COPPER BINDING WITH METHYL SUBSTITUTED ETHYLENEDIAMINES

XU WANG, DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY, 40605-0055*.

Last year, we reported that ethylenediamine ($NH_2CH_2CH_2NH_2$) prefers monodentate binding with a copper atom in the gas phase.[a] In this study, we have learned that methyl substituted ethylenediamines [$(CH_3)HNCH_2CH_2NH_2$, $(CH_3)_2NCH_2CH_2NH_2$, $(CH_3)_2NCH_2CH(CH_3)$, $(CH_3)_2NCH_2CH(CH_3)_2$] favor a bidentate binding mode. Copper complexes with these diamines are produced in laser vaporization molecular beams and investigated by pulsed field ionization zero electron kinetic energy (PFI-ZEKE) spectroscopy and *ab initio* calculations. The ionization potentials of Cu-[$(CH_3)HNCH_2CH_2NH_2$] and -[$(CH_3)_2NCH_2CH_2NH_2$] are determined to be 36022(20) and 36283(20) cm^{-1} from PFI-ZEKE spectra, and those of Cu-[$(CH_3)_2HNCH_2CH_2NH_2(CH_3)$] and -[$(CH_3)_2NCH_2CH_2NH_2(CH_3)_2$] are 36230(250) and 34900(300) cm^{-1} from photoinization efficiency curves. Metal-ligand stretch frequencies are measured to be 202 cm^{-1} for the monomethyl species and 200 cm^{-1} for the dimethyl complex. In addition, a number of ligand-based vibrations are determined to be 450, 574, 743, 1063, and 1103 cm^{-1}. The comparison of the measured and calculated ionization potentials and vibrational structures shows that copper binds to two nitrogens in all four methyl substituted diamines. The different binding between ethylenediamine and the methyl derivatives appears to arise from the weakening or elimination of the intramolecular hydrogen bond by methyl substitutions of the hydrogen atoms.

[a] X. Wang and D. Yang, J. Phys. Chem. 108, 6449 (2004).