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

Yasuhiro Inada, a Ken-ichi Sugimoto, a Kazuhiko Ozutsumi, b and Shigenobu Funahashi * a

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01, Japan, and Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan

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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.4–8 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.6–7 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 d5 high-spin Mn(II) ion in water is negative (e.g., −6.2 cm3 mol−1)11 and thus the solvent exchange proceeds via an associative activation mode, while the solvent exchange of Ni(II) ion with d4 configuration has a positive activation volume of +7.2 cm3 mol−1 in water12,13 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 ± 0.7 cm3 mol−1 (−15 °C) in acetic acid15 and +1.6 ± 0.5 cm3 mol−1 (36.3 °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 hexamethylyphosphoramide (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


(1) (a) Nagoya University. (b) University of Tsukuba.
(2) Marcus, Y. Ion Solvation; John Wiley & Sons Ltd.: Chichester, U.K., 1985; Chapters 4 and 6.
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-Tetramethylbutyleurea (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, 99.99%), and shot-shaped indium (Wako, 99.98%) were dissolved in an aqueous solution of trfluoromethanesulfonic 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 and In, Cd(N03)2•4H2O (Wako, Sp. Gr.) was used without further purification. All TMU solutions were prepared and treated under dry nitrogen gas in a drybox in order to prevent the contamination of water and TMU solutions of metal ions were prepared for EXAFS measurements. The concentration of the metal ion sample solutions, Cm (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 the molar absorption coefficient (ε), where the unit of mol dm⁻³ was converted to mol dm⁻³ with knowledge of the density of solutions.

EXAFS spectra were measured around the K edge of each metal atom 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 K-shell absorption edge was obtained by increasing the number of glass filter sheets.

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 μk was estimated by fitting a smooth curve to the

<table>
<thead>
<tr>
<th>metal</th>
<th>solvent</th>
<th>Cm/ mol kg⁻¹</th>
<th>R/pm</th>
<th>ε/pm</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(ClO₄)₂</td>
<td>water</td>
<td>0.503</td>
<td>217(1)</td>
<td>7.4(0.1)</td>
<td>6h</td>
</tr>
<tr>
<td>Fe(CF₃SO₄)₂</td>
<td>TMU</td>
<td>0.135</td>
<td>209(1)</td>
<td>6.7(0.2)</td>
<td>4.9(0.2)</td>
</tr>
<tr>
<td>Co(CF₃SO₄)₂</td>
<td>water</td>
<td>0.533</td>
<td>211(1)</td>
<td>7.4(0.1)</td>
<td>6h</td>
</tr>
<tr>
<td>Ni(CF₃SO₄)₂</td>
<td>water</td>
<td>0.505</td>
<td>200(1)</td>
<td>6.5(0.1)</td>
<td>4.1(0.2)</td>
</tr>
<tr>
<td>Cu(CF₃SO₄)₂</td>
<td>water</td>
<td>0.505</td>
<td>197(1)</td>
<td>5.7(0.1)</td>
<td>4.8(0.2)</td>
</tr>
<tr>
<td>Zn(CF₃SO₄)₂</td>
<td>water</td>
<td>0.489</td>
<td>192(1)</td>
<td>4.6(0.2)</td>
<td>3.9(0.2)</td>
</tr>
<tr>
<td>Cd(NO₃)₂</td>
<td>water</td>
<td>0.529</td>
<td>207(1)</td>
<td>8.1(0.1)</td>
<td>6h</td>
</tr>
<tr>
<td>In(CF₃SO₄)₃</td>
<td>water</td>
<td>0.484</td>
<td>214(1)</td>
<td>5.4(0.2)</td>
<td>6h</td>
</tr>
</tbody>
</table>

The values of Eo/keV and λ/pm are 6.5517(2) and 548(12) for Mn(II), 6.5126(2) and 522(9) for Fe(II), 6.5039(2) and 513(9) for Ni(II), 6.5039(2) and 513(9) for Cu(II), and 6.5039(2) and 513(9) for Cd(II) and In(III) ions in TMU, respectively. The standard deviations are given in parentheses. The values were kept constant during the least-squares calculations. The values of Eo/keV and λ/pm were first selected 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.

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\[
\chi_{\text{obsd}}(k) = \frac{\mu(k) - \mu_{\text{bg}}(k)}{\mu_{\text{k}}(k)}
\]

where \( E_0 \) is the energy of the incident X-ray, \( E_0 \) is the threshold energy of a K-shell electron, \( \mu \) is the mass of the electron, and \( h \) is the Plank constant. The value of \( E_0 \) was first selected as the position of the half-height of the edge jump in each sample. The \( k^2 \chi_{\text{obsd}}(k) \) values

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Solvation Structures of Metal Ions

Inorganic Chemistry, Vol. 33, No. 9, 1994 1877

Figure 1. Observed EXAFS oscillation $\chi_{\text{obs}}(k)$ 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.

Figure 2. Fourier transforms $|G(R)|$ of $k^3\chi_{\text{obs}}(k)$ 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.

Results and Discussion

The EXAFS spectra $\chi_{\text{obs}}(k)$ 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 $k^3\chi_{\text{obs}}(k)$ values, which correspond to squares in Figure 3, were obtained by the inverse Fourier transformation in the $R$ range from 70 to 235 pm.

$G(R) = \sqrt{\frac{1}{2\pi^2}} \sum_{k_{\text{max}}} k^3 [\chi_{\text{obs}}(k)] W(k) \exp(-2ikR) dk$  \hspace{1cm} (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 $k^3\chi_{\text{obs}}(k)$ values. In order to refine the structure parameters, the model function $k^3\chi_{\text{obs}}(k)$ was fitted to the $k^3\chi_{\text{obs}}(k)$ function given by the single-electron and single-scattering theory (eq 3),

$x_{\text{obs}}(k) = \sum_j \left\{ \frac{\eta_j}{kR_j^2} \right\} \exp \left( \frac{-2\sigma_j k^2}{\lambda} \right) F_j(\pi,k) \sin(2kR_j - \alpha_j(k))$  \hspace{1cm} (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, $\eta_j$ is the number of scatterer $j$, $\sigma_j$ is the Debye–Waller factor, $\lambda$ 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.

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, 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 (6 = 3 M$^{-1}$ 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. 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 [Cu(hmpa)$_4$]$^{2+}$, [Cu(pzpo)$_4$]$^{2-}$ (pzpo = tripentylphosphine oxide), and [Cu(mno)$_4$]$^{2-}$ (mno = trimethylamine N-oxide), and are obviously different from those of square planar complexes, such as [Cu(acac)$_2$]$^{2-}$ (acac = acetylacetonate), [Cu(epo)$_4$]$^{2-}$ (epo = 4-ethoxyphenyldine N-oxide), and [Cu(pmpo)$_4$]$^{2-}$ (pmpo = diphenylphosphine oxide), and from those of tetrahedral complexes, such as [Cu(morpo)$_4$]$^{2-}$ (morpo = trimorpholinophosphine oxide), wavenumber at the absorption maximum ($\nu_{max}$ = ~11 000 cm$^{-1}$) and [CuX$_4$]$^{2-}$ (X is a halogen, $\nu_{max}$ = ~9000 cm$^{-1}$). Furthermore, there has been considerable interest in the relationship between the dihedral angles of pseudotetrahedral copper(II) complexes with CuO$_4$ and CuN$_4$ chromophores and their transition energies, and the absorption spectra in TMU are also similar to those of the copper(II) complexes of bidentate ligands ($\nu_{max}$ = ~13 000 cm$^{-1}$), such as N-tert-butylsalicylideneimin and heterocyclic secondary amine derivatives, which have the distorted tetrahedral structure ($D_4h$). With knowledge of their available spectral data, the four bands seem to be assigned to the transition from $\Gamma_2(\Gamma_4)$ to $\Gamma_2(\Gamma_4)$, $\Gamma_2(\Gamma_2)$, and $\Gamma_2(\Gamma_2)$ in the $D_4h$ symmetry. Thus, it is confirmed that the [Cu(tmu)$_4$]$^{2+}$ ion has the distorted tetrahedral structure ($D_4h$).

The specific spectrum for a TMU solution of the Ni(II) ion has been analyzed to have five bands at 8000 (6 = 4 M$^{-1}$ cm$^{-1}$).
Solvation Structures of Metal Ions

Inorganic Chemistry, Vol. 33, No. 9, 1994 1879

For the Fe(I1) ion in TMU, we can see absorptions at lower than 5000 and at 8600 (ε = 6 M 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 absorbtion pattern is similar to that of [Fe(m3po)(ClO4)](ClO4) (mpo = trimethylphosphine oxide),39 [Fe(m2ao)(ClO4)](ClO4) (m2ao = triethylarsine oxide),40 and [Fe(m2pp)(ClO4)](ClO4),41 which have Cu(I1) symmetry with the FeO2 chromophore. Thus, it is likely that the solvation structure of Fe(I1) ion in TMU is five-coordinate square pyramidal (C5v, 5E(P) = ~10 000 cm-1).

In this symmetry, the peak lower than 5000 cm-1 is assigned to the transition from T2 to A1, and the peak at 8600 cm-1 is from T2 to T1. However, since the five-coordinate Fe(I1) complexes with D5h symmetry (vmax ~ 5000 and ~10 000 cm-1)42 also have absorption maximums similar to those of the TMU solution, the clear distinction between C5v and D5h for the solvation structure of Fe(I1) ion in TMU is difficult to determine by a comparison of electronic spectra.

In the spectrum of the Mn(I1) ion in TMU, there are two peaks at 24 300 (ε = 0.4 M cm-1) 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 MnO	extsubscript{2} chromophore, such as [MnL2(OCO2)](L = a phosphine oxide or an arsine oxide, vmax = ~20 000, ~24 000, and ~29 000 cm-1).55 [Mn(m2pp)(ClO4)](ClO4) (mpo = bis(dimethylamino)phenylnaphthol, vmax = 6200 and 16 500 cm-1).49 Thus, it is acceptable that the structure of the solvated Co(I1) ion in TMU is four-coordinate tetrahedral.

The absorption intensity of transition at 16 700 cm-1 for the Co(I1) ion in TMU, however, is dissimilar to those of previously known regular tetrahedral complexes (ε = 300–500 M cm-1).28,45,48 According to the electronic absorption data for bis(dipivaloylmethanido)cobalt(II) (D2d, e)26,49 [Co(pip mocdo)(ClO4)] (pip = dipivaloylmethane, mocdo = monoprotonated 1-methyl- and 2-methylpiperazine) (vmax = 30–70, 50),29 tetrakis(disopropyl methylphosphonato) cobalt(II) (D2d, e = 63),51 [Co(Xe)2(mpmp)] (X = Cl- or Br-; mpmp = monoprotonated 1-methyl- and 2-methylpiperazine) (vmax = 60–90,52 and [Co(mpmp)X] (X = Cl- or Br-; mpmp = 1-phenyl-2,3-dimethyl-5-pyrazolone) (vmax = 70–80,53) the descending symmetry around Co(II) ion tends to lead the lower absorption intensity. Since the molar absorption coefficient of [Co(m2pp)X]2+ is close to those of the distorted tetrahedral compounds, the TMU solvate of Co(II) ion may have a distorted tetrahedral structure (D2d).


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,\textsuperscript{60} we can estimate the relative energies of the d orbitals in some symmetries. For the d\textsuperscript{8} Ni(II) ion, it can be calculated that the sum of the energies for occupied d orbitals is -10.0 \textit{Dq}(C\textsubscript{4v}) for C\textsubscript{4v} symmetry and -3.56 \textit{Dq}(T\textsubscript{d}) for \textit{Td} symmetry; i.e., the stabilization energy in C\textsubscript{4v} symmetry is expected to be larger than that in T\textsubscript{d} symmetry.\textsuperscript{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)\textsuperscript{57} However, according to the present results in TMU, the value of \textit{n} is 6 for In(III) ion and 5 for Mn(II) ion, and \textit{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);\textsuperscript{58} 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.\textsuperscript{19}

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