Solvation Structure of Solvated Cu(I) Ions in Non-Aqueous Solvents as Studied by EXAFS and *ab initio* Molecular Orbital Methods

Y. Inada[a], Y. Tsutsui[b], H. Wasada[c], S. Funahashi[b,*]

[a] Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan
[b] Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan
[c] Department of Chemistry, Faculty of Regional Studies, Gifu University, 1-1 Yanagido, Gifu 501-1112, Japan

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The structure parameters around the Cu(I) ion in pyridine (PY), 4-methylpyridine (4MPY), 2-methylpyridine (2MPY), 2,6-dimethylpyridine (26DMPY), and acetonitrile (AN) were determined by the extended X-ray absorption fine structure (EXAFS) method. The solvation structures of the Cu(I) ion in PY, 4MPY, and AN are 4-coordinate tetrahedral with Cu–N bond lengths of 205, 205, and 200 pm, respectively. In the case of 2MPY and 26DMPY, the Cu(I) ion has a 3-coordinate triangular structure with a Cu–N bond length of 201 pm. Such a decrease in the coordination number was interpreted in terms of the bulkiness of the solvent molecules. In order to clarify the most stable solvation structure of the Cu(I) ion, we carried out *ab initio* molecular orbital calculations for the solvation system of $[Cu(NCH)_n]^+$ (n = 1 - 6) where the steric effect is negligible. The Gibbs free energy of solvation was the smallest in the case of n = 4 and the 4-coordinate tetrahedral solvation of the Cu(I) ion was theoretically evaluated as most stable. The enthalpy of solvation monotonously decreases with increasing n, while the entropy of solvation proportionally increases. Although a larger gain of enthalpy is observed for the octahedral structure rather than the tetrahedral one, the entropic loss for the former overcomes the enthalpic gain.

* Reprint requests to Prof. Shigenobu Funahashi.