

Table I. Fluorescence Maxima and Lifetimes of the Excited-State Tautomers I* and II*, and Transient Absorption Maxima and Lifetimes of the Ground-State Tautomers I and II

	excited-state tautomers		ground-state tautomers	
	I*	II*	I	II
fluores				
λ_{\max}	530 nm			
τ	0.65 ns ^a	<0.2 ns ^a		
TSLE fluores	518 nm ^b	530 nm ^b		
τ	0.7 ns ^c	<0.2 ns ^c		
trans absorb			60-70 μ s ^d	400 ns ^d
τ			380 nm	420 nm
			65 μ s	380 ns

^aDetermined at ~200 K. ^bDetermined by the TSLE time-resolved fluorescence spectra as mentioned in the text. ^cDetermined by the same method as (b) at 200 K. ^dDetermined by the variable delay technique of the TSLE fluorescence at room temperature.

as mentioned above. If these two types of tautomers may be generated in the excited state, there may be two respective H-bonding conformers in the ground state prior to the photoexcitation: H-bonding to carbonyl and ether oxygens of the pyrone ring in addition to the 7-hydroxyl group.²⁴ In the excited-state proton transfer of 4-methylumbelliferone, Shank et al.²⁵ suggested

(24) According to this argument, the 410-nm fluorescence shown in Figure 1 might consist of two fluorescence spectra of these conformers superimposed. However, the spectral confirmation is impossible at the present stage.

the protonation of the ring oxygen (pyrylium structure) of the α -pyrone ring as well as on the carbonyl oxygen. Since the pyrylium structure of 7-HF (II) seems to be more labile than the other (I), the short-lived tautomer in the ground state may be ascribed to structure II and the long-lived one to structure I. The observed decay times of the ground-state tautomers may reflect the reaction rates of the reverse proton transfer to the parent molecule in the ground state, because no significant photochemical reaction of 7-HF was observed to take place in the deaerated methanol solution. Therefore, the reverse proton transfer seems to take place faster in the tautomer II than I. On the other hand, if the interconversion between two tautomers is possible, the decay time of the short-lived tautomer II might include the interconversion rate of II to I. However, the reverse proton transfer of this tautomer II to the parent molecule N may be predominant compared with the interconversion to the other tautomer (II \rightarrow I), though the possibility of the interconversion between two tautomers in the ground state as well as in the excited state can not be entirely removed at the present stage. These arguments at least for the excited state will be confirmed by picosecond spectroscopy.

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Registry No. 7-HF, 6665-86-7; methanol, 67-56-1.

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Solvation Structure of Silver Ions and Atoms in Acetonitrile

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Abstract: Electron spin-echo modulation studies have been carried out for Ag atoms and Ag²⁺ ions in X-irradiated frozen acetonitrile solution of AgClO₄ to deduce the solvation-shell geometry for these paramagnetic species and the parent Ag⁺ ions. The results indicate that the solvation structure of the Ag²⁺ ion is the same as that of the parent Ag⁺ ion except for the solvation-shell radii. Four acetonitriles are bonded to the Ag²⁺ or Ag⁺ ion in a square-planar configuration by side-on coordination with their molecular dipoles oriented perpendicular to the plane. The distances from the Ag²⁺ ion and the Ag⁺ ion to the center of the C \equiv N bonds are estimated to be 0.20 and 0.23 nm, respectively. The solvation structure of the Ag atom is slightly different from that of the Ag⁺ ion. Four acetonitriles are bonded to the Ag atom in a tetrahedral configuration by side-on coordination. The acetonitriles are not bonded to the silver atoms and ions through nonbonding orbitals on the C \equiv N nitrogens, but σ -bonded through bonding π orbitals on the C \equiv N bonds, because the energy of the nonbonding orbitals is lower than that of the π orbitals. The reason for preferential solvation of Ag⁺ ions by acetonitrile in acetonitrile/water mixtures is discussed.

In mixed solvent, ions are preferentially solvated by one of the solvent components. This phenomenon is known as preferential solvation or selective solvation. Since the study of preferential solvation is not only of physicochemical interest but also of importance for elucidating chemical reactions in solutions,² many methods have been developed for determining the ratio of the solvent components in the solvation shell. These include conductance measurements, optical spectra measurements, NMR measurements,³ and ESR measurements.^{4,5}

One of the most typical examples of preferential solvation is Ag⁺ ions in acetonitrile/water mixture. Acetonitrile generally solvates metal ions very weakly,⁶ so that most metal ions are preferentially solvated by water. However, Strehlow and Koepp found that half of the water molecules around the Ag⁺ ions is replaced by acetonitrile in the mixed solvent of 20 mol % acetonitrile at room temperature.⁷ Alesbury and Symons studied the ESR spectra of Ag atoms and Ag²⁺ ions formed by electron gain

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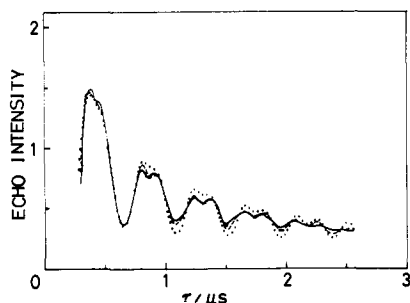


Figure 1. Comparison of the experimental and calculated ESE signals for Ag atoms in CD₃CN. The solid line shows the experimental ESE signal. The dotted line shows the best simulation for the experimental ESE signal under the assumption that four equivalent CD₃CN are bonded to the Ag atom by head-on coordination. The parameters for the calculation are $r = 0.34$ nm, $a = 0$, $n = 12$, and $D(\tau) = \exp(1.88 - 2.95 \times 10^3 \tau^{1/2} + 0.867 \times 10^6 \tau - 0.366 \times 10^{11} \tau^2)$. The dashed line shows the best simulation under the assumption that four equivalent CD₃CN are bonded to the Ag atom by side-on coordination. The parameters for the calculation are $r_1 = 0.29$ nm, $a_1 = 0.1$ MHz, $n_1 = 4$, $r_2 = 0.41$ nm, $a_2 = 0$, and $n_2 = 8$, and $D(\tau) = \exp(1.96 - 3.28 \times 10^3 \tau^{1/2} + 1.21 \times 10^6 \tau - 1.01 \times 10^{11} \tau^2)$.

and electron loss of Ag⁺ ions in the γ -irradiated mixed solvent at 77 K and concluded that each Ag⁺ ion, which is the precursor of the Ag atoms and the Ag²⁺ ions, is solvated by four equivalent acetonitriles and that no water molecule is included in the solvation shell even in a mixture of 50 mol % water.⁴ They suggested that four equivalent acetonitriles are bonded to the Ag atom and the Ag²⁺ ion in tetrahedral and square-planar configurations, respectively, with the molecular dipoles oriented toward the central atom or the ion. However, the detailed solvation geometries of silver ions and atoms in acetonitrile have not been clarified.

Recently we have applied electron spin-echo (ESE) spectroscopy for the study of preferential solvation of paramagnetic ions.⁸ Not only the ratio of the solvent components but also the number and the orientation of the solvent molecules in the first solvation shell have been determined by analyzing the nuclear modulation effects on the ESE signals. We also have determined the detailed solvation structures of Ag atoms in ice,^{9,10} glassy water,¹¹ and methanol¹² by using ESE spectroscopy.

Here we extend ESE studies to the solvation structure of Ag atoms and Ag²⁺ ions in acetonitrile in order to delineate reasons for preferential solvation of Ag⁺ ions by acetonitrile.

Experimental Section

Solution of 0.5 mol/dm³ AgClO₄ in perdeuterated acetonitrile (C-D₃CN) was sealed in Suprasil quartz tubes. The tubes were quickly frozen by liquid N₂ to form polycrystalline samples. The samples were X-irradiated at 77 K to a dose of 0.9 Mrd. ESR spectra of irradiated samples were measured at 77 K with a Varian E-109 ESR spectrometer. The two-pulse ESE signals of Ag atoms and Ag²⁺ ions were measured with a home-built X-band ESE spectrometer.¹² For increasing the lifetime of the ESE signals, the samples were kept at 4.2 K during the ESE measurements. The deuterium nuclear modulations on the ESE signals were analyzed by using a spherical averaging model¹³ combined with a nonlinear least-squares analysis.¹⁴ The experimental ESE signal was compared with the theoretical one by

$$ER = \frac{1}{N} \sum_{i=1}^N [V_{ex}(\tau_i) - D(\tau_i) \prod_{j=1}^n V_{th}(\tau_i, r_j, a_j)]^2$$

$$D(\tau_i) = \exp(d_0 + d_1 \tau_i^{1/2} + d_2 \tau_i + d_3 \tau_i^2)$$

where N is the number of data points, $V_{ex}(\tau_i)$ is the observed intensity of the ESE signal, τ_i is the time interval between the first 90° pulse and

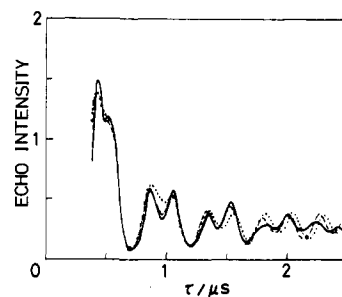


Figure 2. Comparison of the experimental and calculated ESE signals for Ag²⁺ ions in CD₃CN. The dotted line shows the best simulation for the experimental ESE signal under the assumption that four equivalent CD₃CN are bonded to the Ag²⁺ ion by head-on coordination. The parameters for the calculation are $r = 0.31$ nm, $a = 0.1$ MHz, $n = 12$, and $D(\tau) = \exp(3.99 - 8.14 \times 10^3 \tau^{1/2} + 4 \times 10^6 \tau - 0.263 \times 10^{12} \tau^2)$. The dashed line shows the best simulation under the assumption that four equivalent CD₃CN are bonded to the Ag²⁺ ion by side-on coordination. The parameters for the calculation are $r_1 = 0.26$ nm, $a_1 = 0.1$ MHz, $n_1 = 4$, $r_2 = 0.36$ nm, $a_2 = 0$, $n_2 = 8$, and $D(\tau) = \exp(1.91 - 2.32 \times 10^3 \tau^{1/2} - 6.03 \times 10^4 \tau - 0.26 \times 10^{12} \tau^2)$.

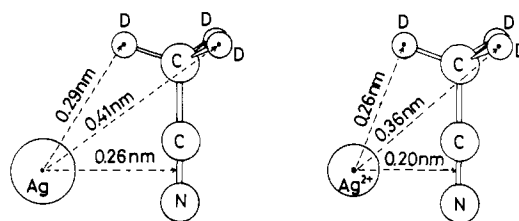


Figure 3. Suggested geometries for a first solvation shell CD₃CN around Ag atom and Ag²⁺ ion.

the second 180° pulse, $D(\tau_i)$ is an unknown monotonic decay function, $V_{th}(\tau_i, r_j, a_j)$ is the angular-averaged theoretical ESE intensity for j th magnetic nucleus with an electron spin-nuclear spin distance of r_j and an isotropic hyperfine coupling constant of a_j , and n is the number of nuclear spins surrounding the electron spin. The explicit representation of $V_{th}(\tau_i, a_j, r_j)$ has been given.¹⁰ The best set of parameters are determined by the equations

$$\partial ER / \partial d_0 = \partial ER / \partial d_1 = \partial ER / \partial d_2 = \partial ER / \partial a_j = \partial ER / \partial r_j = 0$$

The accuracy of the electron spin-nuclear spin distances determined by this analysis is about 0.01 nm.

Results

The solid line in Figure 1 shows the ESE signal of Ag atoms measured at 352 mT. We first simulated the experimental ESE signal under the assumption that 12 deuteriums are approximately equivalently interacting with a central electron spin; that is, four acetonitriles are approximately equivalently coordinated to the Ag atom with their molecular dipoles oriented toward the Ag atom. The dotted line in Figure 1 shows the best simulation under this assumption. Fitting is apparently unsatisfactory. To obtain better simulation, distances to the three methyl deuteriums in each acetonitrile were varied under the restriction that four acetonitriles are still approximately equivalently coordinated to the Ag atom. The best fit shown in Figure 1 with a dashed line corresponds to one Ag to methyl deuterium distance of 0.29 nm and the other two Ag to methyl deuterium distances of 0.41 nm. Assuming that the structure of the acetonitriles in the solvation shell is the same as in the bulk, the geometry of the acetonitrile coordinated to the Ag atom is deduced from the Ag-deuterium distances and is shown in Figure 3. The acetonitrile is bound to the Ag²⁺ ion by side-on coordination with its C≡N bond perpendicular to a line from the center of the C≡N bond to the Ag atom. The distance from the Ag atom to the center of the C≡N bond is 0.26 nm. From the figure it is obvious that the acetonitrile is not coordinated through a nonbonding orbital on nitrogen but is bonded through bonding and/or antibonding π orbitals of the C≡N bond.

The solid line in Figure 2 shows the ESE signal of Ag²⁺ ions obtained at the magnetic field of 315.5 mT. It can be seen that the nuclear modulation is quite different from that of the Ag

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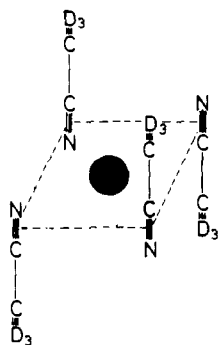


Figure 4. Suggested solvation geometry for Ag^{2+} and Ag^+ ions in CD_3CN . Four CD_3CN are bonded to the central silver ion (full circle) in a square-planar configuration by side-on coordination with their molecular dipoles oriented perpendicular to the plane. The distances from the silver ion to the center of the $\text{C}\equiv\text{N}$ bonds are 0.20 and 0.23 nm for the Ag^{2+} and Ag^+ ions, respectively.

atoms. It is comparatively deeper and has a double frequency component indicative of a strong electron spin-nuclear spin interaction. The best simulation for this modulation was obtained by using a geometrical picture that the Ag^{2+} ion is surrounded by four approximately equivalent deuteriums with the distance of 0.26 nm and eight approximately equivalent deuteriums with the distance of 0.36 nm. The coordination structure of the acetonitrile deduced from these distances is shown in Figure 3. The structure is analogous to that for the Ag atom. The distance from the Ag^{2+} ion to the center of the $\text{C}\equiv\text{N}$ bond is 0.20 nm. The difference between the solvation shell radii of the Ag atom and the Ag^{2+} ion is the same as that between the atomic radius of Ag (0.15 nm) and the ionic radius of Ag^{2+} (0.09 nm).

Discussion

Solvation Structure of Ag^{2+} Ions. Ag^{2+} ions show an ESR spectrum with g_{\parallel} larger than g_{\perp} , indicating a square-planar ligand configuration with an unpaired electron in a $d_{x^2-y^2}$ orbital on Ag^{2+} .⁴ Two configurations can be considered for the acetonitriles coordinated to the Ag^{2+} ion. One is a vertical configuration in which the $\text{C}\equiv\text{N}$ bonds are perpendicular to the plane including the Ag^{2+} ion and the acetonitriles. The other is a coplanar configuration in which the $\text{C}\equiv\text{N}$ bonds are parallel to the plane. The ESR and the ESE signals themselves make no distinction between the two configurations. However the coplanar configuration seems highly improbable because of repulsive steric interactions between the acetonitriles. The repulsive interactions are probably too strong even in the vertical configuration if all the methyl groups of the acetonitriles are aligned above or below the plane. As shown in Figure 4, a sterically reasonable configuration is attained by alternatively changing the direction of the molecular axis relative to the plane.

In this configuration four acetonitriles are σ -bonded to the Ag^{2+} ion by donating electron pairs in the bonding π orbitals on the $\text{C}\equiv\text{N}$ bonds to the Ag^{2+} ion. The order of orbital energies for the Ag^{2+} is $4d_{zx} = 4d_{yz} < 4d_{z^2} \approx 4d_{xy} < 4d_{x^2-y^2}$. The order of orbital energies for acetonitrile is $n < \pi < \pi^*$ where n , π , and π^* denote a nonbonding orbital on the $\text{C}\equiv\text{N}$ nitrogen, a bonding π orbital on the $\text{C}\equiv\text{N}$ bond, and an antibonding π orbital on the $\text{C}\equiv\text{N}$ bond, respectively.¹⁵ The semiffilled orbital of the solvated Ag^{2+} ion is therefore approximately given by $\Phi = a\phi(4d_{x^2-y^2}) + \sum b_i\phi_i(\pi)$. Since the energy of 4d orbitals of Ag^{2+} ion (-21.48 eV) is much lower than that of the π orbital (-12.2 eV), a considerable amount of spin density is expected to be in the π orbitals. The Ag^{2+} ion therefore shows a strong ^{14}N hyperfine coupling of ca. 70 MHz¹⁶ and an axially symmetric ESR spectrum with $g_{\parallel} > g_{\perp}$ characteristic to d^9 ions under D_{4h} symmetry.

The acetonitriles could be π -bonded to the Ag^{2+} ion by back-donation of electron pairs in the nonbonding $4d_{zx}$ and $4d_{yz}$ orbitals

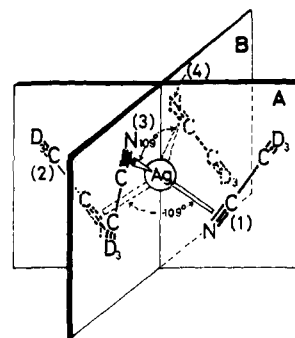
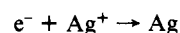
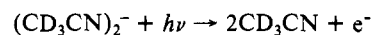


Figure 5. Suggested solvation geometry for Ag atom in CD_3CN . Four CD_3CN are bonded tetrahedrally to the central Ag atom by side-on coordination. The principal molecular axes of CD_3CN (1) and CD_3CN (2) are on the plane A, whereas those of CD_3CN (3) and CD_3CN (4) are on the plane B which is perpendicular to the plane A. The distance from the Ag atom to the center of the $\text{C}\equiv\text{N}$ bond is 0.26 nm for all the four CD_3CN .

to the π^* orbitals on the $\text{C}\equiv\text{N}$ bonds. However, the back-donation may not be important because the energy of the 4d orbitals is about 17 eV lower than that of the π^* orbitals.¹⁷

Solvation Structure of the Ag Atom. Since the unpaired electron of the Ag atom is mostly in a 5s orbital, it is not straightforward to determine whether the four equivalent acetonitriles are in a square-planar configuration or a tetrahedral configuration. However, absence of any marked anisotropy on the ESR spectrum suggests that the four acetonitriles are in the tetrahedral configuration.¹⁸ If the Ag atom is in the square-planar configuration, electron pairs in the $4d_{zx}$ and $4d_{yz}$ orbitals can be back-donated to four π^* orbitals on the $\text{C}\equiv\text{N}$ bonds, producing two sets of three-center two-electron π -bonding. Since the semiffilled orbital in this configuration is the 5s orbital, the Ag atom is expected to show an isotropic ESR spectrum with no ^{14}N hyperfine coupling and a very strong ^{107}Ag or ^{109}Ag hyperfine coupling similar to that of a free Ag atom with no coordinated molecule. Although the yield was too low to detect the ESE signal, the Ag species giving the ESR spectrum similar to that of the free Ag atoms was observed after 4.2 K photoillumination of the 4.2 K X-ray irradiated sample.¹⁶ The reaction taking place during the photoillumination was interpreted as follows:



After annealing at 77 K, this Ag species was converted to the Ag species which we observed in the present investigation. Therefore it is concluded that the Ag atoms generated at 4.2 K by the photoillumination are in the square-planar configuration and are converted to those in the tetrahedral configuration by the annealing at 77 K. In the tetrahedral configuration the four acetonitriles can be π -bonded to the Ag atom by donating electron pairs in the π orbitals to four sp^3 hybrid orbitals on the Ag atom. The semiffilled orbital in this configuration is approximately given by $\Phi = a\phi(5s) + \sum b_i\phi_i(\pi)$. Since the energy of the 5s orbital (-7.57 eV) is higher than that of the π orbital, the spin density in the orbitals is expected to be much lower than that in the 5s orbital. The Ag atom in this configuration shows an isotropic ESR spectrum with a weak ^{14}N hyperfine coupling, which consists with the observed ESR spectrum of the Ag atoms generated at 77 K.^{16,18} The suggested solvation geometry of the Ag atom is shown in Figure 5.

Solvation Structure of Ag^+ Ions. Since no ESR and ESE data are available for Ag^+ ions, it is impossible to obtain direct information on the solvation structure of the Ag^+ ions. However, we conclude that the Ag^+ ion coordinates four acetonitriles in the same manner as the Ag^{2+} ion because of the following reasons.

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(1) The number of solvating acetonitriles for the parent Ag^+ ions should be the same as that for the Ag^{2+} ions and the Ag atoms at 77 K. (2) Ag atoms in the square-planar configuration observed after photoillumination at 4.2 K is considered to retain their original Ag^+ coordination environment. (3) The repulsive steric interactions between the four acetonitriles are minimized by the square-planar configuration shown in Figure 4.

In this configuration the four acetonitriles are σ -bonded by donating electron pairs in the π -orbitals to four dsp^2 hybrid orbitals on the Ag^+ ion. Back-donation of the nonbonding $4d_{zx}$ and $4d_{yz}$ electrons may also contribute to the coordination.

Since the difference between the solvation shell radii of the Ag^{2+} ion and the Ag atom is the same as that between the ionic radius of Ag^{2+} and the atomic radius of Ag, the difference between the solvation shell radii of the Ag^{2+} and the Ag^+ ions should be the same as that between the ionic radii of Ag^{2+} and Ag^+ . When an ionic radius of 0.12 nm is used for the Ag^+ ion, the distance between the Ag^+ ion and the center of the $\text{C}\equiv\text{N}$ bonds is estimated to be 0.23 nm.

Ag atoms and Ag^{2+} ions are also formed by X-ray irradiation at 4.2 K. Although the yields of the Ag atoms and the Ag^{2+} ions are much lower, the ESR parameters for these species at 4.2 K are essentially the same as those at 50 or 77 K.¹⁶ Since the solid acetonitrile might be rigid enough at 4.2 K to prevent diffusion and rotation of acetonitrile, it seems difficult that the solvation geometry is changed from the square-planar configuration to the tetrahedral configuration by electron gain of the Ag^+ ion. However, the ESR spectrum indicates that the solvated Ag atom is in the tetrahedral configuration even at 4.2 K. The change of the solvation geometry is probably induced by the energy released by the reaction with Ag^+ ions and energetic secondary electrons produced by X-ray irradiation. It should be noted that the change of the solvation geometry from the square-planar configuration in Figure 4 to the tetrahedral configuration in Figure 5 can be attained by rotating the acetonitriles merely 35° from the original positions.

In the previous report¹⁶ Kevan et al. suggested that the solvation process of the Ag atom brings the four acetonitriles closer to the Ag atom, which leads to some delocalization of the unpaired electron spin density from the Ag atom to the solvent molecules. However, the present investigation strongly suggests that the delocalization is caused by the change of the coordination from the square-planar configuration to the tetrahedral one.

It is interesting to compare the coordination structure of isocyanides ($\text{RN}\equiv\text{C}$) with that of acetonitrile. Isocyanides are known to be coordinated strongly to transition-metal ions with their molecular dipoles oriented toward the ions by donating nonbonding electrons on the $\text{N}\equiv\text{C}$ carbons to the metal ions and/or accepting nonbonding d electrons on the metal ions to the antibonding π orbitals on the $\text{N}\equiv\text{C}$ carbons. Therefore the $\text{N}\equiv\text{C}$

bonds act concordantly as dipoles and ligands on solvating the metal ions. Such a concordancy is observed in many solvents such as water and alcohols. In the present study it is concluded that the molecular dipole of acetonitrile is not oriented toward the Ag^+ ion. This indicates that the $\text{C}\equiv\text{N}$ nitrogen does not donate its nonbonding electrons to the metal ion or accept back-donated d electrons to its antibonding orbital. This is because the energy of the nonbonding orbital is lower than that of π orbital in acetonitrile. The $\text{C}\equiv\text{N}$ bond dipole (3.5 D) or the molecular dipole of acetonitrile (3.9 D) acts as a more or less isolated dipole not much involved in the coordination interactions with metal ions.

To understand the solvation geometry in acetonitrile we may consider the electrostatic interactions between a metal ion and the molecular dipoles, repulsive steric interactions between the solvating acetonitriles, and the coordination of the acetonitriles to the metal ion by electron donation or back-donation. The electrostatic interactions and the steric interactions are optimized in the configuration with the molecular dipoles oriented toward the metal ion. However the acetonitriles cannot be coordinated to the metal ion because the direction of coordination is perpendicular to that of the molecular dipole. The electrostatic interactions and the steric interactions increase with decreasing radius of the metal ions. Small metal ions therefore prefer a configuration in which the molecular dipoles are oriented toward the ions. In this configuration the acetonitriles act only as molecular dipoles in the solvation interactions, so they only weakly solvate the metal ions. The electrostatic interactions and the steric interactions are decreased by increasing the radius of the metal ions. If the coordinate bond is strong enough to compensate for the decrease in the electrostatic interactions and the increase in the repulsive steric interactions, the acetonitriles can be coordinated to large metal ions with their molecular dipoles perpendicular to the direction of the coordination which is the case we deduce for Ag^+ . The coordinate bond is sufficiently strong for Ag^+ ions because the bond is strengthened by back-donation of nonbonding 4d electrons. This is presumably the main reason why Ag^+ ions are preferentially solvated by acetonitrile in the acetonitrile/water mixture. Since the charge-dipole interactions do not contribute much to the solvation of the Ag^+ ions, the acetonitriles can solvate the Ag atoms and the Ag^{2+} ions without major change of the solvation geometry.

In conclusion acetonitrile is an ideal *dipole solvent* for small metal ions because the direction of the molecular dipole is perpendicular to the direction of the π orbitals which have the potentiality of forming a coordinate bond with a large metal ion.

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Registry No. Ag, 7440-22-4; acetonitrile, 75-05-8.