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The Relationships between the Formation Constants of 2,2′-Bipyridine Metal(II) Complexes and the Donor Numbers of Solvents

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Synopsis. The complex formation constants of cobalt(II) or zinc(II) with 2,2′-bipyridine (bpy) were determined spectrophotometrically in various solvents. The values of log K_1, log K_2, and log K_3 for the Co(II) complexes obtained were 4.06±0.06, 3.09±0.04, and 1.15±0.02 respectively in dimethyl sulfoxide, while those of log K_1 for the Zn(II)–bpy complexes were 6.27±0.10, 4.14±0.01, 4.71±0.03, and 3.44±0.12 in trimethyl phosphate, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and dimethyl sulfoxide respectively. It was found that the linear relationships hold between logarithms of the formation constants of the bpy complexes and the donor numbers of the solvents when both the solvated metal ions and the bpy complexes are octahedral in the solvents.

In recent years, studies of the solvent effects on the chemical reactions have been extensively reported.[1–3] However, there are few quantitative equilibrium data to account for the solvent effects for the first transition metal complexes.[1,4,5]

In this study, we determined spectrophotometrically the complex formation constants of cobalt(II) or zinc(II) with 2,2′-bipyridine (bpy) in dimethyl sulfoxide (DMSO), trimethyl phosphate (TMP), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) for the purpose of clarifying the solvent effects on the chemical equilibria. The linear relationship between the logarithms of the complex formation constants and the donor numbers of the solvents will be discussed on the basis of the experimental data.

Experimental

Materials and Preparations. DMSO and DMF of a guaranteed reagent grade were purified as has been described elsewhere.[6,7] TMP and DMA were distilled under a reduced pressure of nitrogen, after having been dried with 5A molecular sieves. 2,2′-Bipyridine was recrystallized from a hexane solution. Solvated complexes of the metal ions $[M(s)_6](ClO_4)_2$ (M=Co(II) or Zn(II), and s=dmso, dmf, or dma) were synthesized by methods similar to those of $[M(hmpa)_4](ClO_4)_2$:[8] hydrated metal perchlorate was treated with a large excess of 2,2-dimethoxypropane for one hour with stirring. At the end of the dehydration period, a slight excess of the solvent was added. After several minutes, a large excess of anhydrous ether was added, and then the precipitate was filtered. They were dried in a vaccum desiccator. Solvated Zn(II) perchlorate in TMP was prepared as follows: hydrated Zn(II) perchlorate was dissolved in TMP, where 5A molecular sieves were present for the purpose of dehydration. After standing overnight, 5A molecular sieves were removed from the solution. Portions of stock solutions of these metal perchlorates were taken to analyze the metal ion concentrations by the spectrophotometric methods already reported.[9] The bpy complex solutions were prepared by mixing aliquots of the stock solutions of metal perchlorates with those of the bpy solution. The ionic strength was kept at I=0.06 M (mol dm^{-3}) with sodium perchlorate.

Apparatus. The absorptivities of complex solutions were measured by using a Shimadzu Spectrophotometer, Model UV-200S, with a thermostated cell compartment. The temperature was kept at 25±0.1 °C.

Results and Discussion

The value of the first formation constant, K_1=[[M(bpy)]$^{2+}$]/[M^{2+}][bpy], for the Co(II)–bpy complex in DMSO, and those for the Zn(II)–bpy complexes in DMSO, DMF, DMA, and TMP were obtained by the use of Job's curves.[10,11] The value of the second formation constant, K_2=[[M(bpy)$_2$]$^{2+}$]/[[M(bpy)]$^{2+}$][bpy], and that of the third formation constant, K_3=[[M(bpy)$_3$]$^{2+}$]/[[M(bpy)$_2$]$^{2+}$][bpy], for the Co(II)–bpy complex in DMSO were obtained by the linear relationship method.[10,11] The results are summarized in Table 1, together with the results in hexamethylphosphoric triamide (HMPA) and those for the Mn(II)–bpy complex previously reported.[11–13] The log K values decrease roughly in accordance with the increase in the donor number (D) of the solvents, except for the K_1 and K_2 values for the Co(II)–bpy complexes and for the K_1 value for the Mn(II)–bpy complex in HMPA, as shown in Table 1.

It is accepted that, in solvents such as water, methanol, DMSO, and DMF, the solvated ions of first transition metals are mostly octahedral.[14–16] On the other hand, we have already reported that, in HMPA, they prefer the tetrahedral configurations to the octahedral ones since the HMPA molecule is very bulky as compared with the molecules of the other solvents.[9,11] Therefore in all the solvents used here other than in HMPA, [M(s)$_6$]$^{2+}$ (M(II)=Mn(II), Co(II), or Zn(II), s=solvent) is octahedral.[14–16] Their bpy complexes are probably be octahedral also, for the bpy ligand gives a stronger ligand field than the solvents. Nevertheless, [Zn(hmpa)$_6$]$^{2+}$, [Zn(hmpa)$_4$(bpy)]$^{2+}$, and [Co(hmpa)$_2$(bpy)$_2$]$^{2+}$ in HMPA are octahedral, in contrast with the tetrahedral configurations of [M(hmpa)$_4$]$^{2+}$ and [M(hmpa)$_2$(bpy)]$^{2+}$ (M(II)=Mn(II) or Co(II)).[9,11] Therefore, when the octahedral–octahedral equilibria are established in the solvents, the linear relationship can be said to hold roughly between log K vs. D as shown in Table 1. The deviation from the linearity in HMPA may be due to the establishment of a tetrahedral–tetrahedral or tetrahedral–octahedral equilibrium, in consequence of the steric hindrance caused by the bulkiness of the HMPA molecule in the coordination sphere.[11]

When bpy coordinates to a metal ion, the metal ion liberates two solvent molecules from the coordination sphere. Therefore, the true formation constant should

Table 1. Formation Constants of the Complexes of Mn(II), Co(II), and Zn(II) with bpy in Various Solvents at 25 °C and I=0.06 mol dm^{-3}

M^{2+}	Ligand	log $K^{a)}$	Solvent (Donor Number)						
			$H_2O^{12)}$ (18)	$CH_3OH^{13)}$ (19)	TMP (23)	DMF (26.6)	DMA (27.8)	DMSO (29.8)	HMPA$^{11)}$ (38.8)
		log K_1	5.65					4.06	5.84$^{b)}$
Co^{2+}	bpy	log K_2	5.60					3.09	3.58$^{c)}$
		log K_3	4.80					1.15	−0.4
Zn^{2+}	bpy	log K_1	5.20		6.27	4.14	4.71	3.44	1.77
Mn^{2+}	bpy	log K_1	2.62	2.7				2.5	3.10$^{b)}$

a) log K in octahedral-octahedral equilibrium except for b) and c). b) log K_1 in tetrahedral-tetrahedral equilibrium. c) log K_2 in tetrahedral-octahedral equilibrium.

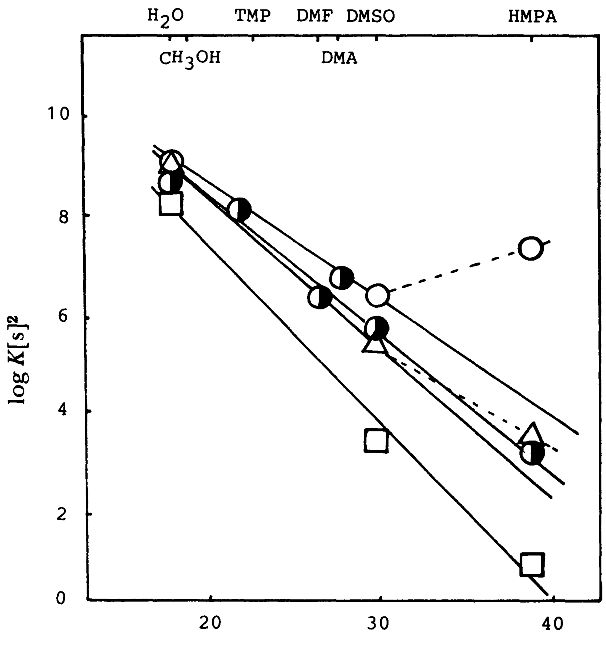

Fig. 1. Linear relations of log $K[s]^2$ vs. donor numbers in various solvents. For Co(II)-bpy complexes, (○): log $K_1[s]^2$, (△): log $K_2[s]^2$, (□): log $K_3[s]^2$. In HMPA, the value of log K_2 is plotted since the tetrahedral-octahedral equilibrium holds at the second step. For Zn(II)-bpy complexes, (◑): log $K_1[s]^2$.

be $K_{x+1}[s]^2$ rather than K_{x+1}=[[M(bpy)$_{x+1}$]$^{2+}$]/[[M(bpy)$_x$]$^{2+}$][bpy] (x=0, 1, or 2) in an octahedral–octahedral equilibrium, where [s] is the molar concentration of the solvent. Since the [s] values are not equal to each other for various solvents, the plots of log $K_{x+1}[s]^2$ *vs.* D are probably more reasonable than those of log K_{x+1}. Figure 1 shows the plots of log $K_{x+1}[s]^2$ *vs.* D. The linearity for the K_1 of the Zn(II)-bpy complex corresponding to the octahedral-octahedral equilibria in all solvents is improved from that in Table 1.

When octahedral-octahedral equilibria hold in various solvents, the following linear equation is given:

$$\log K[s]^2 = \alpha D + \text{const.} \tag{1}$$

where α is the slope of the straight line. Moreover, the following equation holds in the solvents:

$$-RT \ln K[s]^2 = \Delta H - T\Delta S \tag{2}$$

It is considered that the ΔS values of the equilibria in various solvents are roughly equal, because one bpy molecule is taken in, and two solvent molecules are liberated in each reaction. Thus, the changes in the K values upon changing solvents are due mainly to the changes in the ΔH values upon changing solvents, which depend upon the properties of the solvent; the bond strength between the metal ion and the solvent in the coordination sphere increases with the increase in the basicities of the solvents. The donor number is a measure of the basicity of the solvent, being equal to the heat of the reaction between $SbCl_5$ and the solvent in 1,2-dichloroethane.[2] All the solvents used in the present study coordinate with the oxygen atom to the first transition metal ion, with no back donation in the coordination. Thus, it is considered that Eq. 1 might hold for the metal ion in various solvents in octahedral-octahedral equilibria.

It has been reported that, in the cases of halide (X^-), the stabilities of $[Co(X)_4]^{2-}$ are affected by both the donor number and the acceptor number of the solvents.[2] However, since bpy is electrically neutral and the solvation to bpy occurs more weakly than that to the Cl^- ion, the acceptor number is not important here.

In conclusion, log $K[s]^2$ is linear with respect to the donor number only when the solvation to the ligand is weak and the octahedral–octahedral equilibria hold in the solvents, as is shown in Fig. 1.

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