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Novel structural variation of silver(I)–pyridine complexes in nitromethane as studied by X-ray absorption spectroscopy

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ABSTRACT

The XAFS spectra were measured at around the Ag K-edge of the Ag(I) ion in nitromethane (NM) with a variety of concentrations of pyridine (PY). In NM without PY, the Ag(I) ion is tetrahedrally solvated by four NM molecules similar to those in most solvents. The Ag–O bond length in NM solvent is longer than that in aqueous solution, indicating the low donating ability of NM. The mono-, bis-, tris-, and tetrakis-pyridine complexes are formed in NM by the addition of PY. The EXAFS analyses reveal that the structure of the formed PY complex in NM is linear for $Ag(py)(nm)^+$, linear for $Ag(py)_2{}^+$, triangular for $Ag(py)_3{}^+$, and tetrahedral for $Ag(py)_4{}^+$. The longer Ag–O bond length for $Ag(py)(nm)^+$ than that for $Ag(nm)_4{}^+$and the release of bound NM molecules at the formation of $Ag(py)(nm)^+$ are interpreted to be due to the strong σ donating property of PY. The Ag–N bond length (220 pm) for $Ag(py)_3{}^+$ is intermediate between 216 pm for $Ag(py)_2{}^+$ and 228 pm for $Ag(py)_4{}^+$. The formation equilibria of $Ag(py)_3{}^+$ and $Ag(py)_4{}^+$ are analyzed on the basis of the changeover of EXAFS spectra as a function of the total concentrations of Ag^+ and PY in NM.

1. Introduction

The Ag(I) ion takes 4-coordinate tetrahedral solvation structure in water [1–6], *N*,*N*-dimethylformamide [5], dimethyl sulfoxide [5,6], trimethyl phosphate [5], 1,1,3,3-tetramethylurea (TMU) [5], and *N*,*N*′-dimethylpropyleneurea [6] as the oxygen-donating solvents, and in acetonitrile [3,5,7], pyridine (PY) [3,5,8], 2-methylpyridine [5], *n*-propylamine [5], and ethylenediamine [5] as the nitrogen-donating solvents. Although the structure of the Ag(I) ion in liquid ammonia has been reported to be 3-coordinate triangular [9] or 4-coordinate tetrahedral [3], it exists as linear $Ag(NH_3)_2{}^+$ complex in aqueous ammonia solution without water molecules in the first coordination sphere [9,10]. Furthermore, 2-, 3-, and 4-coordinate Ag(I) complexes have been suggested to form in response to the mole ratio of the ligand to the Ag(I) ion for ammonia [11], pyradine [12], and bidentate Schiff base derivatives in aqueous solution [13,14]. The Ag(I) complexes including the nitrogen donating ligand in crystal also have a variety of coordination numbers and structures, which is 2-coordinate linear [15–17], 3-coordinate triangular [18], and 4-coordinate tetrahedral structure [17,19,20]. Interestingly, two types of PY complexes, $Ag(py)_2{}^+$ and $Ag(py)_4{}^+$, have been reported to coexist in the same crystal [17], implying that the stabilities of the Ag(I) complexes are similar for the 2- and 4-coordinate complexes in the crystal.

The solvation structure has been systematically investigated for a variety of metal ions in many solvents [21]. The steric properties, such as the ionic radius of the metal ion and the bulkiness of the solvent molecule, are important to determine the solvation structure. The more positive charge density contributes to attract more solvent molecules around the metal ion, and the larger ionic radius is advantageous to relax the repulsion between the attracted solvent molecules in the first solvation sphere. The large solvation number can lead to the gain of enthalpy, but the steric hindrance is entropically unfavorable because of the crowded first solvation sphere. In solvents with bulky molecular structure, such as TMU and hexamethylphosphoric triamide [22,23], the reduced solvation numbers are thus frequently observed even for the first-row transition metal ions, for which the 6-coordinate octahedral structure is widely seen because of its electronic stability. The attractive interaction between the metal ion and solvent molecules serves as a counterbalance to the repulsive interaction between the coordinating solvent molecules, and the solvation structure is then mainly decided as the result of combination of the charge density of metal ion and the bulkiness of solvent molecule. The electronic stabilization may contribute to the solvation structure as seen in

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the case of the Co(II) and Ni(II) ions in TMU, in which the 4-coordinate tetrahedral structure is more stable for the former with d^7 electronic configuration, but the latter favors the 5-coordinate structure due to its d^8 electronic configuration.

The large ionic radius produces the space around the Ag(I) ion to aggregate the ligand and solvent molecules, however, the electrostatic attraction for solvation becomes weak because of the low positive charge density and thus the entropy term in the coordination sphere is relatively important to control the structure of the Ag(I) complex [5]. Although a variation of the structure has been theoretically reported in the gas phase [5] and experimentally suggested in the aqueous solution [11–14], the detailed structure parameters have never been analyzed experimentally for the Ag(I) ion. The precise structural analysis is necessary to understand the unique characteristics of structure for a series of Ag(I) complexes with different number of coordinating ligands.

Pyridine has high electron donating ability and rigid molecular structure, and therefore can form stable complexes in solution. The electron lone pair at the N atom binds to a metal ion via the σ-type coordination. Furthermore, there are vacant unoccupied orbitals with the π property, for which the d electrons of the metal ion can be accepted by the π back donation. The σ-donating property is more moderate than that of NH_3, which is reported to form a series of Ag(I) complexes with the coordination number of 2, 3, and 4 [10,11], while the π-accepting property is absent for NH_3. The structural investigation for the combination with PY is thus very important for the Ag(I) ion to understand its structural characteristics. The coordination structure of the Ag(I) complex is also greatly affected by the coordination ability of the solvent molecule. When it has a comparable ability to the incoming ligand molecule, the solvent molecules compete against the ligand to occupy the first coordination sphere of the metal ion. Such competition can affect the complex structure, and it will interfere with the intrinsic evaluation of structural properties.

Nitromethane (NM) is a polar nonaqueous solvent and can dissolve many metal salts because of its dielectric nature (the dielectric constant: 35.87 at 30 °C) [24]. In addition, it has a rare electronic characteristic of low electron donating ability. One measure of it is the Gutmann's donor number of 2.7 [25], which is almost comparable to nonpolar solvents. Such low coordinating ability is an advantage for the structural analysis of the Ag(I) complexes, because the NM solvent molecule does not strongly interfere with the complexation of entering ligands. Nitromethane is thus an ideal solvent as a silent dielectric medium to investigate the complex structure. The present work has attempted to reveal coordination chemistry of the Ag(I) ion in solution by determining the structure of the Ag–py complexes formed in NM, in which the solvent molecules weakly coordinate to the Ag(I) ion.

The XRD technique is one of the powerful tools available to determine the structure parameters of metal complexes formed in solution [26]. However, the minor components in the sample solution are almost impossible to detect by the XRD technique. For NM solutions of the Ag–py complexes, the intense intramolecular interactions of the solvent NM molecules and the free PY molecules hide the interesting interactions around the Ag(I) ion, because the solubility of the Ag(I) salts is not high in NM. An experimental method using X-ray absorption fine structure (XAFS) can shed light on such minor species in solution, because the local structural information is potentially included in the XAFS spectrum for a target atom in the sample without any long-range periodic alignments [27]. The radial structure function can be derived mainly for the first coordination sphere of the Ag(I) ion by the analysis of the extended X-ray absorption fine structure (EXAFS) appearing at around the K edge of Ag. Thus, the XAFS technique has been applied in this study to the NM solutions containing the Ag(I) ion and PY. Because the stepwise complexations have been expected to form the Ag–py complexes with different numbers of PY, a variety of NM solutions with different compositions have been subjected to the XAFS measurements. The evaluated novel variation of structure will be discussed on the basis of the EXAFS results for a series of the Ag–py complexes formed in NM.

2. Experimental

2.1. Sample solutions

All chemicals used were of reagent grade. Fifteen Ag(I) NM solutions labeled from N0 to N14 were prepared for XAFS measurements as shown in Table 1. All solutions contained an almost constant total concentration of the Ag(I) ion (C_{Ag}: 0.4–0.6 mol kg^{-1}), and the total concentration of PY (C_{py}) was varied in the C_{py}/C_{Ag} range from 0 to 8.03. The sample solutions were prepared by mixing the NM solutions of the Ag(I) ion and PY under a nitrogen atmosphere. The counter ion of Ag^+ was either ClO_4^- or BF_4^-. The aqueous and pyridine solutions of $AgClO_4$ were prepared as the reference samples for the EXAFS analysis. *Caution:* Be careful to handle the Ag(I) salts in nonaqueous solvents because of the possibility of explosion.

2.2. XAFS measurement

XAFS spectra of all solutions were measured at the vicinity of the Ag K edge in the transmission mode under 295 K using the BL-10B and NW10A stations at the Photon Factory of the High Energy Accelerator Research Organization (KEK) [28,29]. The white synchrotron radiation was monochromatized by the Si(3 1 1) channel-cut crystal monochromator at BL-10B and by the Si(3 1 1) double crystal monochromator at NW10A. Sample solutions were sealed in a cell with windows of boron nitride plates, and the path length was adjusted to get an appropriate jump of absorbance at the absorption edge. The cell was placed between two ionization chambers to detect the incident (I_0) and transmitted X-ray intensity (I). The first ionization chamber was filled with Ar gas and the second one with Kr gas. The X-ray absorbance (μt) in the transmission mode is defined as $\ln(I_0/I)$.

2.3. EXAFS analysis

EXAFS data were analyzed with the ATHENA and ARTEMIS programs in the IFEFFIT package [30,31]. The threshold energy of a K-shell electron, E_0, was selected as the position at half the height of the

Table 1
Concentrations of sample solutions.

	Solvent	C_{Ag} (mol kg^{-1})	C_{py} (mol kg^{-1})	C_{py}/C_{Ag}
W	Water	0.501	–	–
N0	NM	0.581	0	0
N1	NM	0.570	0.242	0.425
N2	NM	0.556	0.532	0.957
N3	NM	0.545	0.773	1.42
N4	NM	0.536	0.951	1.77
N5[a]	NM	0.415	0.917	2.21
N6	NM	0.524	1.209	2.31
N7	NM	0.513	1.455	2.84
N8[a]	NM	0.456	1.31	2.87
N9	NM	0.502	1.690	3.36
N10	NM	0.492	1.887	3.84
N11[a]	NM	0.466	1.84	3.95
N12	NM	0.474	2.271	4.79
N13	NM	0.427	3.271	7.66
N14[a]	NM	0.467	3.75	8.03
PY	PY	0.490	–	–

[a] Counter ion was BF_4^-. For the other samples, ClO_4^-.