

Solvation Structures of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II), and Indium(III) Ions in 1,1,3,3-Tetramethylurea As Studied by EXAFS and Electronic Spectroscopy. Variation of Coordination Number

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The structures of solvated complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and In(III) ions in 1,1,3,3-tetramethylurea (TMU) have been determined by means of EXAFS (extended X-ray absorption fine structure) and electronic spectroscopy. The solvation structures in TMU are square pyramidal for the Mn(II) and Ni(II) ions, distorted tetrahedral for the Co(II) and Cu(II) ions, tetrahedral for the Zn(II) ion, and octahedral for the Cd(II) and In(III) ions, while in water all these metal ions are six-coordinated octahedrons. The solvation structure of Fe(II) ion is square pyramidal or trigonal bipyramidal. In the bulky TMU solvent, the coordination number should be reduced for relaxation of the sterically repulsive interaction around the solvated metal ions. The metal-oxygen (M-O) bond lengths of solvated metal ions in TMU are 209 ± 1 , 205 ± 1 , 200 ± 1 , 200 ± 1 , 192 ± 1 , 195 ± 1 , 228 ± 1 , and 213 ± 1 pm for Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and In(III) ions, respectively. The M-O bond lengths for Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions in TMU are shorter than those of corresponding metal(II) ions in water, while the M-O bond lengths in TMU and water are the same for the six-coordinate Cd(II) and In(III) ions.

Introduction

In donor solvents such as water, methanol, *N,N*-dimethylformamide (DMF), and acetonitrile, metal ions are strongly solvated. Structural information on solvated metal ions in solution is quite important for complete understanding of the thermodynamic and kinetic behaviors of the metal ions.²⁻⁴ Extended X-ray absorption fine structure (EXAFS) spectroscopy has become a powerful tool for obtaining structural information about the nearby environment of a particular atom.⁵⁻⁷ The EXAFS technique has been used to determine structural parameters of solvated metal ions such as the solvation number and the bond length between metal ion and donor atom.⁸

There are a number of studies on solvent exchange for the first-row transition metal ions in familiar solvents, such as water, acetonitrile, and methanol.⁴ Merbach *et al.* have claimed that the mechanisms change gradually from an associative activation mode for the early first-row transition metal elements to a dissociative activation mode for the later elements.^{9,10} This trend can be accounted for by the electronic configuration in the valence shell and the size of the metal ions. The fillings of the *d* orbitals of metal ions electrostatically disfavor the attacking of the donor atom of entering solvent molecules, and furthermore, the decrease in the radii of metal ions leads to a less associative mode of

activation due to crowding around the central metal ion. For example, the activation volume for the solvent exchange on *d*⁵ high-spin Mn(II) ion in water is negative (e.g. $-6.2 \text{ cm}^3 \text{ mol}^{-1}$)¹¹ and thus the solvent exchange proceeds via an associative activation mode, while the solvent exchange of Ni(II) ion with *d*⁸ configuration has a positive activation volume of $+7.2 \text{ cm}^3 \text{ mol}^{-1}$ in water^{12,13} and thus proceeds by a dissociative mode of activation. Previously, we demonstrated the bulkiness effects of solvent molecules for the solvent exchange reaction on the basis of activation volumes obtained by the high-pressure NMR method.^{13,14} The activation volumes for solvent exchange on the Mn(II) ion were determined to be $+0.4 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ ($-15 \text{ }^\circ\text{C}$) in acetic acid¹³ and $+1.6 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ ($36.3 \text{ }^\circ\text{C}$) in DMF.¹⁴ The central Mn(II) ion surrounded by six bulkier solvent molecules such as acetic acid and DMF should be sterically crowded. These positive values have been thought the reaction mechanism to be a dissociative mode due to the bulkiness of the solvent molecule.

In a bulky solvent, the steric repulsion among the solvent molecules bounded in the first coordination sphere of central metal ions must be large. Thus, we can expect that the coordination number of solvated metal ions in the bulky solvent should decrease. In fact, Lincoln *et al.* indicated that the coordination number for the trivalent lanthanides (Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, and Yb³⁺) decreases with an increase in the bulkiness of coordinated solvent molecules: 9 in water, 8 in DMF, and 6 in 1,1,3,3-tetramethylurea (TMU).¹⁵ In addition, the solvation structure of Co(II) ions is tetrahedral in much bulkier hexamethylphosphoric triamide (HMPA).¹⁶ TMU is bulkier than solvents such as water, methanol, acetonitrile, and DMF. Therefore, it can be expected that the solvation structures and reactivities of some metal ions in TMU are different from those in water. According to our preliminary experiments, the reaction

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profile for the reaction of Co(II) and Ni(II) ions with 2,2'-bipyridine and 1,10-phenanthroline in TMU is different from that in water.¹⁷ In this work, we have investigated the structures of solvated Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and In(III) ions in TMU by means of EXAFS and electronic spectroscopy, in order to shed light on the bulkiness effects of TMU molecules on the structure and reactivity of metal ions in TMU.

Experimental Section

Preparation of Sample Solutions. 1,1,3,3-Tetramethylurea (Wako, Sp. Gr.) was purified by distillation under reduced pressure after dehydration by using 4A molecular sieves.

Hexaaquametal trifluoromethanesulfonates of Fe(II), Ni(II), Cu(II), Zn(II), and In(III) ions were prepared by the following method. Iron sponge (Wako, 99.99%), NiCO₃·Ni(OH)₂·4H₂O (Wako, Pr. Gr.), CuO (Wako, 99.9%), zinc metal (Wako, 99.998%), and shot-shaped indium (Wako, 99.98%) were dissolved in an aqueous solution of trifluoromethanesulfonic acid (triflic acid, Wako, 98%). The residue was removed by filtration, and the filtrate was concentrated. In the case of Co(II) ion, CoCl₂·6H₂O (Wako, Sp. Gr.) was dissolved in an aqueous triflic acid solution and the solution was concentrated by use of an infrared lamp. The dissolve-concentrate method was repeated several times until HCl was completely expelled. Manganese(II) perchlorate was used because of the low solubility of the manganese(II) triflate. The hexaaquamanganese(II) perchlorate was prepared from MnCO₃ (Wako, Sp. Gr.) and perchloric acid (Wako, Sp. Gr.). For Cd(II) ion, Cd(NO₃)₂·4H₂O (Wako, Sp. Gr.) was used without further purification. Hydrates of each metal ion were dissolved in TMU, and the water in the solution was removed under reflux in a modified Soxhlet extractor with activated 4A molecular sieves.¹⁸ The reflux was repeated several times until complete removal of the water and TMU solutions of each metal ion were obtained.

Aqueous and TMU solutions of metal ions were prepared for EXAFS measurements. The concentration of the metal ion sample solutions, C_M/mol kg⁻¹, is given in Table 1. The aqueous solutions contained 0.1 mol kg⁻¹ of hydrogen ion in order to prevent the hydrolysis of metal ions. All TMU solutions were prepared and treated under dry nitrogen gas in a drybox in order to prevent the contamination of water.

Measurements. Electronic spectra were recorded on a UV-3100PC spectrophotometer (Shimadzu) over the wavelength range from 250 to 2000 nm at 298 K. The unit of M⁻¹ cm⁻¹ (M ≡ mol dm⁻³) is used for a molar absorption coefficient (ε), where the unit of mol kg⁻¹ was converted to mol dm⁻³ with knowledge of the density of solutions.

EXAFS spectra were measured around the K edge of each metal in the transmission mode using the BL7C and BL10B stations at the Photon Factory of the National Laboratory for High Energy Physics.¹⁹ Monochromatized X-rays were obtained by an Si(111) double crystal at the BL7C and an Si(311) channel-cut crystal at the BL10B. The incident X-ray intensity I₀ and the transmitted X-ray intensity I were simultaneously measured with ionization chambers. The ionization chamber for I₀ measurement was filled with nitrogen gas (100%) in the case of Mn, Fe, Co, Ni, Cu, and Zn and with argon gas (100%) for Cd and In. The chamber for I measurement was filled with nitrogen/argon mixture gas in the case of Mn, Fe, Co, Ni, Cu, and Zn and with argon gas (100%) for Cd and In. The percentage of argon gas in the nitrogen/argon mixture was 15% for Mn, Fe, and Co and 25% for Ni, Cu, and Zn.

A glass filter disk (25-mm diameter and 2-mm thickness) was immersed in a sample solution and then doubly sealed in a PET (poly(ethylene terephthalate), Toray Co.) film bag in order to prevent evaporation of the solvent and contamination of water. An effective jump at the absorption edge was obtained by increasing the number of glass filter disks.

EXAFS Data Analysis. The background absorption was estimated by fitting the Victoreen formula to the data in the pre-edge region,²⁰ which was subtracted from the total absorption μ by extrapolation. The smooth K-shell absorption μ₀ was estimated by fitting a smooth curve to the

Table 1. Structure Parameters for Solvated Metal Ions in Water and TMU^a

metal	solvent	C _M /mol kg ⁻¹	R/pm	σ/pm	n
Mn(ClO ₄) ₂	water	0.503	217(1)	7.4(0.1)	6 ^b
			220 ^c		6 ^{b,c}
			220 ^d		6 ^{b,d}
			220 ^e		6 ^{b,e}
			217 ^f		6 ^{b,f}
			217 ^g		6 ^{b,g}
Fe(CF ₃ SO ₃) ₂	TMU	0.135	209(1) ^h	6.7(0.2)	4.9(0.2)
	water	0.533	211(1)	7.4(0.1)	6 ^b
			212 ^c	6 ^{b,c}	
			210 ^f	8.1 ^f	6 ^{b,f}
			205(1) ^h	7.6(0.1)	4.9(0.2)
			208(1)	6.8(0.1)	6 ^b
Co(CF ₃ SO ₃) ₂	TMU	0.602	205(1) ^h	7.6(0.1)	4.9(0.2)
	water	0.499	208(1)	6.8(0.1)	6 ^b
			208 ^c	6 ^{b,c}	
			209 ^h	5.9 ^h	6 ^{b,i}
			209 ⁱ	6 ^{b,i}	
			200(1) ^h	6.5(0.1)	4.1(0.2)
Ni(CF ₃ SO ₃) ₂	TMU	0.505	205(1)	6.4(0.1)	6 ^b
	water	0.504	204 ^c	6 ^{b,c}	
			207 ^d	6 ^{b,d}	
			207 ^h	5.7 ^h	6 ^{b,j}
			206 ^l	6 ^{b,j}	
			205 ^k	6.7 ^k	6.4 ^k
Cu(CF ₃ SO ₃) ₂	TMU	0.358	200(1) ^h	5.9(0.1)	4.8(0.2)
	water	0.505	197(1) ^l	5.7(0.1) ^l	4 ^{b,l}
			229(3) ^m	12.4(0.4) ^m	2 ^{b,m}
			194 ^{c,l}	4 ^{b,c,l}	
			243 ^{c,m}	2 ^{b,c,m}	
			197 ^{l,n}	4 ^{b,l,n}	
Zn(CF ₃ SO ₃) ₂	TMU	0.489	192(1) ^h	4.6(0.2)	3.9(0.2)
	water	0.498	207(1)	8.1(0.1)	6 ^b
			208 ^c	6 ^{b,c}	
			211 ^h	6.2 ^h	6 ^{b,p}
			210 ^q	6 ^{b,q}	
			213 ^r	6 ^{b,r}	
Cd(NO ₃) ₂	TMU	0.529	195(1) ^h	5.8(0.1)	3.8(0.2)
	water	0.512	227(1)	8.0(0.2)	6 ^b
			231 ^r	6 ^{b,s}	
			226 ^h	5.8 ^h	6 ^{b,t}
			229 ^r	6 ^{b,t}	
			228(1) ^h	9.8(0.2)	5.9(0.2)
In(CF ₃ SO ₃) ₃	TMU	0.851	214(1)	5.4(0.2)	6 ^b
	water	0.484	215 ^u	6 ^{b,u}	
			213(1) ^h	6.2(0.2)	6.1(0.2)

^a The values of E₀/keV and λ/pm are 6.5517(2) and 548(12) for Mn(II), 7.1260(2) and 522(9) for Fe(II), 7.1314(2) and 540(9) for Co(II), 8.3480(2) and 573(10) for Ni(II), 8.9971(3) and 564(15) for Cu(II), 9.6726(2) and 539(9) for Zn(II), 26.7076(2) and 503(8) for Cd(II), and 27.9434(3) and 529(12) for In(III) ion, respectively. The standard deviations are given in parentheses. ^b The values were kept constant during the least-squares calculations. ^c Reference 27a. ^d Reference 27b. ^e Reference 27c. ^f Reference 27d. ^g EXAFS data analysis has been performed by assuming that all the M–O distances of each solvated metal ion in TMU are equal. ^h Reference 27e. ⁱ Reference 27f. ^j Reference 27g. ^k Reference 27h. ^l For the equatorial site. ^m For the axial site. ⁿ Reference 27i. ^o Reference 27j. ^p Reference 27k. ^q Reference 27l. ^r Reference 27m. ^s Reference 27n. ^t Reference 27o. ^u Reference 27p.

subtracted absorption data in the post-edge using a sixth-order polynomial function. The observed EXAFS oscillation χ_{obsd}(k) was extracted and normalized by eq 1. The photoelectron wave vector k is equal to {8m(E

$$\chi_{\text{obsd}}(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} \quad (1)$$

– E₀)^{1/2}/π/h, where E is the energy of the incident X-ray, E₀ is the threshold energy of a K-shell electron, m is the mass of the electron, and h is the Planck constant. The value of E₀ was first selected as the position of the half-height of the edge jump in each sample. The k³χ_{obsd}(k) values

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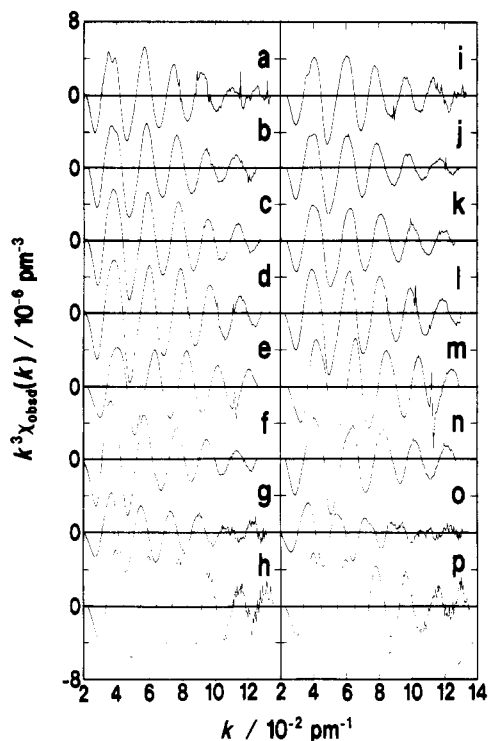


Figure 1. Observed EXAFS oscillation $\chi_{\text{obsd}}(k)$ weighted by k^3 for sample solutions. Key: In water, (a) Mn(II) ion, (b) Fe(II) ion, (c) Co(II) ion, (d) Ni(II) ion, (e) Cu(II) ion, (f) Zn(II) ion, (g) Cd(II) ion, (h) In(III) ion; in TMU, (i) Mn(II) ion, (j) Fe(II) ion, (k) Co(II) ion, (l) Ni(II) ion, (m) Cu(II) ion, (n) Zn(II) ion, (o) Cd(II) ion, (p) In(III) ion.

were converted to the radial distribution function $G(R)$ by the Fourier transformation (eq 2),

$$G(R) = \sqrt{\frac{1}{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} k^3 [\chi_{\text{obsd}}(k)] [W(k)] \exp(-2ikR) dk \quad (2)$$

where $W(k)$ is a window function. The main peak in the $|G(R)|$ curve was extracted and was made into an inverse Fourier transformation to obtain the Fourier filtered $k^3\chi_{\text{filt}}(k)$ values. In order to refine the structure parameters, the model function $k^3\chi_{\text{calcd}}(k)$ was fitted to the $k^3\chi_{\text{filt}}(k)$ values. The $k^3\chi_{\text{calcd}}(k)$ function is given by the single-electron and single-scattering theory (eq 3),²¹⁻²⁴

$$\chi_{\text{calcd}}(k) = \sum_j \left\{ \frac{n_j}{kR_j^2} \right\} \exp\left(-2\sigma_j^2 k^2 - \frac{2R_j}{\lambda}\right) F_j(\pi, k) \sin(2kR_j - \alpha_j(k)) \quad (3)$$

where $F_j(\pi, k)$ is the backscattering amplitude from each of scatterer j at a distance R_j from the X-ray absorbing atom, n_j is the number of scatterer j , σ_j is the Debye-Waller factor, λ is the mean free path of the photoelectron, and $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectron. The values of $F_j(\pi, k)$ and $\alpha_j(k)$ in eq 3 were quoted from the literature.²⁵

Results and Discussion

The EXAFS spectra $\chi_{\text{obsd}}(k)$ weighted by k^3 of the sample solutions and their Fourier transforms $|G(R)|$ are shown in Figures 1 and 2, respectively. The first intense peaks at 160–180 pm in Figure 2 are due to the interactions between metal ions and oxygen atoms of TMU molecules in the first coordination sphere. The Fourier filtered $k^3\chi_{\text{filt}}(k)$ values, which correspond to squares in

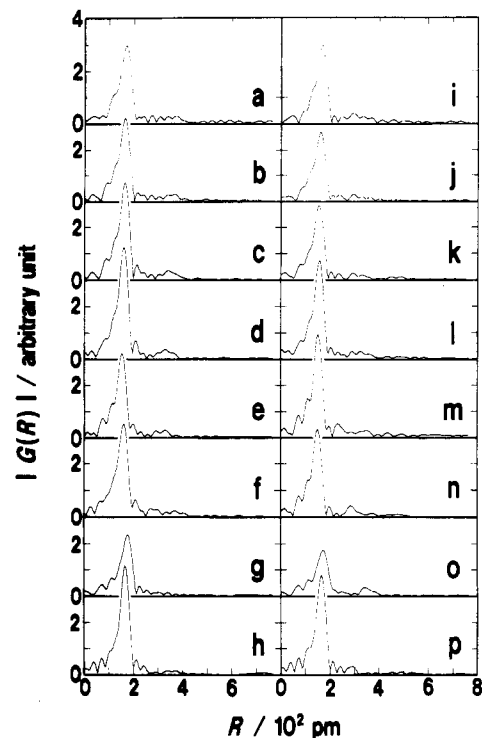


Figure 2. Fourier transforms $|G(R)|$ of $k^3\chi_{\text{obsd}}(k)$ depicted in Figure 1 uncorrected for the phase shift. Key: In water, (a) Mn(II) ion, (b) Fe(II) ion, (c) Co(II) ion, (d) Ni(II) ion, (e) Cu(II) ion, (f) Zn(II) ion, (g) Cd(II) ion, (h) In(III) ion; in TMU, (i) Mn(II) ion, (j) Fe(II) ion, (k) Co(II) ion, (l) Ni(II) ion, (m) Cu(II) ion, (n) Zn(II) ion, (o) Cd(II) ion, (p) In(III) ion.

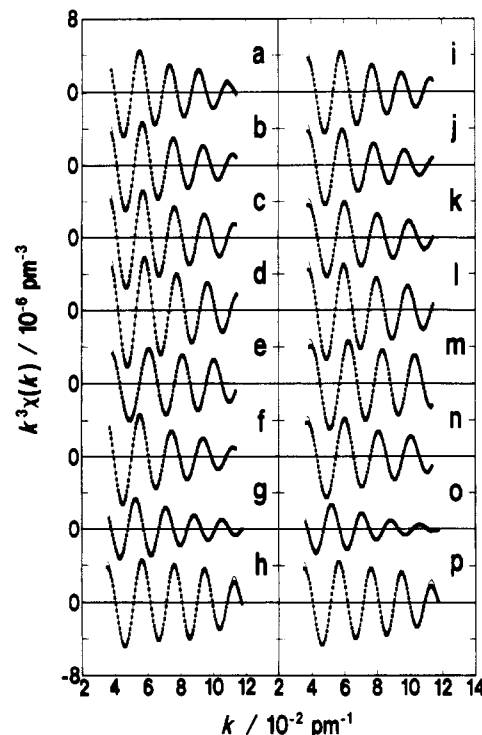


Figure 3. Fourier filtered EXAFS oscillations for sample solutions. The squares are $k^3\chi_{\text{filt}}(k)$ values obtained by the inverse Fourier transformation for $|G(R)|$ in Figure 2, and the solid lines are $k^3\chi_{\text{calcd}}(k)$ curves calculated by using the parameters in Table 1 according to eq 3. Key: In water, (a) Mn(II) ion, (b) Fe(II) ion, (c) Co(II) ion, (d) Ni(II) ion, (e) Cu(II) ion, (f) Zn(II) ion, (g) Cd(II) ion, (h) In(III) ion; in TMU, (i) Mn(II) ion, (j) Fe(II) ion, (k) Co(II) ion, (l) Ni(II) ion, (m) Cu(II) ion, (n) Zn(II) ion, (o) Cd(II) ion, (p) In(III) ion.

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Figure 3, were obtained by the inverse Fourier transformation in the R range from 70 to 235 pm.

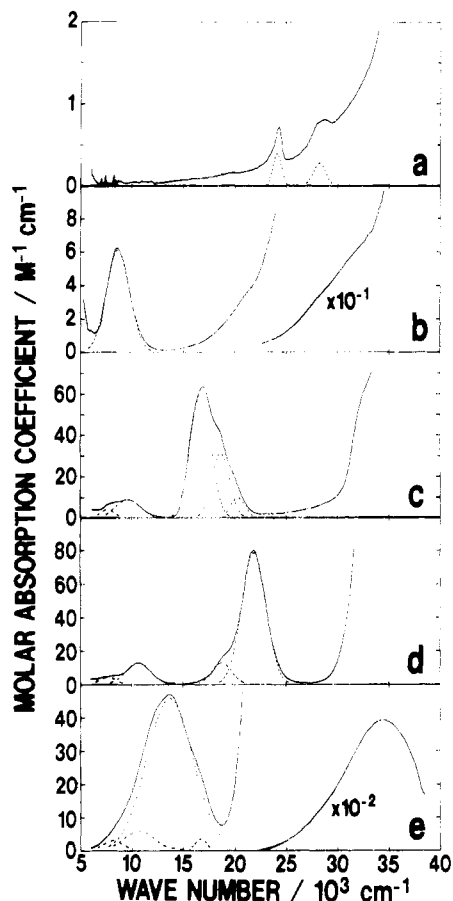


Figure 4. Electronic spectra for Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions in TMU: (a) Mn(II) ion; (b) Fe(II) ion; (c) Co(II) ion; (d) Ni(II) ion; (e) Cu(II) ion. The components of the absorption band are shown by dotted curves.

The structure parameters (E_0 , λ , R , σ , and n) of each metal ion were estimated by a least-squares calculation over the k range from 4.5×10^{-2} to $12.0 \times 10^{-2} \text{ pm}^{-1}$. The values of E_0 , λ , R , and σ for aqueous solutions were determined by fixing the coordination number n to 6, because the six-coordinate octahedral structures of the metal ions are accepted in aqueous solutions.^{8,26,27} In the case of TMU solutions, the values of R , σ , and n were refined by adopting the E_0 and λ values determined for relevant metal ions in aqueous solution. The structure parameters obtained are listed in Table 1 together with metal-oxygen (M-O) bond lengths (R/pm) in aqueous solution previously reported.^{8,27} Solid lines in Figure 3 correspond to the $k^3 \chi_{\text{calc}}(k)$ curves depicted by use of the obtained parameters. The M-O bond lengths obtained for the aqueous solutions are in good agreement with those previously reported,^{8,27} showing that the E_0 and λ values are well approximated in the present study.

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Figure 4 shows the electronic spectra of TMU solutions of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions at 298 K. Molar absorption coefficients ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) are the same over a wide range of the metal(II) ion concentrations (1–100 mM). This indicates that there is no existence of polynuclear metal solvates in TMU.

According to the results of EXAFS measurements (see Table 1), the coordination number is 4 for Co(II), Cu(II), and Zn(II) ions, 5 for Mn(II), Fe(II), and Ni(II) ions, and 6 for Cd(II) and In(III) ions. Since electronic spectra of the first-row transition metal(II) ions are characteristic of coordination symmetry around the central metal ion,²⁸ we will discuss the band energies for observed d-d transitions, their assignments, and the solvation structures for the metal ions in TMU on the basis of the available electronic spectra. The band shape of observed electronic spectra has been simulated on the assumption of the composite of Gaussian curves. The components of the absorption bands obtained by the band shape simulation are depicted in Figure 4.

In the spectrum of the Cu(II) ion, absorption bands are observed at 7600 ($\epsilon = 3 \text{ M}^{-1} \text{ cm}^{-1}$, shoulder), 10 400 (6, shoulder), 13 700 (46), 15 800 (4, shoulder), and 34 500 (3950) cm^{-1} (Figure 4e). The band at 34 500 cm^{-1} comes from charge transfer.²⁸ The other four bands are considered as the d-d transitions, and the transition energies are quite similar to those of pseudotetrahedral complexes with the CuO_4 chromophore, such as $[\text{Cu}(\text{hmpa})_4]^{2+}$,²⁹ $[\text{Cu}(\text{p}_3\text{po})_4]^{2+}$ ($\text{p}_3\text{po} = \text{triphenylphosphine oxide}$),^{30a} and $[\text{Cu}(\text{m}_3\text{no})_4]^{2+}$ ($\text{m}_3\text{no} = \text{trimethylamine } N\text{-oxide}$),³¹ and are obviously different from those of square planar complexes, such as $[\text{Cu}(\text{acac})_2]^{2+}$ ($\text{acac} = \text{acetylacetonate}$),³² $[\text{Cu}(\text{epno})_4]^{2+}$ ($\text{epno} = 4\text{-ethoxypyridine } N\text{-oxide}$),³³ and $[\text{Cu}(\text{np}_2\text{po})_4]^{2+}$ ($\text{np}_2\text{po} = \text{dimethylamino}diphenylphosphine oxide$),³⁴ and from those of tetrahedral complexes, such as $[\text{Cu}(\text{morpo})_4]^{2+}$ ($\text{morpo} = \text{trimorpholinophosphine oxide}$, wavenumber at the absorption maximum (ν_{max}) = $\sim 11\,000 \text{ cm}^{-1}$)³⁵ and $[\text{CuX}_4]^{2-}$ (X is a halogen, $\nu_{\text{max}} = \sim 9000 \text{ cm}^{-1}$).³⁶ Furthermore, there has been considerable interest in the relationship between the dihedral angles of pseudotetrahedral copper(II) complexes with CuN_2O_2 and CuN_4 chromophores and its transition energies, and the absorption spectra in TMU are also similar to those of the copper(II) complexes of bidentate ligands ($\nu_{\text{max}} = \sim 13\,000 \text{ cm}^{-1}$), such as *N-tert*-butylsalicylideneimine and heterocyclic secondary amine derivatives, which have the distorted tetrahedral structure (D_{2d}).^{37,38} With knowledge of their available spectral data,³⁸ the four bands seem to be assigned to the transition from ${}^2\Gamma_1(T_2)$ to ${}^2\Gamma_2(T_2)$, ${}^2\Gamma_1(E)$, ${}^2\Gamma_3(T_2)$, and ${}^2\Gamma_2(E)$ in the D_{2d} symmetry. Thus, it is confirmed that the $[\text{Cu}(\text{tmu})_4]^{2+}$ ion has the distorted tetrahedral structure (D_{2d}).

The specific spectrum for a TMU solution of the Ni(II) ion has been analyzed to have five bands at 8000 ($\epsilon = 4 \text{ M}^{-1} \text{ cm}^{-1}$,

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broad), 10 600 (13), 13 900 (1), 18 700 (13, shoulder), and 21 900 (79) cm^{-1} and a threshold higher than 30 000 cm^{-1} (Figure 4d). The highly intense band upper 30 000 cm^{-1} corresponds to the charge-transfer transition. The same spectral pattern was observed for many Ni(II) complexes of phosphine and arsine oxides with the NiO₂ chromophore in C_{4v} symmetry ($\nu_{\text{max}} = \sim 8500, \sim 11\,500, \sim 13\,500, \sim 18\,000, \text{ and } \sim 22\,000 \text{ cm}^{-1}$).³⁹⁻⁴³ Then, the five peaks may be assigned to the transition from 3B_1 to $^1A_1(D), ^3E(F), ^1B_1(D), ^3A_2(P), \text{ and } ^3E(P)$, respectively,⁴⁴ and it is concluded that the solvated Ni(II) ion in TMU has a five-coordinate square pyramidal structure (C_{4v}). In addition, the spectrum of $[\text{Ni}(\text{tmu})_2]^{2+}$ is clearly different from those of $[\text{Ni}(\text{hmpa})_4]^{2+}$ (T_d),^{29,45} $[\text{Ni}(\text{p}_3\text{po})_4]^{2+}$ (D_{2d}),^{46a} $[\text{Ni}(\text{p}_3\text{po})_2(\text{ONO}_2)_2]^{2+}$ (D_{2d}),^{46b} and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (O_h),⁴⁷ and thus the mixture of 4-coordinate and 6-coordinate solvates in TMU is definitely ruled out.

The spectrum of the Co(II) ion in TMU has absorption bands at 7700 ($\epsilon = 4 \text{ M}^{-1} \text{ cm}^{-1}$, shoulder), 9600 (9), 16 700 (61), 18 600 (32, shoulder), and 20 300 (10, shoulder) cm^{-1} (Figure 4c). The set of transition energies is similar to that of tetrahedral Co(II) complexes with the CoO₄ chromophore, such as $[\text{Co}(\text{hmpa})_4]^{2+}$ ($\nu_{\text{max}} = \sim 6500$ and $\sim 17\,000 \text{ cm}^{-1}$),⁴⁵ $[\text{Co}(\text{p}_3\text{po})_4]^{2+}$ ($\nu_{\text{max}} = 15\,600 \text{ cm}^{-1}$),³⁰ $[\text{Co}(\text{np}_2\text{po})_4]^{2+}$ ($\nu_{\text{max}} = 6400$ and $16\,600 \text{ cm}^{-1}$),³⁴ $[\text{Co}(\text{morpo})_4]^{2+}$ ($\nu_{\text{max}} = \sim 6000$ and $\sim 16\,000 \text{ cm}^{-1}$),³⁵ $[\text{Co}(\text{p}_3\text{-ao})_4]^{2+}$ ($\text{p}_3\text{ao} = \text{triphenylarsine oxide}, \nu_{\text{max}} = \sim 7000$ and $\sim 17\,000 \text{ cm}^{-1}$),⁴⁸ and $[\text{Co}(\text{n}_2\text{ppo})_4]^{2+}$ ($\text{n}_2\text{ppo} = \text{bis(dimethylamino)-phenylphosphine oxide}, \nu_{\text{max}} = 6200$ and $16\,500 \text{ cm}^{-1}$).⁴⁹ Thus, it is acceptable that the structure of the solvated Co(II) ion in TMU is four-coordinate tetrahedral.

The absorption intensity of transition at 16 700 cm^{-1} for the Co(II) ion in TMU, however, is dissimilar to those of previously known regular tetrahedral complexes ($\epsilon = 300\text{--}500 \text{ M}^{-1} \text{ cm}^{-1}$).^{28,45,48} According to the electronic absorption data for bis-(dipivaloylmethanido)cobalt(II) (D_{2d} , $\epsilon = 40$),⁵⁰ $[\text{Co}(\text{acac})_2]^{2+}$ (D_{2d} , $\epsilon = 30\text{--}70$),^{50b} tetrakis(diisopropyl methylphosphonato)cobalt(II) (D_{2d} , $\epsilon = 65$),⁵¹ $[\text{CoX}_3(\text{mpr})]$ ($X = \text{Cl}^- \text{ and } \text{Br}^-$; mpr = monoprotonated 1-methyl- and 2-methylpiperazine) (C_{3v} , $\epsilon = 60\text{--}90$),⁵² and $[\text{Co}(\text{pmp})\text{X}_2]$ ($X = \text{Cl}^-, \text{Br}^-, \text{I}^-$; pmp = 1-phenyl-2,3-dimethyl-5-pyrazolone) (C_{2v} , $\epsilon = 70\text{--}80$),⁵³ the descending symmetry around Co(II) ion tends to lead the lower absorption intensity. Since the molar absorption coefficient of $[\text{Co}(\text{tmu})_4]^{2+}$ is close to those of the distorted tetrahedral compounds, the TMU solvate of Co(II) ion may have a distorted tetrahedral structure (D_{2d}).

For the Fe(II) ion in TMU, we can see absorptions at lower than 5000 and at 8600 ($\epsilon = 6 \text{ M}^{-1} \text{ cm}^{-1}$) cm^{-1} due to the d-d transitions and at higher than 23 000 cm^{-1} with a gradual increase in intensity owing to the charge transfer (Figure 4b). The absorption pattern is similar to that of $[\text{Fe}(\text{m}_3\text{po})_4(\text{OCIO}_3)](\text{ClO}_4)$ ($\text{m}_3\text{po} = \text{trimethylphosphine oxide}$),³⁹ $[\text{Fe}(\text{m}_3\text{ao})_4(\text{OCIO}_3)](\text{ClO}_4)$ ($\text{m}_3\text{ao} = \text{trimethylarsine oxide}$),³⁹ and $[\text{Fe}(\text{n}_2\text{ppo})_4(\text{OCIO}_3)](\text{ClO}_4)$,⁴⁹ which have C_{4v} symmetry with the FeO₂ chromophore. Thus, it is likely that the solvation structure of Fe(II) ion in TMU is five-coordinate square pyramidal (C_{4v} , $\nu_{\text{max}} = \sim 10\,000 \text{ cm}^{-1}$). In this symmetry, the peak lower than 5000 cm^{-1} is assigned to the transition from 5T_2 to 5A_1 and the peak at 8600 cm^{-1} is from 5T_2 to 3B_1 . However, since the five-coordinate Fe(II) complexes with D_{3h} symmetry ($\nu_{\text{max}} \leq 5000$ and $\sim 10\,000 \text{ cm}^{-1}$)⁵⁴ also have absorption maximums similar to those of the TMU solution, the clear distinction between C_{4v} and D_{3h} for the solvation structure of Fe(II) ion in TMU is difficult to determine by a comparison of electronic spectra.

In the spectrum of the Mn(II) ion in TMU, there are two peaks at 24 300 ($\epsilon = 0.4 \text{ M}^{-1} \text{ cm}^{-1}$) and around 28 000 cm^{-1} (0.3, multiplet), a low intensity broad band over the region from 18 000 to 21 000 (0.2) cm^{-1} , and a high-intensity charge-transfer band of 35 000 cm^{-1} or higher (Figure 4a). The spectrum is similar to that observed for the square pyramidal complexes with an MnO₂ chromophore, such as $[\text{MnL}_4(\text{OCIO}_3)](\text{ClO}_4)$ (L is a phosphine oxide or an arsine oxide, $\nu_{\text{max}} = \sim 20\,000, \sim 24\,000, \text{ and } \sim 29\,000 \text{ cm}^{-1}$),⁵⁵ $[\text{Mn}(\text{mpno})_4(\text{OCIO}_3)](\text{ClO}_4)$ (mpno = 2,6-dimethylpyridine *N*-oxide),⁵⁶ and $[\text{Mn}(\text{m}_3\text{no})_5]^{2+}$.³³ Thus, it is concluded that the structure of the solvated Mn(II) ion in TMU is five-coordinate square pyramidal (C_{4v}).

With regard to the Zn(II) ion, the observed Zn-O bond length is 207 ± 1 in water and 195 ± 1 pm in TMU, the difference being 12 pm. According to a number of structural studies of both six-coordinate octahedral and four-coordinate tetrahedral zinc(II) compounds,⁵⁷ the difference in the effective ionic radius of Zn(II) ion of six- and four-coordination is, in fact, ca. 14 pm,⁵⁷ which is very close to the difference between the Zn-O bond lengths in water and in TMU. Thus, the solvated Zn(II) ion in TMU may have a four-coordinate tetrahedral structure (T_d).

In the case of the Cd(II) and In(III) ions, there is no difference in the structure parameters of *R* and *n* between TMU and aqueous solutions. We can conclude that the Cd(II) and In(III) ions are octahedrally six-coordinated (O_h).

Interestingly, a variety of solvation structures of the first-row transition metal(II) ions in TMU have been observed in the present work. As shown previously, the solvation structures of first-row transition metal(II) ions in water²⁷ and DMF^{58,59} are octahedral. TMU has a larger molar volume ($V^\circ = 121 \text{ cm}^3 \text{ mol}^{-1}$) than H₂O ($V^\circ = 18.1 \text{ cm}^3 \text{ mol}^{-1}$) and DMF ($V^\circ = 77.4 \text{ cm}^3 \text{ mol}^{-1}$). In such a bulky solvent TMU, it was found that the solvation numbers for all of these metal(II) ions are decreased and the M(II)-O bond lengths are shortened. These findings are attributable to the sterically repulsive interaction owing to the coordination of bulky TMU molecules.

The effective ionic radii of Cd(II), Mn(II), Fe(II), Co(II), Zn(II), Ni(II), and Cu(II) ions in O_h symmetry gradually shorten in this order.⁵⁷ The coordination number in TMU is 6 for the largest Cd(II) ion and 4 for the smallest Cu(II) ion, and the

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coordination numbers of the middle sized metal(II) ions are decreased from 5 to 4, corresponding to the shortening of the ionic radius. However, there is an exception to this trend in coordination number in that the larger Co(II) ion is four-coordinate, while the smaller Ni(II) ion is five-coordinate. According to a qualitative treatment by Krishnamurthy and Schaap,⁶⁰ we can estimate the relative energies of the d orbitals in some symmetries. For the d^8 Ni(II) ion, it can be calculated that the sum of the energies for occupied d orbitals is $-10.0 Dq(C_{4v})$ for C_{4v} symmetry and $-3.56 Dq(T_d)$ for T_d symmetry; *i.e.*, the stabilization energy in C_{4v} symmetry is expected to be larger than that in T_d symmetry.⁶¹ Thus, the Ni(II) ion in TMU prefers a five-coordinate square pyramidal to a four-coordinate tetrahedral structure.

The effective ionic radius of the In(III) ion in octahedral symmetry is 80 pm, which is shorter than that of the Mn(II) ion (83 pm).⁵⁷ However, according to the present results in TMU, the value of n is 6 for In(III) ion and 5 for Mn(II) ion, and R of the In(III) ion is longer than that of the Mn(II) ion. Therefore, due to the higher charge of the trivalent In(III) ion, the six-

coordinate solvation structure is more advantageous than the structure with a lower coordination number accompanying the shortening of the M–O bond length.

Recently, Ozutsumi et al. have revealed the solvation structures of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions in *N,N*-dimethylacetamide (DMA);⁵⁹ Mn(II), Co(II), and Ni(II) ions are six-coordinate octahedral, Cu(II) ion is six-coordinate axially elongated octahedral, and Zn(II) ion is accepted to be a mixture of four-coordinate and six-coordinate solvates. Since the size of DMA is smaller than TMU, the steric hindrance of bound solvent molecules around the central metal(II) ion in DMA should be smaller than in TMU. The bulkiness of the solvent molecule greatly affects the solvation structure of metal ions.

In conclusion, the coordination number of the solvated metal ions in nonaqueous solvent is mainly determined by the bulkiness of solvent molecules and the size of central metal ions, although the ligand field stabilization energy is added as a perturbation for the determination. We must expect that the mechanisms for solvent exchange and complexation of metal(II) ions in TMU will be different from those in other solvents where the metal(II) ions have octahedral solvation.¹⁷

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(61) Since the Dq value should be a function of R and n , the value of $Dq(C_{4v})$ in C_{4v} symmetry must be different from that in T_d symmetry. In the case of four-coordinated Co(II) ion, the M(II)–O bond length in the tetrahedral solvated complex is 200 pm, which is the same as the value of R in a five-coordinated Ni(II) solvate. If the R value of the four-coordinated tetrahedral Ni(II) solvate is assumed to be equal to that of the Co(II) solvate, the Dq value may depend on the value of n . Thus, the value of $Dq(C_{4v})$ may be larger than that of $Dq(T_d)$.