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The Formation Constants and Configurations of the Complexes of Cr(II), Mn(II), Fe(II), Co(II), Cu(II), and Zn(II) with 2,2′-Bipyridine and of Co(II) with 2,2′:6′,2″-Terpyridine in Hexamethylphosphoric Triamide

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The absorption spectra and the first formation constants, K_1, of complexes $[M(bpy)]^{2+}$ (M(II)=Cr(II), Mn(II), Fe(II), Co(II), Cu(II), and Zn(II), bpy=2,2′-bipyridine) were determined spectrophotometrically in hexamethylphosphoric triamide(HMPA). The values of $\log K_1$ obtained were 4.61 ± 0.02, 3.10 ± 0.12, 4.82 ± 0.04, 5.84 ± 0.07, 7.33 ± 0.02, and 1.77 ± 0.07 for respective metal ions. The configurations of complexes $[M(bpy)]^{2+}$ were discussed on the basis of these data. The K_1 values of $[Cr(bpy)]^{2+}$, $[Mn(bpy)]^{2+}$, $[Fe(bpy)]^{2+}$, and $[Co(bpy)]^{2+}$ in HMPA are slightly larger than those in H_2O, indicating that their configurations are tetrahedral, whereas the value of $[Cu(bpy)]^{2+}$ in HMPA is slightly smaller than that in H_2O, indicating that its configuration in HMPA is either square planar or tetragonal. It seems that $[Zn(bpy)]^{2+}$ is octahedral in HMPA, because its K_1 value is smaller about three orders of magnitude than that in H_2O. In addition, the second formation constant, K_2, of complex $[Co(bpy)_2]^{2+}$, and the first and second formation constants of complexes $[Co(terpy)]^{2+}$ and $[Co(terpy)_2]^{2+}$ (terpy=2,2′:6′,2″-terpyridine) were also determined to be $\log K_2=3.59\pm0.03$ for the bpy complex, and $\log K_1=4.87\pm0.01$ and $\log K_2=3.35\pm0.01$ for the terpy complexes, respectively. These three complexes are concluded to be octahedral.

In a previous paper,[1] the configurations of solvated complex ions of the first transition metals (Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) in hexamethylphosphoric triamide (HMPA) were reported. It was found that the metal ions are tetrahedrally solvated in the cases of Mn(II), Fe(II), Co(II), and Cu(II), while equilibria are established among octahedral, square planar and tetrahedral solvated species in the case of Ni(II), and that Zn(II) forms probably an octahedrally solvated complex ion.

Now the problems on the complex-forming equilibria between the first transition metal ions and a ligand in HMPA are very interesting, since the configurations of the solvated ions in HMPA are widely different from those in water or in a number of other organic solvents, such as dimethyl sulfoxide, *N,N*-dimethylformamide, and methanol, in any of which the solvated ions are generally octahedral.

Up to date, however, no thermodynamic studies have been done yet except for the case of Co(II) complexes in HMPA.[2,3] In the present study, the absorption spectra and the values of the formation constants of the following complexes will be reported: the first formation constants, K_1, of complexes $[M(bpy)]^{2+}$ (M(II)=Cr(II), Mn(II), Fe(II), Co(II), Cu(II), or Zn(II), bpy=2,2′-bipyridine),[†] the second formation constant, K_2, of the complex $[Co(bpy)_2]^{2+}$, and the first and second formation constants of the complexes $[Co(terpy)]^{2+}$ and $[Co(terpy)_2]^{2+}$ (terpy=2,2′:6′,2″-terpyridine). The configurations of $[M(bpy)]^{2+}$ in HMPA will be discussed on the basis of these data.

Experimental

Materials and Procedure. HMPA of guaranteed reagent grade was purified as described elsewhere.[1] Bpy was recrystallized from hexane, and terpy was used without further purification. Anhydrous sodium perchlorate was prepared by heating monohydrous salt which had been recrystallized twice from water. Complexes of various metal ions $[M(hmpa)_4](ClO_4)_2$ (M(II)=Mn(II), Fe(II), Co(II), Cu(II), or Zn(II)) were synthesized according to the methods by Donoghue and Drago.[4,5] Stock solutions of these metal perchlorates were prepared, and portions of them were taken to analyze the metal ion concentrations by the spectrophotometric methods already published.[1] Complex solutions were prepared by mixing the aliquots of stock solutions of metal perchlorates with those of bpy or terpy solutions. The ionic strength was kept at $I=0.06\ \mathrm{mol\ dm^{-3}}$ with sodium perchlorate.

Solution of chromium(II) perchlorate in HMPA was prepared under nitrogen atmosphere as follows. Metallic chromium was dissolved in aqueous solution of perchloric acid, and the hydrated perchlorate was crystallized from it. After the removal of water in vacuum at room temperature until the blue crystals turned white, the white crystals were treated with a slight excess of HMPA and an appropriate amount of ether and crystals of chromium perchlorate solvated by HMPA were obtained and dissolved in HMPA. The total chromium(II) ion concentration in solution was determined spectrophotometrically by diphenylcarbazide method[6] (molar absorptivity $\varepsilon=6.590\times10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 540 nm).

Apparatus. The absorptivities of complex solutions were measured using a Hitachi Spectrophotometer Model 100-40 and a Hitachi Recording Spectrophotometer Model EPS-3T, with a thermostated cell compartment, respectively. The temperature was kept at 25.0±0.1 °C.

Results

The values of K_1 were obtained by a method by use of Job's curves (Method I),[7] the linear relationship method (Method II),[7] and the relative stability constant method (Method III).[8]

Determination of K_1 by Method I. The curves of Job's continuous variation method were obtained at two different total concentrations ($c=c_a$ and c_b) of M(II) (M(II)=Mn(II), Fe(II), Co(II), or Zn(II)) and bpy; an example is given in Fig. 1, essentially

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[†] In this expression, HMPA molecules solvating the metal ions are omitted.

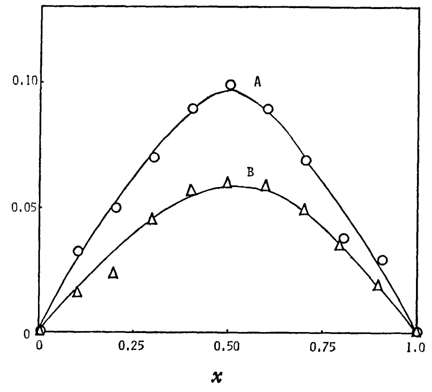

Fig. 1. Job's curves for Mn(II)+bpy system in HMPA at 317 nm.
Curve A: $c_a=1.00\times10^{-3}$ mol dm^{-3}, curve B: $c_b=7.00\times10^{-4}$ mol dm^{-3}.

similar data being obtained in other cases. Curves A and B indicate that the 1:1 complex $[M(bpy)]^{2+}$ is predominantly formed between M(II) and bpy, so that the following relations are established:

$$M^{2+} + bpy \overset{K_1}{\rightleftharpoons} [M(bpy)]^{2+}, \tag{1}$$

$$K_1 = \frac{[[M(bpy)]^{2+}]}{[M^{2+}][bpy]}. \tag{2}$$

In the Figure, the abscissa shows $x=[bpy]_0/c$, and the ordinate Y is defined as follows:

$$Y = (\varepsilon_1-\varepsilon_0-\varepsilon_b)[[M(bpy)]^{2+}] \tag{3}$$

in which ε_0, ε_1, and ε_b are the molar absorptivities of M^{2+}, $[M(bpy)]^{2+}$, and bpy, respectively. The values of K_1 and ε_1 are calculated by Eq. 3 and the following equations from curves A and B.[7)]

$$[[M(bpy)]^{2+}] = \frac{x_a(1-x_a)c_a^2-x_b(1-x_b)c_b^2}{c_a-c_b}, \tag{4}$$

$$[M^{2+}] = x_a c_a - [[M(bpy)]^{2+}], \tag{5}$$

$$[bpy] = (1-x_a)c_a - [[M(bpy)]^{2+}], \tag{6}$$

where x_a and x_b are the x values having a common Y value on curves A and B. The results are summarized in Table 1.

Determination of K_1 and K_2 by Method II.[7)] At concentrations of both M(II) and bpy low enough so that the amount of $[M(bpy)_2]^{2+}$ formed is negligibly small, the apparent molar absorptivity of M(II), ε, is expressed by a linear relationship, Eq. 7, with $(\varepsilon_0-\varepsilon)/[bpy]$.[7)] When the molar absorptivity of M^{2+}, ε_0, is zero, Eq. 8 holds.

$$\varepsilon = \varepsilon_1 + \frac{1}{K_1}\frac{(\varepsilon_0-\varepsilon)}{[bpy]} \tag{7}$$

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_1} + \frac{1}{K_1\varepsilon_1}\frac{1}{[bpy]} \tag{8}$$

Accordingly, plotting ε *vs.* $(\varepsilon_0-\varepsilon)/[bpy]$ or $1/\varepsilon$ *vs.* $1/[bpy]$ will give the values of K_1 and ε_1 from the slope and the intercept. Figure 2 shows the linear relationship of Co(II)+bpy system; similar relationships were obtained for Mn(II)+bpy and Fe(II)+bpy systems, respectively. The values of K_1 and ε_1 thus obtained are also summarized in Table 1. These values of K_1 are in good agreement with those obtained by Method I.

The second complex formation constant of $[Co(bpy)_2]^{2+}$, $K_2=[[Co(bpy)_2]^{2+}]/[[Co(bpy)]^{2+}][bpy]$, is obtained from Eq. 9 in the more concentrated regions for both Co(II) and bpy than in Fig. 2,

$$\varepsilon = \varepsilon_2 + \frac{1}{K_2}\frac{(\varepsilon_0-\varepsilon)+(\varepsilon_1-\varepsilon)K_1[bpy]}{K_1[bpy]^2}, \tag{9}$$

where ε_2 is the molar absorptivity of $[Co(bpy)_2]^{2+}$. The linearity is obvious between ε and $\{(\varepsilon_0-\varepsilon)+(\varepsilon_1-\varepsilon)K_1[bpy]\}/K_1[bpy]^2$ as shown in Fig. 3, giving the value of K_2 from the slope. The first and second formation constants of Co(II)-terpy complexes are also determined by the same method, the results being listed in Table 2.

Determination of K_1 by Method III.[8)] When both M^{2+} and M_a^{2+} ions coexist in HMPA, equilibria (1)

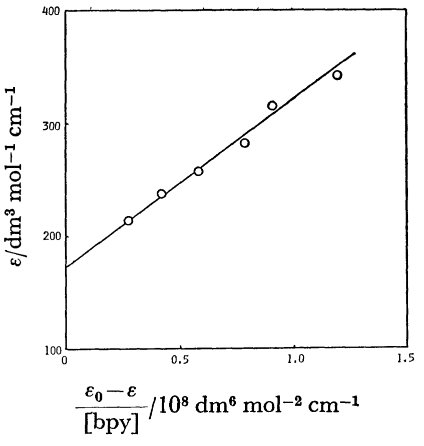

Fig. 2. Linear relation of ε against $(\varepsilon_0-\varepsilon)/[bpy]$ in HMPA at 630 nm.
$[Co(II)]=8.00\times10^{-4}$ mol dm^{-3}, $[bpy]_0=1.00\times10^{-4}$—$6.00\times10^{-4}$ mol dm^{-3}.

TABLE 1. FIRST FORMATION CONSTANTS OF THE COMPLEXES OF Mn(II), Fe(II), Co(II), OR Zn(II) WITH bpy IN HMPA BY METHOD I AND METHOD II

Method		Mn(II)	Fe(II)	Co(II)	Zn(II)
Method I	$\log K_1$	3.21 ± 0.24	4.86 ± 0.11	5.77 ± 0.22	1.77 ± 0.07
	$\log \varepsilon_1$	2.81 ± 0.07[a)]	3.88 ± 0.02[b)]	3.95 ± 0.03[c)]	3.10 ± 0.06[d)]
Method II	$\log K_1$	2.98 ± 0.02	4.78 ± 0.02	5.90 ± 0.02	—
	$\log \varepsilon_1$	1.26 ± 0.09[e)]	2.42 ± 0.04[f)]	2.25 ± 0.05[g)]	—

The following values were adopted in Method I: a) $\log\varepsilon_0=0.60$, $\log\varepsilon_b=2.02$ at 317 nm, b) $\log\varepsilon_0=3.20$, $\log\varepsilon_b=2.90$ at 310 nm, c) $\varepsilon_0=0$, $\log\varepsilon_b=3.36$ at 305 nm, d) $\log\varepsilon_0=0.48$, $\log\varepsilon_b=2.02$ at 317 nm. The following wavelengths were used in Method II: e) 380 nm, f) 522 nm, g) 630 nm.

and (10) hold simultaneously among those ions and bpy,

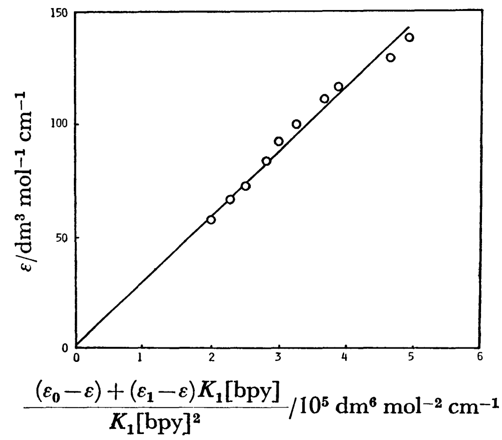

Fig. 3. Linear relation of ε against $((\varepsilon_0-\varepsilon)+(\varepsilon_1-\varepsilon)\times K_1[\text{bpy}])/K_1[\text{bpy}]^2$ in HMPA at 580 nm. $[\text{Co(II)}]=3.20\times10^{-3}$ mol dm^{-3}, $[\text{bpy}]_0=3.80\times10^{-3}$—$5.60\times10^{-3}$ mol dm^{-3}.

TABLE 2. COMPARISON OF FIRST AND SECOND FORMATION CONSTANTS OF THE COMPLEXES OF Co(II) WITH bpy OR terpy IN HMPA AND H_2O

Ligand	Solvent	$\log K_1$	$\log K_2$	$\log K_3$
bpy	HMPA	5.84±0.07	3.59±0.03	<1[a]
	H_2O[9]	5.65	5.60	4.80
terpy	HMPA	4.87±0.01	3.35±0.01	
	H_2O[9]	8.4	9.9	

a) This value was calculated on an assumption that ε of $[\text{Co(bpy)}_3]^{2+}$ in HMPA is the same value as that in H_2O. $[\text{Co(II)}]=1.00\times10^{-2}$ mol dm^{-3}, $[\text{bpy}]_0=1.50\times10^{-1}$ mol dm^{-3}.

$$\text{M}_\text{a}^{2+} + \text{bpy} \underset{}{\overset{K_\text{a}}{\rightleftharpoons}} [\text{M}_\text{a}(\text{bpy})]^{2+}, \tag{10}$$

where K_a is the formation constant of $[\text{M}_\text{a}(\text{bpy})]^{2+}$. Therefore, an equilibrium (11) is also established with a formation constant K_r as expressed by Eq. 12.

$$\text{M}^{2+} + [\text{M}_\text{a}(\text{bpy})]^{2+} \overset{K_\text{r}}{\rightleftharpoons} \text{M}_\text{a}^{2+} + [\text{M}(\text{bpy})]^{2+}, \tag{11}$$

$$K_\text{r} = \frac{[\text{M}_\text{a}^{2+}][[\text{M}(\text{bpy})]^{2+}]}{[\text{M}^{2+}][[\text{M}_\text{a}(\text{bpy})]^{2+}]} = \frac{K_1}{K_\text{a}}. \tag{12}$$

The absorptivity of the solution, A, is defined by the following equation:

$$A = \varepsilon_0[\text{M}^{2+}] + \varepsilon_1[[\text{M}(\text{bpy})]^{2+}] + \varepsilon_\text{a}[\text{M}_\text{a}^{2+}] + \varepsilon'_\text{a}[[\text{M}_\text{a}(\text{bpy})]^{2+}], \tag{13}$$

where ε_a and ε_a' are the molar absorptivities of M_a^{2+} and $[\text{M}_\text{a}(\text{bpy})]^{2+}$, respectively. When both the values of K_1 and K_a are considerably large, the concentration of free bpy will be negligibly small, and therefore, the total concentration of bpy, $[\text{bpy}]_0$, will be equal to the sum of $[[\text{M}(\text{bpy})]^{2+}]$ and $[[\text{M}_\text{a}(\text{bpy})]^{2+}]$. Consequently, when the molar absorptivities of M^{2+}, $[\text{M}(\text{bpy})]^{2+}$, M_a^{2+}, and $[\text{M}_\text{a}(\text{bpy})]^{2+}$ are known, the value of K_r can be obtained because the total concentrations of M(II), M_a(II), and bpy and observed A are known. Therefore, the value of K_1 is given by virtue of the relationship $K_1=K_aK_r$ and the known K_a value. For the determination of the formation constants, K_1, of $[\text{Cu}(\text{bpy})]^{2+}$ and $[\text{Cr}(\text{bpy})]^{2+}$, Co(II) was used as M_a^{2+} ion in equilibrium (10). Since the molar absorptivity of $[\text{M}(\text{bpy})]^{2+}$ can not be obtained directly, the absorptivity of the solution, A, was determined at the wavelength of the isosbestic point between M^{2+} and $[\text{M}(\text{bpy})]^{2+}$ ($\varepsilon_0=\varepsilon_1$). The results are summarized in Tables 3 and 4.

Absorption Spectra of bpy- and terpy-Complexes. The absorption spectra of pure bpy- or terpy-complexes can be calculated from the apparent spectra of the

TABLE 3. FIRST FORMATION CONSTANT OF THE COMPLEX OF Cu(II) WITH bpy IN HMPA BY METHOD III[a]

[Cu(II)] / 10^{-4} mol dm^{-3}	[Co(II)] / 10^{-3} mol dm^{-3}	$[\text{bpy}]_0$ / 10^{-4} mol dm^{-3}	$\log K_r$	$\log K_1$[b]
2.00	3.00	2.00	1.48	7.32
2.00	4.00	2.00	1.52	7.36
2.00	5.00	2.00	1.50	7.34
				mean 7.33±0.02

a) Measured at the isosbestic point 580 nm between Cu^{2+} and $[\text{Cu}(\text{bpy})]^{2+}$. $\log\varepsilon_0(\text{Cu}^{2+})=\log\varepsilon_1([\text{Cu}(\text{bpy})]^{2+})=0.88$, $\log\varepsilon_a(\text{Co}^{2+})=2.50$, $\log\varepsilon_a'([\text{Co}(\text{bpy})]^{2+})=2.12$. b) $\log K_a=5.84$ was used.

TABLE 4. FIRST FORMATION CONSTANT OF THE COMPLEX OF Cr(II) WITH bpy IN HMPA BY METHOD III[a]

[Cr(II)] / 10^{-2} mol dm^{-3}	[Co(II)] / 10^{-3} mol dm^{-3}	$[\text{bpy}]_0$ / 10^{-3} mol dm^{-3}	$\log K_r$	$\log K_1$[b]
3.20	2.53	2.33	−1.21	4.63
2.85	2.12	2.40	−1.21	4.63
1.75	3.04	2.95	−1.25	4.59
1.50	2.92	2.65	−1.27	4.57
1.15	3.04	2.92	−1.27	4.57
0.91	2.63	2.60	−1.19	4.65
				mean 4.61±0.02

a) Measured at the isosbestic point 650 nm between Cr^{2+} and $[\text{Cr}(\text{bpy})]^{2+}$. $\log\varepsilon_0(\text{Cr}^{2+})=\log\varepsilon_1([\text{Cr}(\text{bpy})]^{2+})=1.11$, $\log\varepsilon_0(\text{Co}^{2+})=2.45$, $\log\varepsilon_a'([\text{Co}(\text{bpy})]^{2+})=2.00$. b) $\log K_a=5.84$ was used.

mixture of M^{2+} and bpy- or terpy-complexed M^{2+} ions by using the values of K_1 and K_2 listed in Tables 1—4. The observed absorption spectra of the solvated Mn^{2+}, Fe^{2+}, and Zn^{2+}, and the calculated ones of $[Mn(bpy)]^{2+}$, $[Fe(bpy)]^{2+}$, and $[Zn(bpy)]^{2+}$ are shown in Fig. 4, those of Co^{2+}, $[Co(bpy)]^{2+}$, $[Co(bpy)_2]^{2+}$, and $[Co(terpy)]^{2+}$ in Fig. 5, and those of Cu^{2+} and $[Cu(bpy)]^{2+}$ in Fig. 6, respectively.

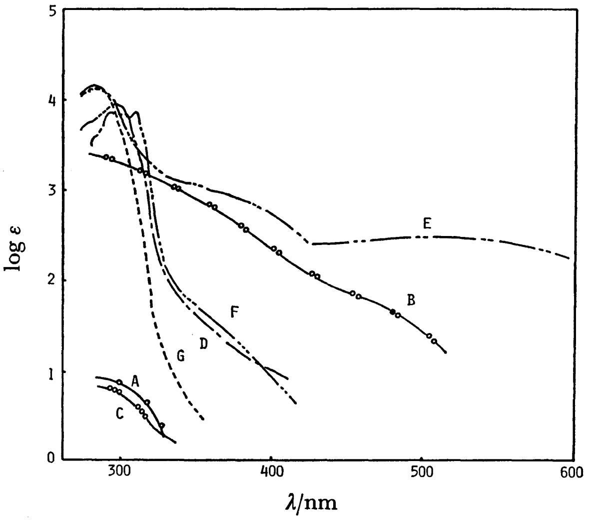

Fig. 4. Absorption spectra of solvated Mn^{2+} (A: —o—), Fe^{2+} (B: —oo—), Zn^{2+} (C: —ooo—), and those of $[Mn(bpy)]^{2+}$ (D: – – –), $[Fe(bpy)]^{2+}$ (E: ——), $[Zn(bpy)]^{2+}$ (F: ———), and bpy (G: ----) in HMPA.

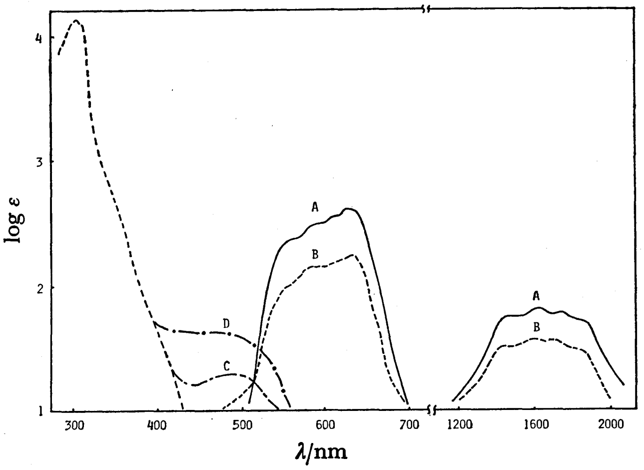

Fig. 5. Absorption spectra of solvated Co^{2+} (A:——), $[Co(bpy)]^{2+}$ (B:- - -), $[Co(bpy)_2]^{2+}$ (C:———), and $[Co(terpy)]^{2+}$ (D:—·—) in HMPA.

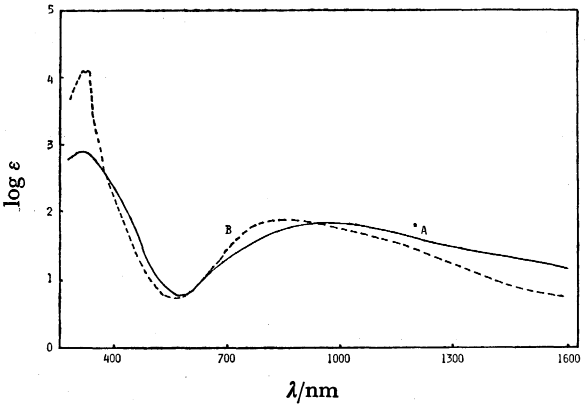

Fig. 6. Absorption spectra of solvated Cu^{2+} (A:——) and $[Cu(bpy)]^{2+}$ (B:----) in HMPA.

Discussion

Configurations of $[Cr(bpy)]^{2+}$, $[Mn(bpy)]^{2+}$, $[Fe(bpy)]^{2+}$, *and* $[Co(bpy)]^{2+}$ *in HMPA.* The K_1 values observed for bpy-complexes are in a sequence $Cr(II) > Mn(II) < Fe(II) < Co(II) < Cu(II) > Zn(II)$ in HMPA. Figure 7 shows the comparison of the K_1 values in HMPA and in H_2O.[9] The factors which would make the values of the formation constants (K) in HMPA differ from those in H_2O or in other organic solvents might be the dielectric constants, basicities, and steric effects of the solvents. Since bpy and terpy ligands are electrically neutral, the K values might be little affected by the dielectric constant of the solvents. Since the competitive coordination to a metal ion occurs between bpy (or terpy) and the solvent molecules, the increase in basicity and in the degree of steric hindrance of the solvent would result in a decrease in K value.

It was reported[1] that the solvated Mn^{2+}, Fe^{2+}, Co^{2+}, and Cu^{2+} ions are tetrahedral in contrast with the octahedrally solvated Zn^{2+} ion in HMPA. Because an HMPA molecule is very bulky, solvated metal ions in HMPA will prefer the tetrahedral configurations to the octahedral ones.[1] If their bpy-complexes tend to form octahedral configurations in HMPA, K_1 values in HMPA would become smaller than those in H_2O or in DMSO because of a larger basicity and steric hindrance of HMPA molecules which would be more closely packed in the octahedral coordination sphere. However, since the observed K_1 values of Cr(II), Mn(II), Fe(II), and Co(II) in HMPA are slightly larger than those in H_2O as shown in Fig. 7, it is supposed that their bpy-complexes would not be octahedral. According to Gutmann *et al.*,[10] the donor strength of HMPA towards Co(II) is smaller

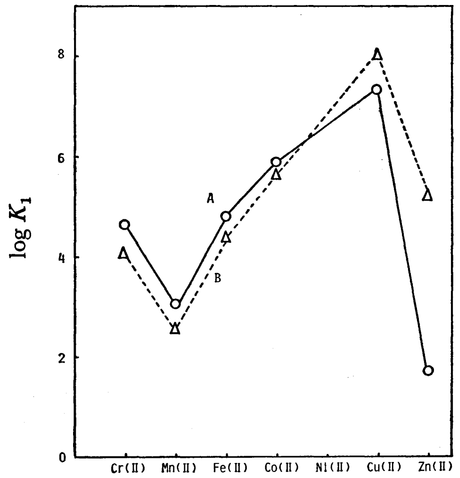

Fig. 7. Comparison of log K_1 in HMPA (A:—) and in H_2O (B:- - -).

than that expected from its donor number and the coordination center in $[\mathrm{Co(hmpa)_4}]^{2+}$ is rattling within the tetrahedron formed by the bulky HMPA molecules. When their bpy-complexes in HMPA are also assumed to be tetrahedral, the K_1 values in HMPA would not be much smaller than those in H_2O because of the smaller steric hindrance and the decreased donor strength of HMPA molecules. Actually, the absorption spectrum of $[\mathrm{Co(bpy)}]^{2+}$ in HMPA exhibits the spectral pattern characteristic of tetrahedral complexes as is seen in Fig. 5, having the absorption band due to $\nu_3(^4\mathrm{T}_1(\mathrm{P})\leftarrow{}^4\mathrm{A}_2)$, ($\varepsilon$=100—2000 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) in the visible region.[11] Although the configurations of bpy-complexes of Cr(II), Mn(II), and Fe(II) can not be judged from the observed absorption spectra, they would be also tetrahedral because their K_1 values in HMPA, as well as the K_1 value of tetrahedral $[\mathrm{Co(bpy)(hmpa)_2}]^{2+}$, are similarly larger than those in H_2O. Then, the following equilibrium seems to be established in all these cases.

$$\underset{\text{tetrahedral}}{[\mathrm{M(hmpa)_4}]^{2+}} + \mathrm{bpy} \overset{K_1}{\rightleftharpoons} \underset{\text{tetrahedral}}{[\mathrm{M(bpy)(hmpa)_2}]^{2+}} + 2\mathrm{hmpa} \tag{14}$$

M(II) = Cr(II), Mn(II), Fe(II), or Co(II)

On the other hand, the absorption spectrum of bis(bpy)cobalt(II) complex in HMPA as is shown in Fig. 5 has a spectral pattern characteristic of the octahedral complexes, having the absorption band near 500 nm (ε=5—40 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$).[11] Therefore, the following tetrahedral↔octahedral configurational equilibrium must be established;

$$\underset{\text{tetrahedral}}{[\mathrm{Co(bpy)(hmpa)_2}]^{2+}} + \mathrm{bpy} \overset{K_2}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Co(bpy)_2(hmpa)_2}]^{2+}}, \tag{15}$$

$$\underset{\text{octahedral}}{[\mathrm{Co(bpy)_2(hmpa)_2}]^{2+}} + \mathrm{bpy} \overset{K_3}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Co(bpy)_3}]^{2+}} + 2\mathrm{hmpa}. \tag{16}$$

When terpy as a terdentate ligand coordinates to Co^{2+} ion, the 1:1 complex is octahedral as is shown from its absorption spectrum[11] in Fig. 5. Accordingly, this equilibrium is also a tetrahedral↔octahedral configurational change;

$$\underset{\text{tetrahedral}}{[\mathrm{Co(hmpa)_4}]^{2+}} + \mathrm{terpy} \overset{K_1}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Co(terpy)(hmpa)_3}]^{2+}} + \mathrm{hmpa}, \tag{17}$$

$$\underset{\text{octahedral}}{[\mathrm{Co(terpy)(hmpa)_3}]^{2+}} + \mathrm{terpy} \overset{K_2}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Co(terpy)_2}]^{2+}} + 3\mathrm{hmpa}. \tag{18}$$

As is evident from Table 2, the K_2 value of $[\mathrm{Co(bpy)_2}]^{2+}$ and the K_1 value of $[\mathrm{Co(terpy)}]^{2+}$ are remarkably smaller than those in H_2O, because the steric hindrance of HMPA molecules in octahedral $[\mathrm{Co(bpy)_2}]^{2+}$ and octahedral $[\mathrm{Co(terpy)}]^{2+}$ may be large. The reason why the K_3 value of $[\mathrm{Co(bpy)_3}]^{2+}$ and the K_2 value of $[\mathrm{Co(terpy)_2}]^{2+}$ in HMPA are extremely smaller than those in H_2O is probably the larger effect of the basicity of HMPA molecules than that due to their steric hindrance.

Configurations of $[\mathit{Cu(bpy)}]^{2+}$, *and* $[\mathit{Zn(bpy)}]^{2+}$ *in HMPA.* Since the steric hindrance caused by HMPA in the square planar complex or tetragonal complex is larger than that in the tetrahedral complex, but smaller than that in the octahedral one, it seems that K_1 value of the square planar or tetragonal complex in HMPA would be smaller than that in H_2O. According to both the K_1 value and the absorption spectrum observed for Cu(II)–bpy complex, it is safely said that its configuration is square planar or tetragonal.[11] Therefore, one of the following two equilibria may hold:

$$\left.\begin{aligned}
&\underset{\text{tetrahedral}}{[\mathrm{Cu(hmpa)_4}]^{2+}} + \mathrm{bpy} \overset{K_1}{\rightleftharpoons} \underset{\text{square planar}}{[\mathrm{Cu(bpy)(hmpa)_2}]^{2+}} + 2\mathrm{hmpa}\\
&\text{or}\\
&\underset{\text{tetrahedral}}{[\mathrm{Cu(hmpa)_4}]^{2+}} + \mathrm{bpy} \overset{K_1}{\rightleftharpoons} \underset{\text{tetragonal}}{[\mathrm{Cu(bpy)(hmpa)_4}]^{2+}}.
\end{aligned}\right\} \tag{19}$$

We have reported that the solvated Zn^{2+} ion in HMPA may be octahedral, since its Stokes radius is larger than that expected if it were tetrahedral.[1] The fact that the K_1 value in HMPA is smaller about three orders of magnitude than that in H_2O is accounted for by a larger steric hindrance of HMPA molecules in octahedral $[\mathrm{Zn(bpy)(hmpa)_4}]^{2+}$ and their larger basicity than those in the case of H_2O molecules. Accordingly, the following equilibrium seems to be established;

$$\underset{\text{octahedral}}{[\mathrm{Zn(hmpa)_6}]^{2+}} + \mathrm{bpy} \overset{K_1}{\rightleftharpoons} \underset{\text{octahedral}}{[\mathrm{Zn(bpy)(hmpa)_4}]^{2+}} + 2\mathrm{hmpa}. \tag{20}$$

General Conclusion. In HMPA, solvated Mn^{2+}, Fe^{2+}, Co^{2+}, and Cu^{2+} are tetrahedral, while solvated Zn^{2+} ion is octahedral.[1] Since an HMPA molecule is very bulky, it seems that solvated metal ions prefer the tetrahedral configurations to the octahedral ones. Gutmann and Weisz reported that mono-, di-, tri-, and tetrahalo complexes of cobalt(II) are tetrahedral in HMPA (halide ion=$\mathrm{Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{I^-}$).[2] When multidentate ligands such as bpy and terpy coordinate to metal ions in HMPA, the configurations of $[\mathrm{Cr(bpy)}]^{2+}$, $[\mathrm{Mn(bpy)}]^{2+}$, $[\mathrm{Fe(bpy)}]^{2+}$, and $[\mathrm{Co(bpy)}]^{2+}$ are also tetrahedral, while that of $[\mathrm{Cu(bpy)}]^{2+}$ is either square planar or tetragonal. In the case of Zn(II), its configuration seems to be octahedral. The K_1 value and the absorption spectrum of Ni(II)-complex was not obtained, because the equilibria among the tetrahedral, square planar and octahedral solvated-species were too complicated to analyze them.[1] The configurations of both $[\mathrm{Co(bpy)_2}]^{2+}$ and $[\mathrm{Co(terpy)}]^{2+}$ are octahedral. In conclusion, it is likely that the complexes coordinated by more than three nitrogen atoms are mostly octahedral in HMPA.

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