes closely mimic the striking spectroscopic characteristics of blue copper proteins. The five-coordinate thiolato copper(II) complex was also prepared by the reaction of μ -hydroxo complex with 2-mercapto-1-methylimidazole at low temperature. In this presentation, we will describe the physicochemical differences between four- and five-coordinate thiolato copper(II) complexes. Both electron transfer rate constants and the activation parameters of Cu(II/I) redox pairs were determined by dynamic 1H -NMR line-broadening techniques. Moreover, we will also present the first row transition metal(II) substituted thiolato complexes.

References

- N. Kitajima, K. Fujisawa, et al., *J. Am. Chem. Soc.*, **114**, 9232-9233 (1992).
K. Fujisawa, K. Fujita, N. Kitajima, et al., *Inorg. Chem. Commun.*, **7**, 1188-1190 (2004).
Y. Matsunaga, K. Fujisawa, et al., *Inorg. Chem.*, **44**, 325-335 (2005).