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Solvent Influence on UV, ^{59}Co, and ^{13}C NMR of $[Co(CN)_6]^{3-}$ and Its Solvation Site

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The electronic absorption (UV) spectrum, ^{59}Co, and ^{13}C NMR of potassium hexacyanocobaltate(III), $K_3[Co(CN)_6]$, were measured in water and a variety of organic solvents: ethylene glycol, methanol, formamide, ethanol, chloroform, nitromethane, dichloromethane, dimethyl sulfoxide, acetonitrile, *N,N*-dimethylformamide, benzonitrile, and nitrobenzene. The complex salt was dissolved in organic solvents by macrobicyclic polyether, cryptand 222. It was found that the spectra are influenced by the solvent, and vary according to the electrophilic ability (Gutmann's acceptor number) of solvents. Especially, the ^{13}C NMR chemical shifts of coordinated cyano carbons (octet) have shifted downfield as the acceptor number becomes larger. This means that the solvent influence is caused by direct interaction between the ligand CN^- and solvent molecules as electron acceptors. The result concerning the linear correlation between the solvent influence on the peak position (nm) of the first d-d transition band and on the chemical shift of ^{59}Co NMR suggests that this influence is due to the d-d transition-energy change of $[Co(CN)_6]^{3-}$ by solvation. Finally, the plausible structure of the outersphere complex of $[Co(CN)_6]^{3-}$ with solvent molecules is proposed on the basis of the result obtained and an examination of molecular models.

In this work, we found that the UV, ^{59}Co, and ^{13}C NMR of $K_3[Co(CN)_6]$ are fairly solvent-dependent. This solvent dependence is due to an outersphere interaction between the complex anion and solvent molecules, since this complex anion is inert and stable against the ligand substitution or a redox reaction in solvents without light. The innersphere coordination has so far been investigated in photochemistry while studies of outersphere coordination have been very few.[1] This is because the outersphere coordination of solvent molecules is flexible, causing the structure of this outersphere complex to be merely speculative. It is therefore essential to clarify what kind of interaction exists between $[Co(CN)_6]^{3-}$ and solvent molecules for investigating the solvent influence on the spectra of $K_3[Co(CN)_6]$. As for the other complexes, it has been investigated that the d-d transition spectrum,[2] the circular dichroism spectrum,[3] ^{59}Co NMR,[4] and ^{13}C NMR[5] of $[Co(edta)]^-$ (edta=ethylenediaminetetraacetate), are remarkably subject to solvent influence through hydrogen-bonded solvation in a solvent of great electrophilic ability (e.g. H_2O and methanol). Then, the influence of the solvent could be quantitatively estimated by the use of acceptor numbers, which were proposed by Mayer, et al. as a measure of the electrophilic ability of solvents.[6] The $[Co(edta)]^-$ anion of C_2 symmetry shows a broad ^{59}Co NMR signal and ambiguity in the peak position of the UV spectra; the symmetry of $[Co(CN)_6]^{3-}$ is rather high (Oh symmetry). We can thus easily compare the UV and ^{59}Co NMR spectra with the electronic states.

In the present work, the solvent influence of $K_3[Co(CN)_6]$ was investigated on the electronic spectra, ^{59}Co NMR, and ^{13}C NMR spectra. We describe (1) the correlation between the solvent influence on the spectra or the d-electronic state of the cobalt(III) ion and the electrophilic ability of solvent molecules, and (2) what kind of interaction between solvent molecules and $[Co(CN)_6]^{3-}$ plays an important role in solvent influence.

Experimental

Materials. $K_3[Co(CN)_6]$ was prepared by the usual method.[7] The purity of this complex was checked by spectroscopic methods. The organic solvents were of the purest commercial grade available and were used without further purification. The solvents used here are as follows: water, ethylene glycol, methanol, formamide, ethanol, chloroform, nitromethane, dichloromethane, dimethyl sulfoxide, acetonitrile, *N,N*-dimethylformamide, benzonitrile, and nitrobenzene.

Measurements. Electronic Spectrum: The electronic absorption spectra were measured at ambient temperature on the solutions of $K_3[Co(CN)_6]$ (0.004 M: M=mol dm^{-3}) for water, and for organic solvents containing cryptand 222 (0.013 M: the amount of 3.3 times for the concentration of the complex ion and 1.1 times for that of K^+ ion). A Shimadzu UV-240 recording spectrometer was used for this measurement. The spectrum is not influenced by the addition of various amounts of cryptand 222 or by a change in the concentration of the cobalt(III) complex, and also by a change in the temperature.

^{59}Co NMR: The ^{59}Co NMR spectra were recorded on a 0.1 M solution of $K_3[Co(CN)_6]$ at 25 °C. Solutions of organic solvents were prepared by the addition of an excess amount of cryptand 222 (3.3 times of amount). The ^{59}Co chemical shift is slightly dependent on the concentration of the complex. Therefore, measurements were carried out in solutions of various concentrations: 0.1, 0.05, 0.01, and 0.001 M. A JEOL JNM-GX400 NMR spectrometer was operated in a Fourier transform mode at 94.862 MHz. The 10-mm NMR tube used here contained $K_3[Co(CN)_6]$ in D_2O as a reference; the sample solutions for the NMR measurements were kept in a 5-mm tube that was fixed inside a 10-mm tube during accumulation. The signals appeared quite sharply,

and the spectrum was obtained after 16—64 accumulation of 0.1 sec pulse interval.

^{13}C NMR: The ^{13}C NMR were obtained at ambient temperature for the 0.1 M solutions that were also prepared by the addition of cryptand 222 (0.33 M). A JEOL JNM-GX400 NMR spectrometer was operated in the Fourier transform mode at 100.535 MHz. Dioxane in D_2O, which was sealed in a 1-mm tube and kept inside a 5-mm sample tube, was taken as an external reference (67.4 ppm from TMS). Pulse intervals of 3—30 s were used and each spectrum was obtained after 5000—10000 scans. The chemical shifts were not influenced by changes in the amount of added cryptand 222, the concentration of the cobalt(III) complex, and temperature.

In this work, the author payed attention to the shielding of the sample solution from light. Complex $K_3[Co(CN)_6]$ is somewhat sensitive to UV radiation, as is well-known. It is confirmed that there is no change in the observed value during measurements under the conditions used here.

Results and Discussion

Electronic Spectra in a Variety of Solvents. The electronic spectra of $K_3[Co(CN)_6]$ in water, ethanol, chloroform, and acetonitrile are shown in Fig. 1. The bands in this figure correspond to the first d-d transition (A_{1g}-T_{1g}) of a cobalt(III) center. This figure suggests that the peak positions of the first d-d transition band appear in the shortest wavelength region in water of these solvents. Since the $[Co(CN)_6]^{3-}$ anion is inert and stable in these solvents under the conditions used, the difference in the peak position is due to the outersphere interaction between the complex anion and solvent molecules.

Since $[Co(CN)_6]^{3-}$ is an anion, this solvent influence could be correlated with the electrophilic ability of solvents. The author estimates this influence on the basis of the acceptor number (*AN*) that was proposed by Mayer et al.[6] as a measure of estimating the electrophilic ability of solvents. These *AN* values of solvents were determined on the basis of ^{31}P NMR chemical shifts of triethylphosphine oxide ($(C_2H_5)_3P{=}O$) in solvents. The acceptor number indicates that a solvent having a large *AN* value is a strong electron acceptor. Therefore, solvent molecules could interact strongly with an anion like $[Co(CN)_6]^{3-}$ if the solvent has a large value of the acceptor number.

All data of the peak positions[8] obtained are presented in Table 1 for a variety of solvents: H_2O, ethylene glycol (EG), methanol (CH_3OH), formamide (FA), ethanol (C_2H_5OH), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethyl sulfoxide (Me_2SO), acetonitrile (CH_3CN), and *N*,*N*-dimethylformamide (DMF). This table also includes the acceptor numbers (*AN*).

This table indicates that the peak positions of the $[Co(CN)_6]^{3-}$ shift to a shorter wavelength as the accep-

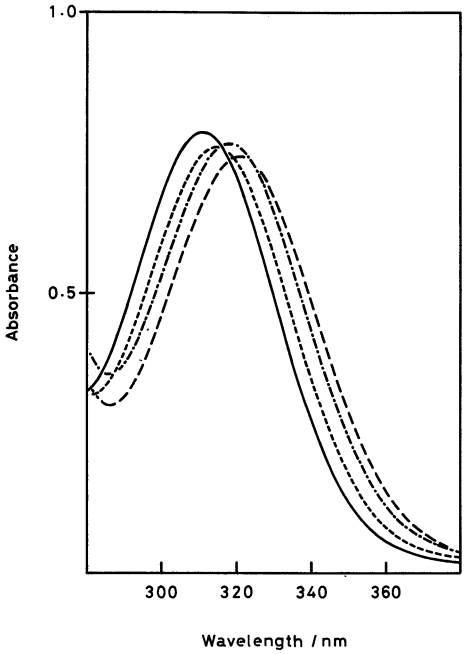


Fig. 1. Electronic absorption spectra of $K_3[Co(CN)_6]$ in water (——), ethanol (----), chloroform (— - —), and acetonitrile (— —).

Table 1. The Peak Positions of the d-d Transition Band and the Chemical Shifts of Cobalt-59 and Carbon-13 NMR of $K_3[Co(CN)_6]$ in a Variety of Solvents

Solvent	*AN*[a]	λ_1/nm[b]	λ_2/nm[c]	$\delta(^{59}Co)$/ppm	$\delta(^{13}C)$/ppm
H_2O	54.8	311.5	257.0	0	139.8
EG		312.5	258.0	39	
CH_3OH	41.3	313.5	258.0	69	138.7
FA	39.8	314.5		74	
C_2H_5OH	37.1	314.5	259.0	109	138.2
$CHCl_3$	23.1	318.0			
CH_3NO_2	20.5			260	137.1
CH_2Cl_2	20.4	318.5		262	137.5
Me_2SO	19.3	321.0		289	137.2
CH_3CN	18.9	320.5	263.0	293	137.5
DMF	16.0	322.5		352	137.4
C_6H_5CN	15.5			315	
$C_6H_5NO_2$	14.8			305	

a) *AN* refers to the acceptor number of the solvent. b) ±0.5 nm. c) ±0.5 nm.

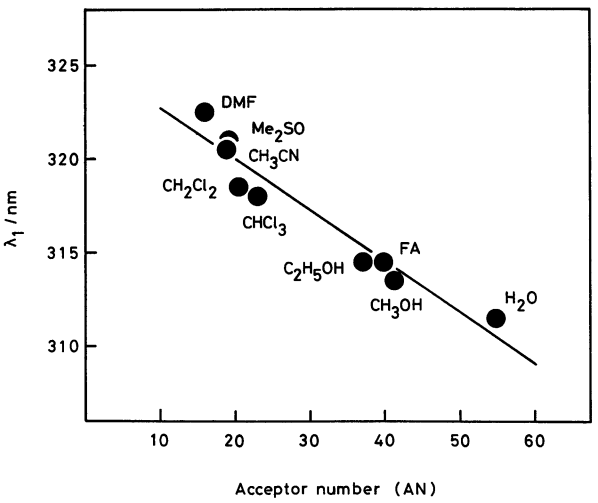


Fig. 2. The correlation between the peak positions (λ_1 in Table 1) in the electronic spectrum and the acceptor numbers (AN) of the solvents.

tor number (AN) increases and the solvent interacts strongly with this anion. Furthermore, as shown in Fig. 2, a plot of the λ_1 values in Table 1 against the acceptor numbers of solvents gives a straight line (the correlation coefficient is −0.965).[9] The linearity of the line suggests that the contribution of the solvent molecules to the peak position (λ_1 value) is linearly correlated to the acceptor number of the solvent. The λ_1 value of the peak position in the solvent was calculated by the following equation (error bars are one standard deviation):

$$\lambda_1 = \lambda_1^\circ - (0.272 \pm 0.028) \times AN \quad (1)$$

where λ_1° and AN refer to the peak positions (λ_1°=325.4±0.9 nm determined by a linear least-squares analysis) in hexane as a standard solvent (AN=0) and the acceptor number of the solvent, respectively. The first term in this equation could correspond to the inherent peak position of the first d-d transition band for $[Co(CN)_6]^{3-}$ that is not solvated and the second term to the contribution of solvating molecules. Therefore, this estimation leads to the result that the contribution of solvating molecules to the λ_1 value in the first d-d transition band is linearly correlated to the electrophilic ability of the solvent. Also, the interaction with water molecules of the largest acceptor number (54.8) makes this value shift to the shortest wavelength and induces the largest energy split of a d-d transition. This should be due to the largest electron-withdrawing effect of water molecules.

The peak position (λ_2) of the second d-d transition band was also obtained for H_2O, EG, CH_3OH, C_2H_5OH, and CH_3CN (Table 1). On the basis of the λ_1 and λ_2 values, the interelectronic repulsion parameter (Racah parameter: B) could be determined for H_2O, EG, CH_3OH, C_2H_5OH, and CH_3CN as follows; B=460, 456, 463, 460, and 461, respectively.[10] According to the literature, this parameter corresponds to an expansion of the d-orbital of the cobalt(III) center and the covalency in Co-C bonding; the expansion becomes great as the B value decreases. However, parameter B seems to be independent of the solvent in this case. This result indicates no drastic expansion of the d-orbital by an electron-withdrawing effect of solvent molecules, though a more detailed examination and data should be essential.

Correlation between the Peak Positions in Electronic Spectra and the Chemical Shifts in the ^{59}Co NMR. If the energy of the d-d electronic transition of $[Co(CN)_6]^{3-}$ could be changed by the interaction between the solvent molecules and this complex anion, the ^{59}Co NMR chemical shifts should also vary according to a change of the electronic spectrum. This is because the chemical shift of ^{59}Co NMR is correlated to the peak position in the electronic spectrum, as shown in the following equation (which is abbreviated):[11]

$$\delta(^{59}Co) \propto 1/\Delta E \quad (2)$$

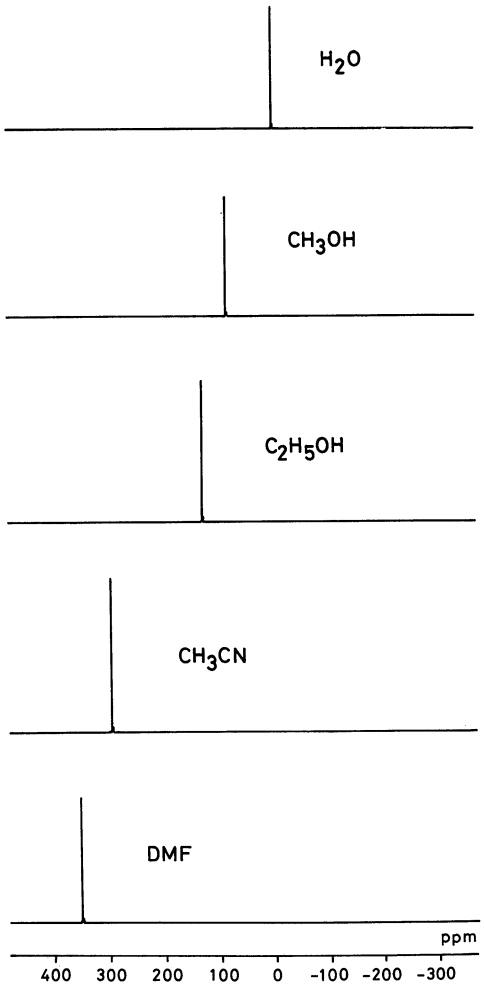


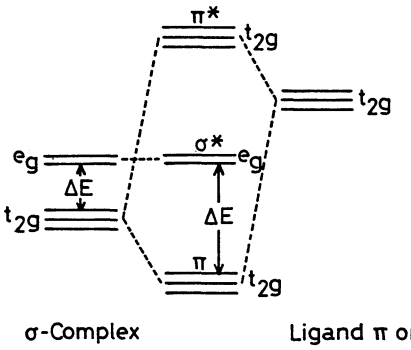
Fig. 3. ^{59}Co NMR spectra of $K_3[Co(CN)_6]$ (0.1 mol dm^{-3}) in a variety of solvents.

where $\delta(^{59}Co)$ and ΔE are the ^{59}Co chemical shift and the energy difference for the first d-d transition band of the cobalt(III) complex, respectively.

Figure 3 shows the ^{59}Co NMR spectra of $K_3[Co(CN)_6]$ in H_2O, CH_3OH, C_2H_5OH, CH_3CN, and DMF. In all solvents, only one sharp signal appears. The chemical shifts of the ^{59}Co NMR are fairly solvent-dependent. The chemical shifts obtained are shown in Table 1; the solvents used were H_2O, EG, CH_3OH, FA, C_2H_5OH, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, and $C_6H_5NO_2$. The chemical shifts are also shifted upfield as the concentration of the complex decreases. This may be due to the ion association between $[Co(CN)_6]^{3-}$ and K^+ with cryptand 222. The chemical shifts, which are obtained by extrapolation to the concentration zero, should be the value without any influence of the counter cation. Therefore, the extrapolated values are listed in Table 1 instead of the observed values.

It seems that the ^{59}Co chemical shifts are linearly correlated to the λ_1 values in Table 1. In order to confirm this correlation, in Fig. 4 are plotted the chemical shifts ($\delta(^{59}Co)$) against the λ_1 values of the first d-d transition band (A_{1g}-T_{1g}) in the corresponding solvents: H_2O, EG, CH_3OH, FA, C_2H_5OH, CH_2Cl_2, Me_2SO, CH_3CN, and DMF. It is clear that the $\delta(^{59}Co)$ values are linearly correlated to the λ_1 value (the intercept is −9968.75 ppm and the slope is 32.01). This result indicates that the d-d transition energy (ΔE in Eq. 2) is influenced by the solvent molecules, and this influence changes the electronic spectrum and the ^{59}Co NMR of $[Co(CN)_6]^{3-}$.

The influence of the solvent on the d-d transition energy (ΔE) is speculatively interpreted by a change in the contribution of the empty π orbital of the ligand carbon.[12] The orbital scheme can be illustrated as follows for a complex that is composed of the σ and π



bonding between Co and the ligand. If the contribution of the π orbital in this case increases, the orbital split should become great, leading to the blue shifts in hydrogen-bonding solvents.

Carbon-13 NMR of $[Co(CN)_6]^{3-}$ in a Variety of Solvents. The next problem is what kind of interaction between solvent molecules and the complex anion influences the d-d electronic transition state of the cobalt(III) center. Solvent molecules interact

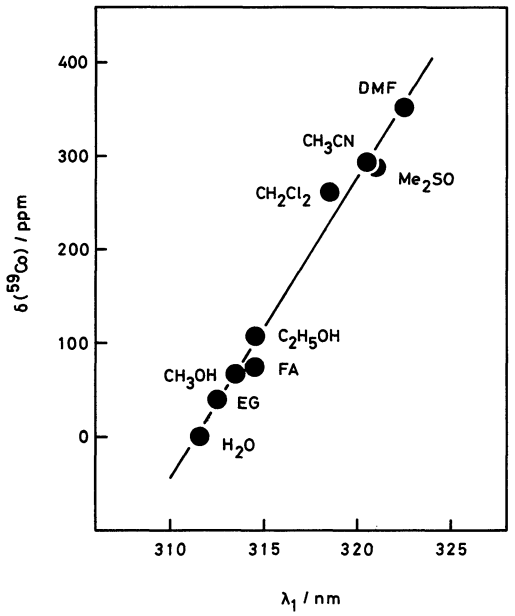


Fig. 4. The correlation between the ^{59}Co chemical shifts ($\delta(^{59}Co)$ in Table 1) and the peak positions (λ_1) in the electronic spectrum.

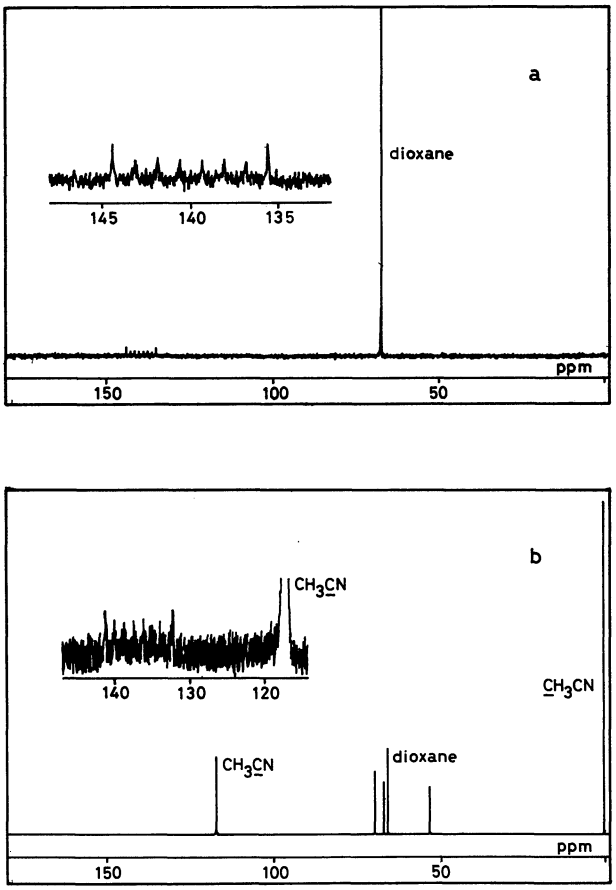


Fig. 5. ^{13}C NMR spectra of $K_3[Co(CN)_6]$ in water (a) and in acetonitrile (b). There are some signals of cryptand 222 near the signal of dioxane in Fig. 5b.

with $[Co(CN)_6]^{3-}$ in the outer coordination sphere. One possibility is the interaction with the ligand CN^-. In order to confirm this interaction, the ^{13}C NMR spectrum is observed in a variety of solvents.

The ^{13}C NMR spectra of $[Co(CN)_6]^{3-}$ in H_2O and CH_3CN are shown in Figs. 5a and 5b, respectively. In aqueous solution (Fig. 5a), the eight weak signals that are assigned to the carbons of the coordinated CN^- and are coupled with the nuclei spin of ^{59}Co (I=7/2) appear at the low magnetic field (135—145 ppm).[13] These signals are expanded in Fig. 5a. Eight signals were clear after about 6000 accumulations over 10-s pulse intervals. In acetonitrile, signals also appear as octet lines. The spectrum is shown in Fig. 5b after about 10000 accumulations over 30-s pulse intervals. Weak signals of the CN^- carbons are shown as eight signals (132—142 ppm) in the expanded spectrum, which is beside the solvent signal of nitrile carbon. The signals in solvents other than the solvents listed in Table 1 are rather broad and obscure, even after 10000 accumulations; chemical shifts were not accurately obtained in this work.

The chemical shifts of carbon-13 in Table 1 also varies from one solvent to other; the solvents used are H_2O, CH_3OH, C_2H_5OH, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, and DMF. This solvent influence should be due to the outersphere interaction between solvent molecules and the $[Co(CN)_6]^{3-}$ ion. Another influence, for example the influence of ion association and a slight amount of water included in the solvent used, is quite small in this system.[14]

The chemical shift of ^{13}C signals is plotted against the acceptor number in order to compare the magnitude of solvation with the electrophilic ability of the solvent. In Fig. 6, are plotted the chemical shifts of ^{13}C NMR against the acceptor numbers of the solvents. A plot of the $\delta(^{13}C)$ values gives a straight line (the correlation coefficient is 0.970) as shown for the plots of λ_1 and $\delta(^{59}Co)$.[15] This line is represented by the following equation (error bars are for one standard deviation):

$$\delta(^{13}C) = \delta(^{13}C)^\circ + (0.0639 \pm 0.0065) \times AN \qquad (3)$$

where $\delta(^{13}C)^\circ$ and AN refer to the ^{13}C chemical shift ($\delta(^{13}C)^\circ$=136.1±0.2 ppm determined by a linear least-squares analysis) and the acceptor number of the solvent, respectively. This linearity shows that the ^{13}C NMR chemical shifts are correlated to the electrophilic ability of solvents in the same manner as the λ_1 values and $\delta(^{59}Co)$ are and the interaction with solvent molecules causes the downfield shifts. The downfield shifts correspond to an electron-withdrawing effect of solvent molecules on the cyano groups.

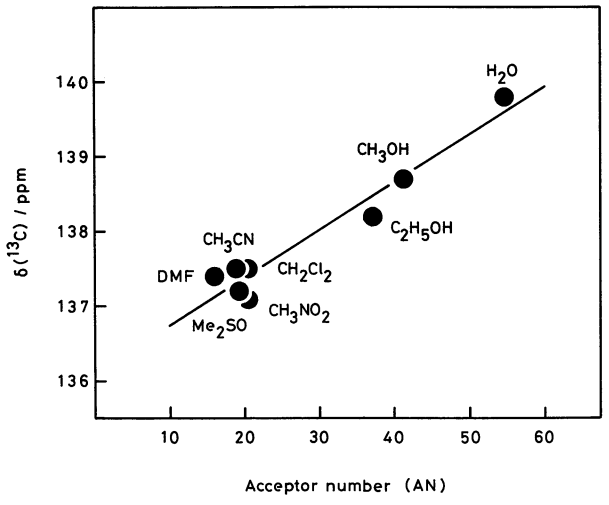


Fig. 6. The correlation between the ^{13}C chemical shifts ($\delta(^{13}C)$ in Table 1) and the acceptor numbers (AN) of the solvents.

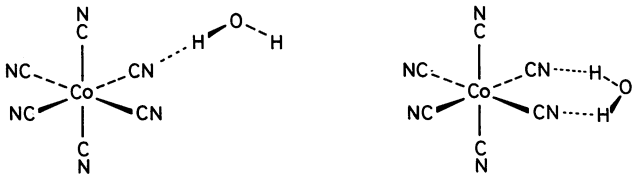


Fig. 7. Solvation model for $[Co(CN)_6]^{3-}$-H_2O system.

On the basis of the correlation it is concluded that the solvent molecules interact with the $[Co(CN)_6]^{3-}$ ion through the ligand CN^- directly. This interaction could be hydrogen bonding for protic solvents like water and methanol.

Solvation Site. The ^{14}N NMR spectrum of $[Co(CN)_6]^{3-}$ could be obtained in aqueous solution, but those in organic solvents are not detected because of the broadness of the nitrogen-14 signal. Therefore, we can not at present confirm the exact site of the interaction of solvation. However, molecular models indicate that direct interaction like hydrogen bonding is possible between the nitrogen and solvent hydrogens, but that the interaction seems to be impossible between the carbon and solvent hydrogens. Eventually, we could propose the solvation model shown in Fig. 7 for water. This species of an outersphere complex exhibits electronic and ^{59}Co NMR spectra which are different from the inherent ones by a change in the d-d transition state of $[Co(CN)_6]^{3-}$. A detailed examination of the correlation between the solvation mode and the change of the d-d transition state of the complex anion is now being studied by MO calculations.

Conclusion

It is concluded that the solvent molecules interact with the $[Co(CN)_6]^{3-}$ ion as electron acceptors through the ligand CN^-, probably at the cyanide nitrogen, and that the solvent influence on the UV, ^{59}Co, and ^{13}C NMR spectra of $K_3[Co(CN)_6]$ measured in this work is all caused by the electron-withdrawing

effect of the solvents. The blue shift of the first d-d transition band and the upfield shift of the ^{59}Co signal of this complex anion correspond to the expansion of the d-d transition-energy split caused by the electron-withdrawing effect.

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8) The solvent influence on the extinction coefficient of $[Co(CN)_6]^{3-}$ is also checked in these solvents, and there is only 10% change and is no definite correlation with the acceptor numbers or dielectric constants.

9) The plot of the wavenumbers (cm^{-1}) of the peak positions against the acceptor number also gives the straight line. The intercepts and correlation coefficients are quite similar to those obtained from the plots of the wavelengths (nm). The intercept and correlation coefficient are 30720 ± 90 cm^{-1} (325.5 nm) and 0.966.

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14) The author measured the ^{13}C NMR spectra of $K_3[Co(CN)_6]$ of 0.05 M aqueous solution, of 0.1 M acetonitrile solution including 0.45 M cryptand 222 (1.5 times amount for the potassium ion) and of acetonitrile solution including added 1 vol% H_2O. The chemical shifts are the same as those of 0.1 M aqueous solution, of 0.1 M acetonitrile solution including 0.33 M cryptand 222 and of acetonitrile (commercially available) solution, respectively, within experimental error (±0.1 ppm). Therefore, the influence of ion association, cryptand 222 and the including water molecules seems to be negligible.

15) The ^{59}Co NMR chemical shift is also correlated linearly to the electrophilic ability of solvents. The chemical shift of the ^{59}Co NMR in the solvent is calculated by the following equation (error bars are one standard deviation):

$$\delta(^{59}Co) = \delta(^{59}Co)^{\circ} - (8.89\pm0.52) \times AN$$

where $\delta(^{59}Co)^{\circ}=453\pm16$ ppm (the correlation coefficient is -0.985).