

Solvation structure of metal ions in nitrogen-donating solvents

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Introduction

Solvation structure of metal ions is the most fundamental aspect for the metal ion in solution, since the structure, the thermodynamic properties, and the kinetic reactivity are largely affected by the solvation structure. In the case of oxygen-donating solvents, in which there is a donating oxygen atom in the solvent molecule, the solvation structure has been systematically determined for many metal ions [1], while in contrast the knowledge in nitrogen-donating solvents is quite limited because of the low solubility of metal ions in such solvents.

The nitrogen-donating solvents have a large variation for the electron-donating ability in comparison with the oxygen-donating solvents, and we have previously demonstrated that the reactivity and mechanism for the ligand exchange reactions in nitrogen-donating solvents are largely different from those in oxygen-donating solvents [1]. The evaluation of the solvation structure is thus very important to interpret the differences in reactivity and mechanisms. In this study, we have determined the solvation structures of the first-row transition metal(II) ions in a series of nitrogen-donating solvents, such as aliphatic amines, pyridine derivatives, and nitriles by means of fluorescent XAFS technique.

Experiments

Sample solutions were prepared by dissolving anhydrous trifluoromethane sulfonate salts of Mn(II), Fe(II), Co(II), and Zn(II) in dehydrated and distilled solvents. In the case of Ni(II), the hexahydrate trifluoromethane sulfonate was dissolved and the solution was then dehydrated using molecular sieves.

The fluorescent XAFS spectra at the Cu K edge were measured at the BL-9A and 10B stations. The incident and fluorescent X-ray intensities were measured by an ionization chamber and the Lytle detector, respectively. The Si(111) double-crystal monochromator was detuned to 80 % of the maximal intensity at the edge energy. The X-ray energy was calibrated using a Cu foil.

The obtained EXAFS spectra were analyzed by a usual procedure. The scattering amplitudes, the phase shifts, and the mean free paths of the photoelectron were cited from the FEFF-generated data for the model compounds. The observed EXAFS data were fitted in the R space in considering the long-range direct interactions and the multiple scattering paths.

Results and Discussion

The determined solvation numbers are summarized in Table 1 and the M–N distances are plotted in Figure 1. It is clearly demonstrated that the solvation structures are

affected by both the electron donating ability and the bulkiness of the solvent molecule.

Table 1: Solvation number

Solv ^a	Mn(II)	Fe(II)	Co(II)	Ni(II)	Zn(II)
PA	6.1	5.8	6+4	6.0	4.2
TN	6.0	6.0	6.2	6.0	6+4
PY	6.4	5.8	5.8	6.1	6.2
4PY	6.3			5.9	5.9
2PY				6.4	4.3
AN	6	6.0	6.2	6	6
PN	6.0	5.9		5.8	6.2

^aPN = 1-aminopropane, TN = 1,3-diaminopropane, PY = pyridine, 4PY = 4-methylpyridine, 2PY = 2-methylpyridine, AN = acetonitrile, and PN = propionitrile.

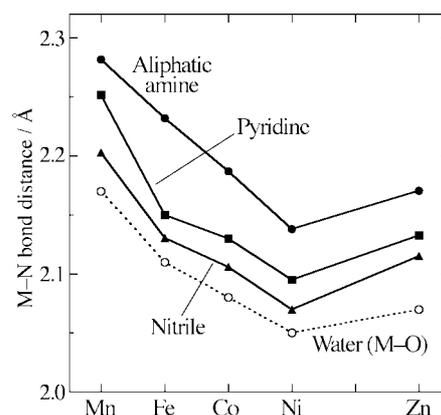


Figure 1: M–N bond distance

In the case of the Co(II) ion with the d^7 electronic configuration, the 4-coordinate tetrahedral structure is mixed in a strong electron donor PA. This is the case for the Zn(II) ion without the ligand-field stabilization in the d orbitals. In a bulky solvent 2PY, the solvation number of Zn(II) is reduced to 4 due to the intermolecular repulsion in the first solvation shell.

Interestingly, the M–N bond distances are systematically varied by the kind of donating nitrogen atom, *i.e.*, $M-N(sp^3) > M-N(sp^2) > M-N(sp)$. The σ donating orbital is expected to radially spread larger for the nitrogen atom having the higher contribution from the p orbital. In addition, the stronger π accepting ability for nitriles can contribute to shorten the M–N bond distance due to the effective π -back bonding interaction.

Reference

[1] Funahashi, S.; Inada, Y. *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 1901.

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