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Solvation Structures of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II), and Gallium(III) Ions in Methanol, Ethanol, Dimethyl Sulfoxide, and Trimethyl Phosphate As Studied by EXAFS and Electronic Spectroscopies

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Solvation structures of the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Ga(III) ions in methanol (MeOH), ethanol (EtOH), dimethyl sulfoxide (DMSO), and trimethyl phosphate (TMP) have been determined using extended X-ray absorption fine structure (EXAFS) spectroscopy. In MeOH, EtOH, and DMSO, the solvation structures of all metal(II,III) ions are 6-coordinate octahedral as in water, and the M−O bond lengths are similar to those in water. In the bulky solvent TMP, the 5-coordinate solvation structure is observed for the Zn(II) ion without ligand-field stabilization. The Ga(III) ion has the 6-coordinate solvation structure in TMP despite its smaller ionic radius than the Zn(II) ion because of the higher charge density on the Ga(III) ion. In the cases of the Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions, the electronic absorption spectra have been measured in MeOH, EtOH, and DMSO. All solutions for each metal(II) ion show a spectral pattern similar to that in water, which is consistent with the results of the EXAFS measurements.

Introduction

A metal ion in solvents is solvated by some solvent molecules, and knowledge of the solvation structure around the metal ion is very important for quantitative interpretation of the equilibrium and kinetic properties of the chemical reactions concerning the metal ion. The hydration structures of many mono-, di-, and trivalent metal ions in water were extensively investigated using X-ray and neutron diffraction methods and extended X-ray absorption fine structure (EXAFS) spectroscopy, and the results were thoroughly reviewed.[1,2] For the first-row transition metal(II) ions later than Mn(II), it is accepted that the hydration structure is 6-coordinate octahedral because there is the greatest electronic stability in the octahedral complex. Recently, solvation structures of the first-row transition metal(II) ions in some nonaqueous solvents have been studied, and it has been pointed out that the bulkiness of the solvent molecule reduces the coordination number of the metal(II) ion. For example, the coordination number of the Mn(II), Fe(II), and Ni(II) ions is 5 and that of the Co(II), Cu(II), and Zn(II) ions is 4 in the bulky solvent 1,1,3,3-tetramethylurea (TMU).[3] A similar decrease in solvation number is observed in the much bulkier solvent hexamethylphosphoric triamide (HMPA).[4] However, such a decrease is not seen in *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) except for the Zn(II) ion in DMA.[5] Thus, the reduction of the solvation number is interpreted as being the result of steric repulsion between the bound solvent molecules in the first coordination sphere of the metal(II) ion for these oxygen-donating solvents. The solvation structures in some nitrogen-donating solvents, such as 1-aminopropane (PA),[6,7] 1,2-diaminoethane,[8,9] 1,3-diaminopropane,[6] 3- and 4-methylpyridine,[10] and nitriles,[9,11] were progressively investigated. Interestingly, in the strong σ-donating solvent PA, the solvation equilibrium between octahedral and tetrahedral structures is observed for the Co(II) ion with d^7 electronic configuration, in which the steric repulsion of bound PA molecules is not expected.[7] As also seen for the Co(II) (4-coordinate pseudotetrahedral) and the Ni(II) (5-coordinate square pyramidal) ions in TMU,[3] the d electron configration of the metal(II) ion sometimes plays a key role in the selection of the solvation structure. Furthermore, as we have recently pointed out,[11,12] the M−N bond length of the solvated metal ion in nitrogen-donating solvents becomes longer according to the following order: nitriles with sp hybridizing nitrogen < pyridines with sp^2 hybridizing nitrogen < aliphatic amines with sp^3 hybridizing nitrogen. This is because the increase in the p character of the donating orbital of the solvent molecule causes expansion of the electron-density distribution. In the case of the Cu(I) and Ag(I) ions, the solvation structures in some nonaqueous solvents are 4-coordinate tetrahedral.[13−16] Thus, the electrostatic attraction between the M(I) ion and the solvent dipole does not overcome either the interligand steric repulsion or the entropic contribution needed to form a structure with a coordination number greater than 4, even if the solvent molecules are small in size.[15,16] On the other hand, the solvation structure of the In(III) ion in some nonaqueous, bulky solvents such as TMU, TMP, triethyl phosphate, and tributyl phosphate, is 6-coordinate octahedral as in water because of its high charge.[3,12] The solvation structure is also affected by the charge density on the metal ion. As shown in the findings previously described, the solvation number of the metal ion is determined by keeping a balance among the increasing contribution due to higher charge of the metal ion, the decreasing contribution due to bulkiness of the solvent molecule, and the ligand-field stabilization on the metal ion. In this study, to shed further light on the solvation phenomena of metal ions, we studied the solvation structures of the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Ga(III) ions in MeOH, EtOH, DMSO, and TMP by measuring the EXAFS and electronic absorption spectra. The structural characteristics of these metal(II,III) ions in these nonaqueous solvents of different

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levels of bulkiness will be demonstrated, and the bulkiness of the solvent molecules will be rationalized on the basis of the solvation structures. Whether the M−O bond length is affected by the type of donating oxygen atom will also be discussed.

Experimental Section

Solvents. Reagent-grade methanol (Wako), ethanol (Wako), dimethyl sulfoxide (Wako), and trimethyl phosphate (Wako) were dried over 4-Å molecular sieves and distilled before use. The water content in each solvent was confirmed to be less than 5×10^{-3} mol kg^{-1} by the Karl−Fisher method.

$M(H_2O)_6\cdot(CF_3SO_3)_2$ (M = Mn, Fe, Co, Ni, Cu, and Zn). $MnCO_3$ (Wako), iron sponge (Wako, 99.99%), $CoCO_3$ (Wako), $NiCO_3$ (Wako), CuO (Wako, 99.99%), and zinc metal (Wako, 99.995%) were respectively suspended in an aqueous solution of CF_3SO_3H (Wako, 98%). Each solution was stirred for a few days, and the residue was filtered. The filtrate was concentrated to obtain each hexahydrate salt. The number of water molecules contained in the salt was 6, which was determined by the molecular weight of the salt measured by EDTA titration. For $Fe(CF_3SO_3)_2\cdot 6H_2O$, all procedures were carried out under argon gas to prevent the oxidation of the Fe(II) ion.

$Ga(H_2O)_n\cdot(CF_3SO_3)_3$ (n = 9−10). The salt of $Ga(H_2O)_n\cdot(CF_3SO_3)_3$ using gallium metal (Wako, 99.99%) was obtained by the same procedure as described just above, where n was determined to be 9−10.

$Mn(tmp)_6\cdot(CF_3SO_3)_2$ and $Ga(tmp)_6\cdot(CF_3SO_3)_3$. An excess amount of *o*-ethylformate relative to water was added to each TMP solution of $Mn(H_2O)_6\cdot(CF_3SO_3)_2$ and $Ga(H_2O)_n\cdot(CF_3SO_3)_3$. The solution was stirred for a few hours at 50 °C, and the residue was filtered. The filtrate for Mn(II) was concentrated under reduced pressure to obtain the light red crystals of $Mn(tmp)_6\cdot(CF_3SO_3)_2$. The filtrate for Ga(III) was washed by dry diethyl ether, and the white crystals of $Ga(tmp)_6\cdot(CF_3SO_3)_3$ were obtained. The number of TMP molecules in both salts was confirmed to be 6 by EDTA titration.

$M(CF_3SO_3)_2$ (M = Mn, Fe, Co, Cu, and Zn). Hexahydrates of the Mn(II), Co(II), Cu(II), and Zn(II) ions were dried at 300 °C for a few hours to obtain the corresponding anhydrous salts. $Fe(H_2O)_6\cdot(CF_3SO_3)_2$ was dried at room temperature in vacuo to prevent the oxidation of the Fe(II) ion. The amount of the metal(II) ion was confirmed by the EDTA titration method.

Sample Solutions for Measurements of EXAFS and Electronic Absorption Spectra. Aqueous sample solutions of metal trifluoromethanesulfonates were prepared by dissolving the corresponding hydrates in doubly distilled water. In the case of the Ga(III) ion, 0.1 mol dm^{-3} CF_3SO_3H was added to prevent hydrolysis. To prepare the aqueous solution of $[Ga(ox)_3]^{3-}$ (ox = $C_2O_4^{2-}$), which was used as the standard sample for the EXAFS analysis, 2.1 g of $Ga(NO_3)_3\cdot mH_2O$ (Wako), 2.2 g of $(NH_4)_2C_2O_4$ (Wako), and 0.08 g of $H_2C_2O_4$ (Wako) were dissolved in water, where the pH was 1.87. Under the present experimental conditions, $[Ga(ox)_3]^{3-}$ was quantitatively formed in the solution, according to the reported stability constants of the oxalato complexes of the Ga(III) ion.[17] MeOH, EtOH, and DMSO solutions of the Mn(II), Fe(II), Co(II), Cu(II), and Zn(II) ions were prepared by dissolving the corresponding anhydrous $M(CF_3SO_3)_2$ in each solvent. On the other hand, MeOH, EtOH, and DMSO solutions of the Ni(II) ion were prepared by dissolving $Ni(H_2O)_6\cdot(CF_3SO_3)_2$ in each solvent, and the water contained in the solution was removed using 4-Å molecular sieves. It was confirmed by the Karl−Fisher titration method that the amount of water contained in the sample solutions was negligible relative to the concentration of the Ni(II) ion. TMP solutions of the Mn(II) and Ga(III) ions were prepared by dissolving the TMP solvates in TMP, respectively. In the case of the Fe(II), Cu(II), and Zn(II) ions, the corresponding anhydrous salts, $M(CF_3SO_3)_2$, were dissolved in TMP. In the case of the Co(II) and Ni(II) ion, the sample solutions were prepared as follows: Excess amounts of *o*-ethylformate relative to the containing water were added to the TMP solution of $M(H_2O)_6\cdot(CF_3SO_3)_2$ (M = Co and Ni). The solution was stirred for 1 h at 50 °C and concentrated at 60 °C under reduced pressure to remove the resulting *o*-ethylformate, ethanol, and ethylformate.[18] The solution obtained was then used for the measurements. The concentrations of the metal(II,III) ions in all sample solutions for the measurements of EXAFS and electronic absorption spectra were determined by EDTA titration and summarized in Tables S1 and S2 (S: Supporting Information), respectively.

Measurements. The sample solutions for the EXAFS measurements were adsorbed in porous glass disks (radius = 2 cm and thickness = 2 mm) which were sealed in a polyethylene bag to prevent moisture ingress and evaporation of the solvent. X-ray absorption spectra were measured at 295 K for all sample solutions and at various temperatures (281−311 K) for the TMP solution of the Zn(II) ion using the BL-6B and BL-12C stations at the Photon Factory of the National Laboratory for High Energy Physics.[19,20] The white synchrotron radiations were monochromatized by a monochromator with an Si(111) double crystal, which was detuned to 50%, 60%, 70%, 70%, 80%, 80%, and 90% of the maximal intensity at the K edge for Mn, Fe, Co, Ni, Cu, Zn, and Ga, respectively, to remove the higher-order reflection.[21] The incident and transmitted X-ray intensities (I_0 and I) were simultaneously measured by the ionization chambers with lengths of 17 and 31 cm, respectively. The ionization chamber for the I_0 measurement was filled with N_2 gas and that for the I measurement was filled with a 1:3 mixture of Ar and N_2 gas for the measurements at the Mn, Fe, and Co K edges and with a 3:17 mixture of Ar and N_2 gas at the Ni, Cu, Zn, and Ga K edges. Electronic absorption spectra were recorded on a V-570 spectrophotometer (JASCO) over the wavelength range 300−1400 nm at 298 K. Units of M^{-1} cm^{-1} (M ≡ mol dm^{-3}) are used for the molar absorption coefficient (ϵ), where the mol kg^{-1} was converted to M, knowing the density of the solutions.

EXAFS Data Analysis. The details of the EXAFS data analysis were the same as previously reported.[3,8,9,11,12] The structure parameters around the metal ion, such as the coordination number (N), the M−O bond length (R), and the Debye−Waller factor (σ), were analyzed by the least-squares calculation using the model function of EXAFS oscillation, $\chi_{calc}(k)$[22−28]

$$\chi_{calc}(k) = \sum_j \left\{\frac{N_j}{kR_j^{\,2}}\right\} \exp\left(-2\sigma_j^{\,2}k^2 - \frac{2R_j}{\lambda}\right) F_j(\pi,k) \sin\{2kR_j - \alpha_j(k)\} \quad (1)$$

where $F_j(\pi,k)$ is the backscattering amplitude from each of the N_j scatterers at distance R_j from the X-ray absorbing atom, σ_j is the Debye−Waller factor, λ is the mean free path of a photoelectron, and $\alpha_j(k)$ is the total phase shift. The values of $F_j(\pi,k)$ and $\alpha_j(k)$ were determined using the EXAFS spectra of the corresponding aqueous solution on the basis of the structure parameters previously determined[1,2] and used during the course of the structural analysis of the other sample solutions while optimizing the values of R_j, σ_j, and N_j as variables. Because the hydration structure of the Ga(III) ion was not available, we

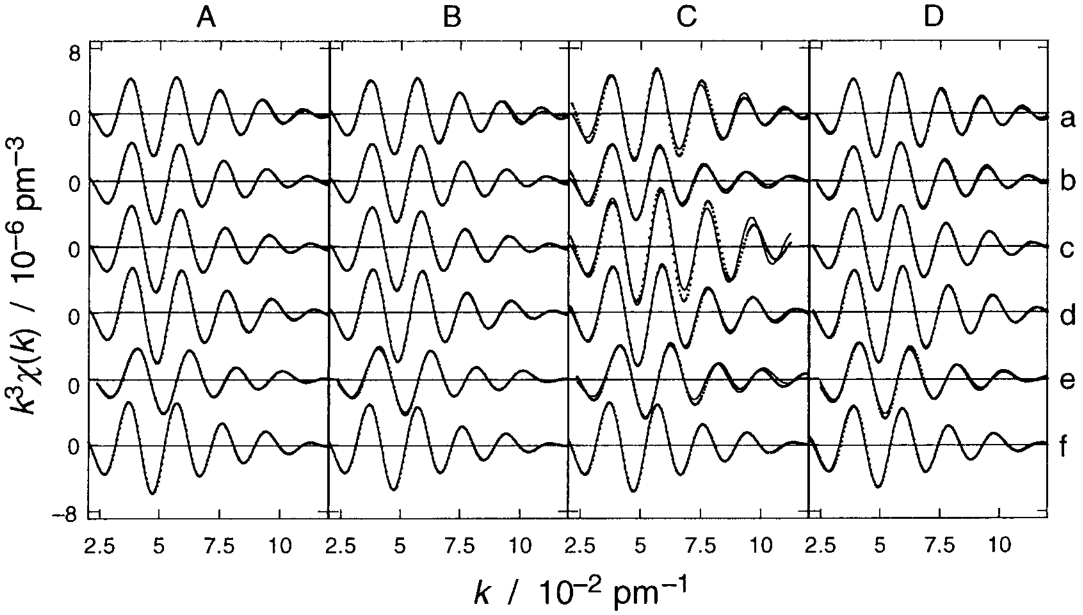

Figure 1. Fourier filtered $k^3\chi(k)$ values (dots) and $k^3\chi_{\text{calc}}(k)$ curves (solid lines) for Mn(II) (a), Fe(II) (b), Co(II) (c), Ni(II) (d), Cu(II) (e), and Zn(II) (f) in MeOH (A), EtOH (B), DMSO (C), and TMP (D).

used the aqueous solution of $[\text{Ga(ox)}_3]^{3-}$ as the structural standard. The structure of the complex in a single crystal was reported.[29] A curve-fitting procedure for the refinement of the structure parameters was applied to the Fourier filtered $k^3\chi_{\text{filt}}(k)$ values to minimize the error-squares sum, $\sum\{k^3\chi_{\text{filt}}(k) - k^3\chi_{\text{calc}}(k)\}^2$, using the program REX.[30]

TABLE 1: Structure Parameters around the Metal Ions[a]

		H_2O[b]	MeOH	EtOH	DMSO	TMP
Mn(II)[c]	N	6	5.8	5.8	6.1	5.9
	R/pm	217	217	217	216	216
	σ/pm		8.2	8.7	7.3	8.0
Fe(II)[d]	N	6	6.0	5.9	6.0	6.0
	R/pm	211	211	211	211	212
	σ/pm		9.2	9.4	10.1	9.9
Co(II)[e]	N	6	6.0	6.0	6.0	5.6
	R/pm	208	208	208	207	209
	σ/pm		9.7	9.9	6.1	8.7
Ni(II)[f]	N	6	5.9	6.0	6.0	5.8
	R/pm	205	205	205	205	205
	σ/pm		9.0	9.5	8.6	7.9
Cu(II)[g]	N	4 2	3.8[h]	3.9[h]	4.0[h]	3.9 1.7
	R/pm	197 229	197[h]	197[h]	196[h]	197 214
	σ/pm		9.3[h]	10.8[h]	8.6[h]	7.4 15.7
Zn(II)[i]	N	6	6.0	5.9	6.0	4.8[j] 5.0[k] 4.9[l] 5.0[m]
	R/pm	207	208	208	208	204[j] 205[k] 204[l] 205[m]
	σ/pm		8.6	9.1	8.8	9.5[j] 9.6[k] 9.8[l] 9.6[m]
Ga(III)[n]	N	5.9				6.0
	R/pm	197				197
	σ/pm	8.3				8.6

[a] At 295 K. Errors of N, R, and σ are estimated to be ca. 0.1, 1 pm, and 0.2 pm, respectively. [b] Reported values by means of X-ray diffraction technique except for the Ga(III) ion determined in this study. [c] $E_0 = 6.546$ keV and $\lambda = 607.5$ pm. [d] $E_0 = 7.121$ keV and $\lambda = 609.1$ pm. [e] $E_0 = 7.719$ keV and $\lambda = 653.3$ pm. [f] $E_0 = 8.343$ keV and $\lambda = 703.1$ pm. [g] $E_0 = 8.987$ keV and $\lambda = 536.1$ pm. The values in the upper row are those for the equatorial site and the lower are for the axial site. [h] Corresponding values for the axial site were not determined. [i] $E_0 = 9.665$ keV and $\lambda = 564.7$ pm. [j] At 295 K. [k] At 281 K. [l] At 302 K. [m] At 311 K. [n] $E_0 = 10.382$ keV and $\lambda = 1213.0$ pm.

Results

The observed EXAFS oscillations weighted by k^3 are shown in Figure S1 for the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions and in Figure S2A for the Ga(III) ion. The symmetrical oscillations are observed for the $k^3\chi_{\text{obsd}}(k)$ curves in water, whereas they are unsymmetrical in MeOH, EtOH, DMSO, and TMP. The $k^3\chi_{\text{obsd}}(k)$ values over the k range of (2−13) × 10^{-2} pm^{-1} were Fourier transformed, and the Fourier transformations, as shown in Figures S2B and S3, were obtained. The main peak observed in the Fourier transformations is attributable to the nearest bonding M−O interaction. In addition to the main peak, the longer interactions appear over the R range of 250−300 pm in MeOH and EtOH, 250−350 pm in DMSO, and 300−350 pm in TMP. They can be assigned to the nonbonding interactions with the next nearest neighboring atoms, C for MeOH and EtOH, S for DMSO, and P for TMP. The peak intensities of these nonbonding interactions in DMSO and TMP are relatively greater than those in MeOH, EtOH, DMF,[5] DMA,[5] and TMU,[3] in which the second sphere is composed of the carbon atom. In this study, because we focused on the local structure around the metal(II,III) center, only the main peaks were analyzed. In Figure S2C for the Ga(III) ion and Figure 1 for the other metal(II) ions, the Fourier filtered $k^3\chi_{\text{filt}}(k)$ values and the $k^3\chi_{\text{calc}}(k)$ curves calculated using eq 1 and the optimized structure parameters are depicted. The calculated curves are perfectly in agreement with the values of $k^3\chi_{\text{filt}}(k)$ in all k ranges used in the least-squares calculation ($3 \le k/10^{-2}$ pm$^{-1} \le 12$). The obtained structure parameters around the metal(II,III) centers are summarized in Table 1. In the case of a TMP solution of the Zn(II) ion, because the N value of 4.8 was obtained at 295 K, we carried out the variable-temperature EXAFS measurements in the temperature range between 281 and 311 K in order to evaluate whether the solvation structure of the Zn(II) ion at 295 K is 5-coordinate or there is solvation equilibrium between the 4- and 6-coordinate structures. The

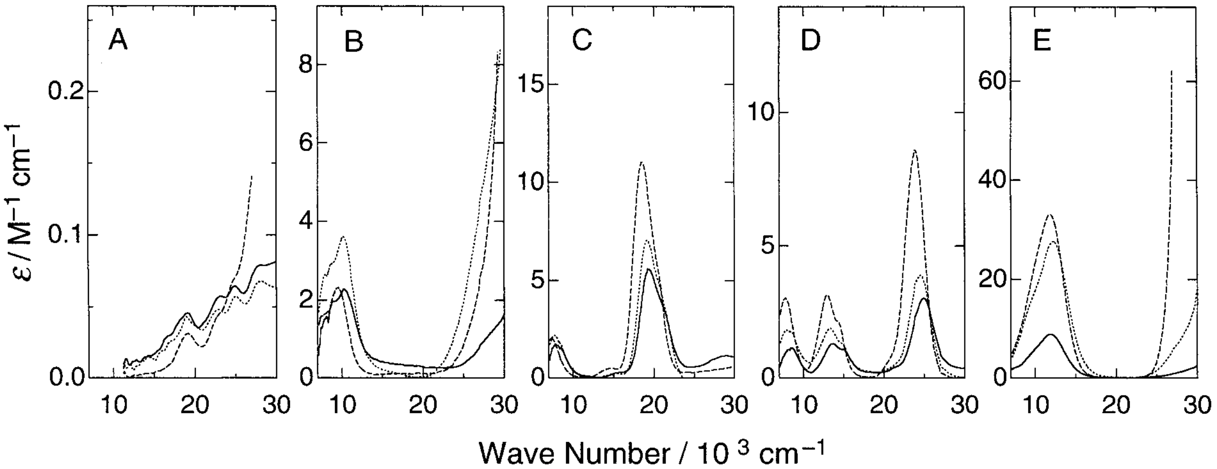

Figure 2. Electronic absorption spectra in MeOH (solid lines), EtOH (dotted lines), and DMSO (broken lines) for the Mn(II) (A), Fe(II) (B), Co(II) (C), Ni(II) (D), and Cu(II) (E) ions at 298 K.

TABLE 2: Spectral Data for the Metal(II) Ions at 298 K

M(II)	solvent	$\lambda_{max}/10^3$ cm^{-1} (ϵ_{max}/M^{-1} cm^{-1})
Mn(II)	H_2O^a	18.7, 23.1, 25.0, 28.0, 29.8
	MeOH	19.1 (0.05), 23.4 (0.06), 25.0 (0.07), 27.8 (0.08), 29.1 (0.08)
	EtOH	19.0 (0.05), 23.3 (0.05), 24.9 (0.06), 27.8 (0.07), 29.6 (0.07)
	DMSO	19.1 (0.03), 23.1 (0.05), 24.6 (0.07), 27.9 (0.17), 28.8 (0.17)
Fe(II)	H_2O^a	8.3, 10.4
	MeOH	8.6 (1.0), 10.2 (1.8)
	EtOH	8.7 (2.4), 10.1 (3.1)
	DMSO	7.9 (1.8), 9.6 (2.2)
Co(II)	H_2O^a	8.1, 19.4
	MeOH	8.0 (1.6), 19.3 (5.5)
	EtOH	7.8 (2.1), 19.1 (7.0)
	DMSO	7.4 (2.0), 18.6 (11.0)
Ni(II)	H_2O^a	8.5, 13.8, 25.3
	MeOH	8.3 (1.1), 13.7 (1.3), 25.0 (3.0)
	EtOH	8.0 (1.2), 13.3 (3.1), 24.5 (3.3)
	DMSO	7.8 (3.0), 13.0 (3.1), 23.8 (8.7)
Cu(II)	H_2O^a	12.4
	MeOH	11.8 (8.9)
	EtOH	12.2 (26.5)
	DMSO	11.8 (33.0)

[a] Reference 31.

obtained $k^3\chi_{obsd}(k)$ curves, Fourier transform magnitudes, $k^3\chi_{filt}(k)$ values, and $k^3\chi_{calc}(k)$ curves are shown in Figure S4, and the structure parameters are given in Table 1.

The observed absorption spectra for the Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions in MeOH, EtOH, and DMSO are depicted in Figure 2. The spectral data are summarized in Table 2, in which the corresponding values in water previously compiled are included.[31] These values are assigned to the d−d transitions.

Discussion

In all solvents used in this study, the coordination numbers of the Mn(II), Fe(II), Co(II), and Ni(II) ions are close to 6, and the M−O bond lengths are similar to the corresponding values in water (see Table 1). Furthermore, all solutions for each metal(II) ion show a spectral pattern of d−d electronic transitions similar to that in water as shown in Table 2. Therefore, it is concluded that the solvation structures of the Mn(II), Fe(II), Co(II), and Ni(II) ions are 6-coordinate octahedral as in water. These results are reasonable because the solvent molecules of MeOH, EtOH, DMSO, and TMP are not so bulky. The hydration structure of the Cu(II) ion has been confirmed to be axially-elongated, distorted-octahedral due to the Jahn−Teller effect. As in water, the four interactions with the Cu−O bond length of 197 pm are at the equatorial sites, and the two interactions of 214 pm are at the axial sites in TMP (see Table 1). Although the structure parameters for the axial sites of the Cu(II) ion in MeOH, EtOH, and DMSO could not be determined by EXAFS spectroscopy, the electronic absorption spectra clearly show the existence of the axial interactions on the Cu(II) ion in MeOH, EtOH, and DMSO (see Figure 2E). The solvation structure of the Cu(II) ion in these solvents is thus the axially-elongated distorted-octahedral. On the basis of the EXAFS analysis, the solvation structures of the Zn(II) ion in MeOH, EtOH, and DMSO are concluded to be 6-coordinate octahedral as in water. Interestingly, the solvation structure in TMP, however, is different from that in the other solvents. As shown in Table 1, the *N* value of the Zn(II) ion in TMP is ca. 5, and the *R* value is shorter than those in the other solvents by ~4 pm. A similar decrease in *N* and *R* has been observed for the Zn(II) ion in DMA, and the authors have pointed out that there is solvation equilibrium between the tetrahedral and octahedral structures.[5] Though the decrease in *N* can be certainly expected due to such a solvation equilibrium, the *N* value should be 5 in the case of the 5-coordinate solvation structure. Because the distinction is difficult using EXAFS measurement at a single temperature, we carried out variable-temperature EXAFS measurements between 281 and 311 K in order to experimentally clarify the solvation structure. In the case of the Co(II) ion, with an ionic radius similar to that of the Zn(II) ion, the solvation equilibrium between tetrahedral and octahedral is familiar due to the d^7 electronic configuration, and the enthalpy change, $\Delta H°$, from the octahedral species (CoS_6^{2+}, S = solvent) to the tetrahedral species (CoS_4^{2+}) is reported to be 36.1 kJ mol^{-1} in PA[7] and ca. 50 kJ mol^{-1} in DMA.[32] Although the $\Delta H°$ value for the octahedral−tetrahedral equilibrium of the Zn(II) ion may be different from those of the Co(II) ion, the reported $\Delta H°$ values for the Co(II) ion become a criterion to estimate the component change in the solution of the Zn(II) ion in TMP for the variable-temperature EXAFS measurements. According to the observed *N* value of 4.8 at 295 K, the mole ratio of ZnS_6^{2+}: ZnS_4^{2+} is estimated to be 4:6, and the conditional equilibrium constant, *K*, for the reaction of $ZnS_6^{2+} \rightleftharpoons ZnS_4^{2+}$ is ca. 1.5. If the value of $\Delta H°$ is approximated to be 15 kJ mol^{-1} as a lower limit, which is still smaller than half of the smaller value of 36.1 kJ mol^{-1} in the case of the Co(II) ion, for the solvation equilibrium of the Zn(II) ion in TMP, the entropy change, $\Delta S°$, is calculated to be 54 J mol^{-1} K^{-1}. The mole ratio of ZnS_6^{2+}/ZnS_4^{2+} should be varied from 5:5 at 280 K to 3:7 at 310 K, and the N and R values should be changed in response to the change in the component ratio. However, the finding that there is no change in the obtained structure parameters for the Zn(II) ion in TMP at 281, 295, 302, and 311 K indicates that there is no equilibrium between octahedral and tetrahedral. Furthermore, as pointed out in the previous study on the octahedral−tetrahedral solvation equilibrium for the Co(II) ion in PA,[7] the Fourier transformation function in the solvation equlibrium shows a distorted Co−N interaction peak because of the large difference (ca. 15 pm) in the Co−N bond lengths between $[Co(pa)_6]^{2+}$ (Co−N = 217 pm) and $[Co(pa)_4]^{2+}$ (Co−N = 201 pm). This difference in the Co−N bond lengths is consistent with the difference in the ionic radii of the Co(II) ions with the coordination numbers of 6 and 4, and the value of the ionic radius of the Zn(II) ion is similarly different by ca. 14 pm between the 4- and 6-coordinate species.[33] Thus, the distorted Fourier transformation should be observed for the Zn(II) ion in TMP, if there is solvation equilibrium. As is apparent from Figures S3 and S4B, any distortion of the main peak assigned to the Zn−O interactions is not observed. We have concluded, then, that the Zn(II) ion has the 5-coordinate solvation structure in TMP with a Zn−O bond length of 204 pm. Considering no ligand-field stabilization of the Zn(II) ion, the 5-coordinate solvation structure is completely acceptable, while the Co(II) ion, with an ionic radius similar to the Zn(II) ion, is 6-coordinate octahedral. As given in Table 1, the N values of the Ga(III) ion in water and in TMP are 5.9 and 6.0, respectively. The Ga(III) ion, thus, has the 6-coordinate octahedral structure with a Ga−O bond length of 197 pm in both solvents. Interestingly, in TMP the smaller Ga(III) ion is 6-coordinate, while the larger Zn(II) ion is 5-coordinate. This finding indicates that, as observed for the In(III) ion in TMU,[3] the higher charge of the metal ion makes the solvation number large, because the electrostatic attraction between the metal ion and solvent molecules exceeds the energetic loss due to the steric repulsion between the coordinating solvent molecules. On the other hand, we have recently reported that the Ga(III) ion in TMU, which is still bulkier than TMP, is 4-coordinate tetrahedral,[12] because the effect of the steric repulsion between the coordinating TMU molecules around the Ga(III) center overrides the effect of the charge on the center. The N value of 5.6 for the Co(II) ion in TMP at 295 K determined in this study is somewhat smaller than 6. A similar trend in N for the Co(II) ion has been observed in DMA.[5] Thus, we have measured the electronic absorption spectra of the Co(II) ion in TMP and DMA at a variety of temperatures to clarify the existence of the solvation equilibrium. As is apparent from the spectra shown in Figure S5, the absorption maxima are shifted to longer wavelengths and the molar absorption coefficients are significantly increased with increasing temperature. This characteristic clearly indicates that there is solvation equilibrium between the octahedral and tetrahedral structures. Because the 4-coordinate species is favored to exist at extremely high temperatures, the main species at room temperature is the octahedral one, and the solvation structure of the Co(II) ion in TMP and DMA at 295 K can be concluded to be 6-coordinate octahedral. In this study, we determined the solvation structures of a series of metal ions from Mn to Ga, belonging to the fourth row of the periodic table, in four oxygen-donating solvents. Considering the solvation structures already determined in other nonaqueous solvents, the bulkiness of the solvent molecules becomes clear. In MeOH, EtOH, DMSO, and DMF,[5] all of the metal ions take 6-coordinate octahedral solvation structures, while the decrease in the solvation number of the Zn(II) ion is observed in DMA[5] and TMP. A gradual decrease in the solvation number, from 5 to 4, with increasing atomic number of the metal ion is seen in TMU,[3] and the 4-coordinate tetrahedral structure is dominant in HMPA with the exception that the Mn(II) ion has a 5-coordinate structure.[4] In conclusion, the order in bulkiness of the solvent molecules is MeOH ∼ EtOH ∼ DMSO ∼ DMF < DMA ∼ TMP < TMU < HMPA, which was determined on the basis of the solvation number of the metal ions. It has been noticed that the M−N bond length of solvated metal ions varies with the kind of nitrogen atoms in the nitrogen-donating solvents.[11,12] There is, however, no difference in the M−O bond length of the hexasolvated metal ions in the solvents with sp^3 hybridizing oxygen, such as water, MeOH, and EtOH, and those with sp^2 hybridizing oxygen, such as DMSO, TMP, DMF, and DMA. This suggests that the electron-distribution area on different kinds of oxygen atoms in these oxygen-donating solvents is almost the same, which is consistent with the harder character of the oxygen atom relative to the nitrogen atom.

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Supporting Information Available: The concentrations of the metal(II,III) ions for the measurements of EXAFS (Table S1) and electronic absorption specta (Table S2), the observed EXAFS oscillations for the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions (Figure S1), the results of the EXAFS measurements for the Ga(III) ion (Figure S2), Fourier transform magnitudes for the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions (Figure S3), the results of the variable-temperature EXAFS measurements for the Zn(II) ion in TMP (Figure S4), and the electronic absorption spectra of the Co(II) ion in TMP and DMA (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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