June, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***66****, 1669—1674(1993)* 1669

Coordination of Water Hydrogen-Bonded to Pyridine Derivatives to the (1*R*,4*S*,8*R*,11*S*)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Cation in Nitrobenzene

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(Received January 5, 1993)

The axial coordination of pyridine, 2-methylpyridine, 4-methylpyridine and water (W) hydrogen-bonded to each donor solvent (S) to the (1*R*,4*S*,8*R*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) cation ($[Ni(tmc)]^{2+}$) in nitrobenzene has been investigated spectrophotometrically. Pyridine and its derivatives are hardly coordinated to $[Ni(tmc)]^{2+}$ owing to steric hindrance, but the water which is hydrogen-bonded to the donor solvent as a 1 : 1 complex (WS) can be easily coordinated to form the five coordinated $[Ni(tmc)(WS)]^{2+}$ cation with a coordination constant (K_{MWS} in $dm^3 mol^{-1}$) of 6.5 for pyridine, 5.7 for 2-methylpyridine, and 11.5 for 4-methylpyridine. The smaller K_{MWS} value for 2-methylpyridine is due to steric hindrance. It was found that the residual hydrogen atom of the coordinated water in WS can be hydrogen-bonded to further species such as S and WS to form additional kinds of five-coordinated complexes, $[Ni(tmc)(WS–S)]^{2+}$ and $[Ni(tmc)(WS–WS)]^{2+}$. Coordination of the doubly hydrogen-bonded water (WS–S) which is induced as a result is stronger for 4-methylpyridine than for pyridine. This reflects the substituent effect of 4-methyl group on the basicity. The basicity of pyridine and its derivatives has been discussed in connection with the electrostatic/charge-transfer balance for hydrogen-bonding, compared with dimethyl sulfoxide.

The (1*R*,4*S*,8*R*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) cation ($[Ni(tmc)]^{2+}$) exists in solutions as an equilibrium mixture of a red, four-coordinated square species and a green, five-coordinated square-pyramidal species.[1,2)]

In the previous study,[3)] it was shown that water dissolved in nitrobenzene is barely coordinated to $[Ni(tmc)]^{2+}$, but water which is hydrogen-bonded to dimethyl sulfoxide as a 1 : 1 complex in nitrobenzene is easily coordinated. Further, it was found that two additional kinds of five-coordinated complexes were formed as a result of hydrogen-bonding of water and dimethyl sulfoxide to the residual hydrogen of the coordinated water.

In the present work, the change of the basicity and hydrogen-bonding donicity for water was studied with respect to formation of the 1 : 1 complex (WS) of water (W) and donor solvent (S), and of its five-coordinated complex $[Ni(tmc)(WS)]^{2+}$ in nitrobenzene. Donor number of pyridine is larger than that of dimethyl sulfoxide.[4)] The pyridine and its derivatives have different degree in basicity (pyridine ($pK_a = 5.19$) < 2-methylpyridine (5.97) ≈ 4-methylpyridine (6.02)) and steric factor.[5)] The substituent effect on the coordination of WS to $[Ni(tmc)]^{2+}$ will be discussed with respect to the basicity and the hydrogen-bonding donicity of water which is hydrogen-bonded to the donor solvents.

Experimental

The metal complex salt, $[Ni(tmc)](ClO_4)_2$ was prepared according to the procedure in the literature.[1,6)] Analysis was as follows. Found: C, 32.62; H, 6.40; N, 10.84%. Calcd for $C_{14}H_{32}O_8N_4Cl_2Ni$: C, 32.71; H, 6.27; N, 10.90%. Nitrobenzene, pyridine, 2-methylpyridine (more than 98%), and 4-methylpyridine (more than 97%) was purchased from Wako Pure Chemical Industries, Ltd. Purification of nitrobenzene was described previously.[2,7)] Pyridine, 2-methylpyridine, and 4-methylpyridine were purified by fractional distillation through a 1.2 m-column. $[^2H_5]$nitrobenzene (^2H= 99.5%) and $[^2H_5]$pyridine (^2H=99%) (both from Aldrich Chemical Company), 2-methylpyridine and 4-methylpyridine without deuteration were used for NMR measurements after standing over molecular sieves (type 4A) for 1 week.

The instrumentation and procedures used to obtain the water content in the solvents, the IR spectra and the visible absorption spectra were the same as described previously.[2,7)] Absorbances for the estimation of equilibrium constants of the complex cation were measured at ca. 1×10^{-3} mol dm^{-3} $[Ni(tmc)]^{2+}$ throughout the experiment. ^{1}H NMR spectra were obtained on a JEOL model JNM-GSX270 NMR spectrometer (270 MHz) at 25±1°C. Tetramethylsilane was used as internal standard.

All solutions were prepared by weight. An Anton Paar model DMA O2D digital density meter was used for measurements of density at 25±0.002°C.

Results and Discussion

Water Species in Nitrobenzene Containing Pyridine and Its Derivatives. Figure 1 shows the IR spectra of water in binary nitrobenzene–pyridine mixtures over the full composition range. In nitrobenzene, the sharp band at 3694 cm^{-1} is assigned to stretching of the free O–H bond, and the bands at 3655 and 3570 cm^{-1} are assigned to the O–H bond for a 1 : 2 water–nitrobenzene species.[3)] These bands are weakened with an increase in the pyridine content.

A shoulder at 3645 cm^{-1} and a broad band at 3360 cm^{-1} are assigned to the free O–H bond and the hydrogen-bonded O–H bond for a 1 : 1 water–pyridine species, respectively, on the basis of the dependency on the water concentration and the assignment by Mohr et al.[8)]

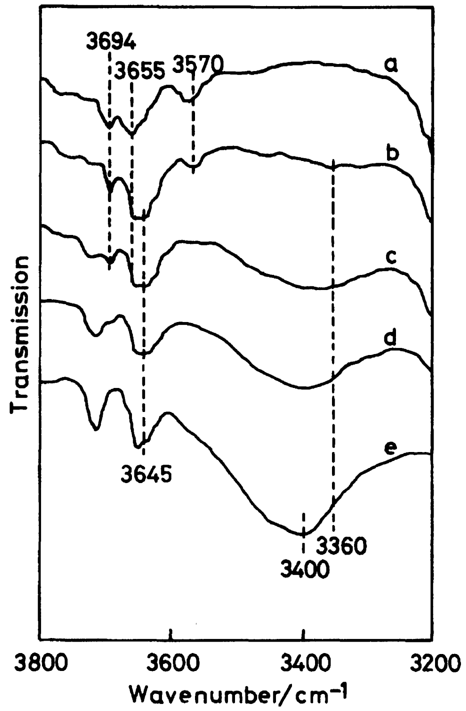

Fig. 1. IR spectra of water in pyridine–nitrobenzene mixed solvents. Mole fraction of pyridine ([water]/mol dm^{-3}): (a) 0.0 (0.081), (b) 0.081 (0.116), (c) 0.385 (0.100), (d) 0.674 (0.122), (e) 1.00 (0.092).

for the 1 : 1 water–pyridine complex in tetrachloromethane. Increasing the pyridine mole fraction decreases the shoulder and the broad band, and produces a broad band at 3400 cm^{-1} which is ascribed to the two bonded O–H groups for a 1 : 2 water–pyridine species. Similar spectra were obtained for 2-methylpyridine and 4-methylpyridine.

From an inspection of the IR data, it can be said that in binary nitrobenzene–donor solvent mixtures with a mole fraction of less than 0.081 for pyridine, 0.098 for 2-methylpyridine, and 0.049 for 4-methylpyridine, W and WS are predominant. The 1 : 1 W–S complex formation and the formation constant (K_{WS}) in nitrobenzene are written as

$$\mathrm{W} + \mathrm{S} \rightleftharpoons \mathrm{WS} \tag{1}$$

$$K_{\mathrm{WS}} = [\mathrm{WS}]/[\mathrm{W}][\mathrm{S}] \tag{2}$$

K_{WS} was evaluated using the Eq. 3 by ^{1}H NMR as described previously.[3)]

$$1/(\delta - \delta_0) = 1/(\delta_1 - \delta_0) + 1/(\delta_1 - \delta_0)K_{\mathrm{WS}}[\mathrm{S}] \tag{3}$$

where δ_0 (=647.7 Hz) is the chemical shift of monomer water in nitrobenzene, δ_1 is the chemical shift of WS, and [S] is the concentration of pyridine, 2-methylpyridine, or 4-methylpyridine. The ^{1}H chemical shift, δ, of water was investigated in nitrobenzene solutions containing the donor solvent of a mole fraction of less than 0.02. Since the chemical shift, δ, depends slightly on the water concentration due to the formation of water dimer etc., values of δ extrapolated to zero water concentration were used. In Eq. 3 the total concentration of donor solvent was used for [S] because the concentration of WS is negligible compared with the total concentration of S. A typical plot of Eq. 3 for 2-methylpyridine is shown in Fig. 2 where a good linear relationship was obtained. K_{WS} was obtained from the intercept and the slope. Table 1 lists K_{WS} with δ_1 obtained for donor solvents. Formation constants for the 1 : 1 water–donor solvent complex in tetrachloromethane obtained from IR are 2.4[9)] dm^3 mol^{-1} and 2.7[10)] for pyridine, 3.05[9)] for 4-methylpyridine and 8.4[10)] for dimethyl sulfoxide (1.5[3)] dm^3 mol^{-1} for dimethyl sulfoxide in nitrobenzene). The formation constant in nitrobenzene is smaller than that in tetrachloromethane. This may be due to stronger interactions of water with nitrobenzene which has a stronger solute hydrogen-bond parameter[11)] than tetrachloromethane. The difference in K_{WS} among pyridine and its derivatives in nitrobenzene is indistinguishable owing to experimental errors.

Spectral Change of the Nickel Complex. The present experiments were carried out with the mixed

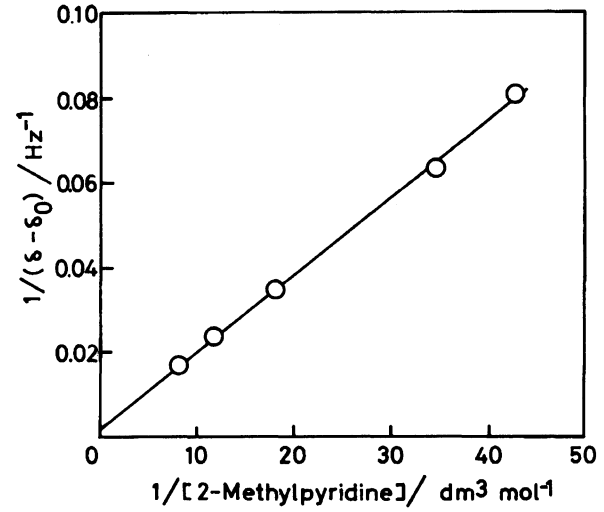

Fig. 2. Plot of $1/(\delta-\delta_0)$ vs. 1/[2-methylpyridine] for water hydrogen-bonded to 2-methylpyridine in nitrobenzene at 25 °C.

Table 1. K_{WS} and δ_1 for 1 : 1 Water–Donor Solvent Complex in Nitrobenzene at 25 °C

Donor solvent	K_{WS}	δ_1/Hz
DMSO [a)]	1.5±0.2	1159±67
Py [b)]	1.0±0.4	1079±166
2-MePy [c)]	1.0±0.6	1183±284
4-MePy [d)]	0.9±0.5	1290±337

a) Dimethyl sulfoxide, Ref. 3. b) Pyridine. c) 2-Methylpyridine. d) 4-Methylpyridine.

solvent systems where the mole fraction of pyridine, 2-methylpyridine, and 4-methylpyridine in nitrobenzene is less than 0.1, 0.03, and 0.03, respectively. In these solvents there was no change in the spectrum of $[Ni(tmc)]^{2+}$ with *R*,*S*,*R*,*S*-configuration for 2 h, showing no interconversion into the *R*,*S*,*S*,*R*-isomer.[12,13]

Typical visible spectra of $[Ni(tmc)]^{2+}$ in nitrobenzene containing pyridine and water are shown in Fig. 3. The absorption peak at 519 nm is ascribed to the red, four-coordinated, planar complex and the peak at 654 nm is ascribed to the blue, five-coordinated, square-pyramidal complex.

Figure 4 shows the variation of molar absorptivity at 519 nm with the concentration of water and pyridine in nitrobenzene. When pyridine is not present the molar absorptivity hardly changes with the water content, showing that no nitrobenzene-solvated water is coordinated. The molar absorptivity extrapolated to zero water concentration is unchanged with increasing pyridine content. Similar results were obtained for 2-methylpyridine and 4-methylpyridine. This shows that these donor solvents are not coordinated to $[Ni(tmc)]^{2+}$ in spite of their high basicity. This is due to the sterical interaction between the methyl groups in tmc and the pyridine ring.[2,14]

Coordination of the Water Complex. Since in the present nitrobenzene–donor solvent system only the predominant species which can be coordinated is water which is hydrogen-bonded to S, axial coordination of the water complex to $[Ni(tmc)]^{2+}$ is described as follows.

$$M + WS \rightleftharpoons MWS \tag{4}$$

$$K_{MWS} = [MWS]/[M][WS] \tag{5}$$

where M is $[Ni(tmc)]^{2+}$ and K_{MWS} are the coordination constant.

However, it was found that the absorptivity behavior in Fig. 4 cannot be explained by reaction 4 alone, because in this case the K_{MWS} value obtained depended on the concentration of the donor solvent, as will be shown later in Fig. 5 where the apparent coordination constant, K_{ap}, is the varying value of K_{MWS}. Similar results were obtained for 2-methylpyridine and 4-meth-

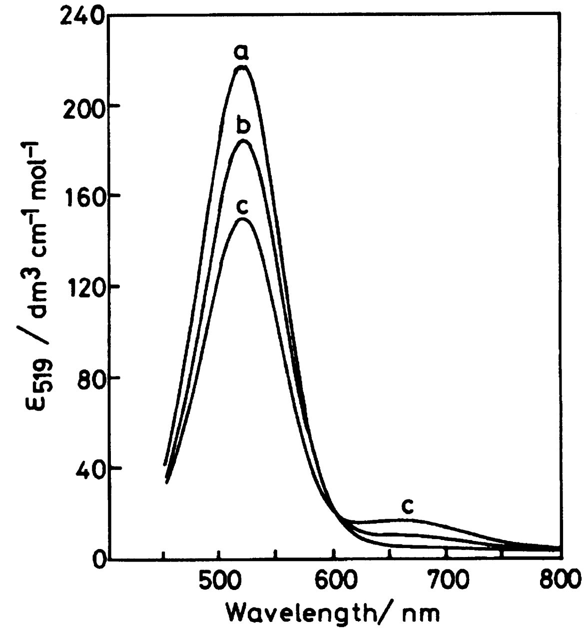

Fig. 3. Visible spectrum variation of a 1.0×10^{-3} mol dm^{-3} solution of $[Ni(tmc)](ClO_4)_2$ with the concentration of pyridine and water in nitrobenzene at 25 °C. ([pyridine]/mol dm^{-3}, [water]/mol dm^{-3}): (a) (0.733, 0.00678), (b) (0.733, 0.0433), (c) (0.733, 0.0982).

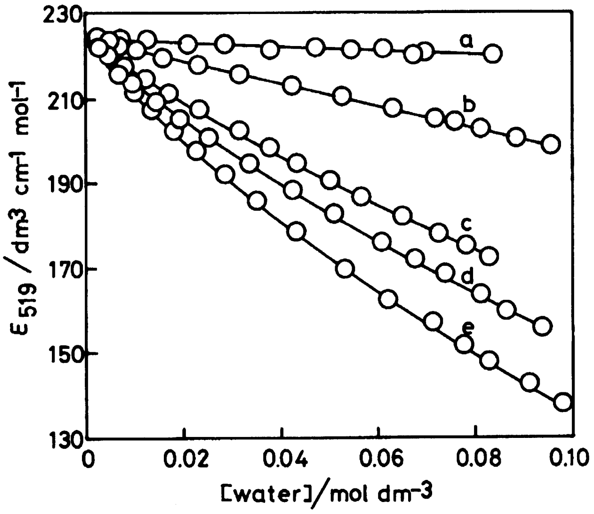

Fig. 4. Variation of molar absorptivity at 519 nm with the concentration of pyridine and water in nitrobenzene at 25 °C. [pyridine]/mol dm^{-3}: (a) 0.0, (b) 0.186, (c) 0.460, (d) 0.546, (e) 0.733.

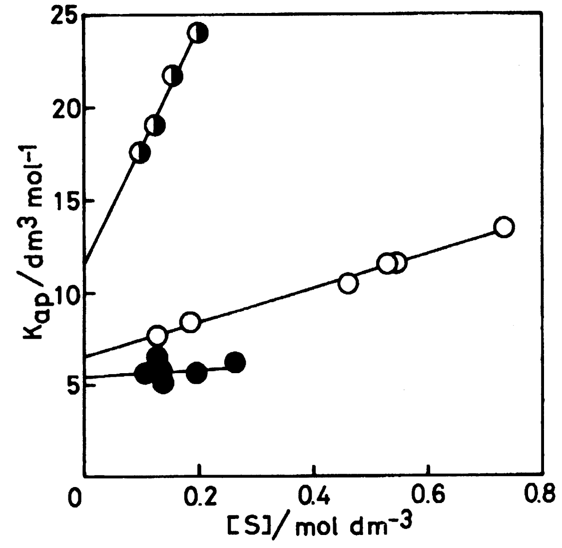

Fig. 5. Dependence of K_{ap} on the pyridine (○), 2-methylpyridine (●), and 4-methylpyridine (◑) concentration in nitrobenzene at 25 °C.

ylpyridine. Therefore, additional association involving the donor solvent should be considered. It is likely that the electron density on hydrogen atoms of the coordinated WS in reaction 4 is lowered because the electrons on the coordinated oxygen atom are drawn to the positive central nickel atom. This may result in a stronger hydrogen-bonding donor of the hydrogen atoms. In water the maximum wavelength for the five-coordinated species is shifted from 654 nm for $[\mathrm{Ni(tmc)(H_2O)}]^{2+}$ to 711 nm for $[\mathrm{Ni(tmc)(OH)}]^{+}$. However, as seen in Fig. 3, no shift in the maximum wavelength was observed on adding pyridine and water to the nitrobenzene solution at the concentration used, indicating that the presence of $[\mathrm{Ni(tmc)(OH)}]^{+}$ is negligible. Similar results were obtained for 2-mythylpyridine and 4-methylpyridine.

We now consider three hydrogen-bonding reactions involving the coordinated water to form a doubly hydrogen-bonded water molecule with a further species, namely, with donor solvent itself:

$$\mathrm{MWS} + \mathrm{S} \rightleftharpoons \mathrm{MWS{-}S} \tag{6}$$

$$K_{\mathrm{MWS-S}} = [\mathrm{MWS{-}S}]/[\mathrm{MWS}][\mathrm{S}] \tag{7}$$

with WS:

$$\mathrm{MWS} + \mathrm{WS} \rightleftharpoons \mathrm{MWS{-}WS} \tag{8}$$

$$K_{\mathrm{MWS-WS}} = [\mathrm{MWS{-}WS}]/[\mathrm{MWS}][\mathrm{WS}] \tag{9}$$

and with W of which the mole fraction is 0.6–0.9 in the total water content:

$$\mathrm{MWS} + \mathrm{W} \rightleftharpoons \mathrm{MWS{-}W} \tag{10}$$

$$K_{\mathrm{MWS-W}} = [\mathrm{MWS{-}W}]/[\mathrm{MWS}][\mathrm{W}] \tag{11}$$

The formation constants $K_{\mathrm{MWS-S}}$, $K_{\mathrm{MWS-WS}}$, and $K_{\mathrm{MWS-W}}$ are the respective hydrogen-bonding formation constants. It is assumed that the activity coefficients of all the coordinating species are unity and that the activity coefficients of the nickel complex cation are unchanged, because their concentration is low.

In the case of pyridine, the decrease in molar absorptivity as shown in Fig. 4 with increasing pyridine and water contents can be attributed to the coordination of water complexes. The molar absorptivity, ε observed at 519 nm is given by Eq. 12,

$$\varepsilon = (1-\alpha)\varepsilon_0 + \alpha\varepsilon_{\mathrm{s}} \tag{12}$$

where ε_0 is the molar absorptivity (224 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) of the four-coordinated complex cation in nitrobenzene. ε_{s} is the molar absorptivity (10 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$)2) of the five-coordinated complex cation and α is the fraction of the five-coordinated complex cation. The apparent coordination constant K_{ap} is defined as

$$\begin{aligned} K_{\mathrm{ap}} = ([\mathrm{MWS}] &+ [\mathrm{MWS{-}S}] \\ &+ [\mathrm{MWS{-}WS}] + [\mathrm{MWS{-}W}])/[\mathrm{M}][\mathrm{WS}] \end{aligned} \tag{13}$$

and is rewritten by using the equilibrium constants defined above:

$$\begin{aligned} K_{\mathrm{ap}} = K_{\mathrm{MWS}}(1 &+ K_{\mathrm{MWS-S}}[\mathrm{S}] \\ &+ K_{\mathrm{MWS-WS}}K_{\mathrm{WS}}[\mathrm{W}][\mathrm{S}] + K_{\mathrm{MWS-W}}[\mathrm{W}]) \end{aligned} \tag{14}$$

Then, the fraction α is written as

$$\begin{aligned} \alpha = ([\mathrm{MWS}] &+ [\mathrm{MWS{-}S}] \\ &+ [\mathrm{MWS{-}WS}] + [\mathrm{MWS{-}W}])/[\mathrm{M}]_{\mathrm{t}} \end{aligned} \tag{15}$$

where $[\mathrm{M}]_{\mathrm{t}}$ is the total concentration of the complex cation. In the range of low water concentration, $[\mathrm{H_2O}] < 0.02\ \mathrm{mol\,dm^{-3}}$, the contribution of reactions 8 and 10 is reduced. In this case, K_{ap} is reduced to the following, as a first approximation.

$$K_{\mathrm{ap}} = K_{\mathrm{MWS}}(1 + K_{\mathrm{MWS-S}}[\mathrm{S}]) \tag{16}$$

Thus, plotting K_{ap} against [S] gives K_{MWS} at [S]=0. Because the complex species containing S were found to be less than 2% of the total concentration for donor solvent, the total concentration of donor solvent was used for [S]. As shown in Fig. 5, there are good linear relationships. K_{MWS} values obtained from the intercepts were 6.5±0.1 for pyridine, 5.7±0.3 for 2-methylpyridine, and 11.5±0.5 for 4-methylpyridine. Unfortunately, as reactions 8 and 10 cannot be discriminated from each other, it was necessary to make three best-fit calculations for unknown formation constants: (i) $K_{\mathrm{MWS-S}}$, (ii) $K_{\mathrm{MWS-S}}$ and $K_{\mathrm{MWS-WS}}$, and (iii) $K_{\mathrm{MWS-S}}$ and $K_{\mathrm{MWS-W}}$. Tables 2, 3, and 4 give the best fit results obtained for each case using a range of the water concentration (0—0.1 $\mathrm{mol\,dm^{-3}}$), together with the standard deviations, σ which was calculated from

$$\sigma^2 = \Sigma(\varepsilon - \varepsilon_{\mathrm{cal}})^2/(N-1) \tag{17}$$

Table 2. Equilibrium Constants a) for Pyridine in Nitrobenzene at 25 °C

[Py b)] / mol dm^{-3}	$K_{\mathrm{MWS-S}}$ c) / dm^3 mol^{-1}	$K_{\mathrm{MWS-WS}}$ c) / dm^3 mol^{-1}	$K_{\mathrm{MWS-W}}$ c) / dm^3 mol^{-1}	σ
0.128	1.5±0.7			0.192
	1.3±0.6	4±9		0.180
	1.3±0.6		0.5±1.0	0.180
0.186	1.7+0.6			0.371
	1.1±0.4	9±7		0.277
	1.1±0.4		1.5±1.3	0.273
0.461	1.4±0.2			0.564
	1.2±0.2	4±4		0.375
	1.2±0.2		1.9±1.8	0.360
0.530	1.5±0.2			0.446
	1.4±0.2	3±3		0.334
	1.4±0.2		1.4±1.2	0.312
0.546	1.5±0.3			0.916
	1.3±0.2	5±4		0.631
	1.3±0.2		2.4±2.1	0.606
0.733	1.5±0.2			0.798
	1.4±0.2	3±3		0.562
	1.4±0.2		2.0±2.1	0.546

a) K_{WS}=1.0 dm^3 mol^{-1} and K_{MWS}=6.5 dm^3 mol^{-1}.
b) Pyridine. c) Errors correspond to 3σ.

Table 3. Equilibrium Constants [a] for 2-Methylpyridine in Nitrobenzene at 25 °C

[2MePy [b]]	$K_{\mathrm{MWS-S}}$ [c]	$K_{\mathrm{MWS-WS}}$ [c]	$K_{\mathrm{MWS-W}}$ [c]	σ
$\mathrm{mol\,dm^{-3}}$	$\mathrm{dm^3\,mol^{-1}}$	$\mathrm{dm^3\,mol^{-1}}$	$\mathrm{dm^3\,mol^{-1}}$	
0.110	0.0±1.5			0.441
	0.0±1.5	0±23		0.441
	0.0±1.5		0.0±2.3	0.441
0.131	0.4±0.9			0.330
	0.0±0.9	1±16		0.264
	0.0±0.9		0.1±1.9	0.264
0.140	0.0±1.0			0.411
	0.0±1.0	0±16		0.411
	0.0±1.0		0.0±2.1	0.411
0.142	0.3±1.4			0.408
	0.0±0.9	0±14		0.408
	0.0±0.9		0.0±1.8	0.408
0.201	0.4±1.0			0.589
	0.0±0.4	8±8		0.348
	0.0±0.4		1.4±1.4	0.348
0.264	0.3±0.4			0.416
	0.2±0.4	2±6		0.368
	0.1±0.4		0.9±1.6	0.364

a) $K_{\mathrm{WS}}=1.0\ \mathrm{dm^3\,mol^{-1}}$ and $K_{\mathrm{MWS}}=5.7\ \mathrm{dm^3\,mol^{-1}}$. b) 2-Methylpyridine. c) Errors correspond to 3σ.

Table 4. Equilibrium Constants [a] for 4-Methylpyridine in Nitrobenzene at 25 °C

[4MePy [b]]	$K_{\mathrm{MWS-S}}$ [c]	$K_{\mathrm{MWS-WS}}$ [c]	$K_{\mathrm{MWS-W}}$ [c]	σ
$\mathrm{mol\,dm^{-3}}$	$\mathrm{dm^3\,mol^{-1}}$	$\mathrm{dm^3\,mol^{-1}}$	$\mathrm{dm^3\,mol^{-1}}$	
0.0975	5.9±1.2			0.373
	4.9±1.1	16±17		0.309
	4.9±1.1		1.3±1.4	0.307
0.124	5.6±1.0			0.408
	4.9±0.7	13±11		0.286
	4.9±0.7		1.3±1.2	0.282
0.156	6.1±0.6			0.389
	5.4±0.4	11±6		0.231
	5.4±0.4		1.5±0.8	0.232
0.201	5.8±0.6			0.525
	5.6±0.6	3±10		0.488
	5.6±0.6		0.5±1.8	0.488

a) $K_{\mathrm{WS}}=0.9\ \mathrm{dm^3\,mol^{-1}}$ and $K_{\mathrm{MWS}}=11.5\ \mathrm{dm^3\,mol^{-1}}$. b) 4-Methylpyridine. c) Errors correspond to 3σ.

and the errors are the values giving 3σ.

Christian et al.[15,16] and Ödberg and Högfeldt[17] reported a dimerization constant of 1.054 and 1.20 $\mathrm{dm^3\,mol^{-1}}$, respectively for water in nitrobenzene. In the present calculation, however, no useful information on a water dimer contribution was obtained by using these values.

Although for the 2-methylpyridine system the two-parameter fitting does not always gives better fitting results, for the pyridine and 4-methylpyridine systems the two-parameter fitting gives significantly small σ values than one-parameter fitting and almost constant values of $K_{\mathrm{MWS-S}}$ were obtained. This shows that in these systems a contribution of $K_{\mathrm{MWS-S}}$ is significant. In view of the errors the contribution of $K_{\mathrm{MWS-WS}}$ and $K_{\mathrm{MWS-W}}$ is small for all the system.

Table 5 summarizes the averaged values for $K_{\mathrm{MWS-S}}$, $K_{\mathrm{MWS-WS}}$, and $K_{\mathrm{MWS-W}}$, together with those for dimethyl sulfoxide. Although pyridine, its derivatives, and nitrobenzene-solvated water are barely coordinated to the cation, the water which is hydrogen-bonded to pyridine and its derivatives is easily coordinated with a coordination constant larger than that of dimethyl sulfoxide itself. Thus, the coordinating ability of water is enhanced by formation of the 1 : 1 W–S complex. We can regard water molecules as an "arrow head" for coordinating solutes. This comes from both a steric advantage and the enhanced basicity due to charge transfer through hydrogen bonding.

The K_{WS} value for pyridine in nitrobenzene (Table 5) is smaller than that for dimethyl sulfoxide. This trend also holds in tetrachloromethane: K_{WS} is 2.7 $\mathrm{dm^3\,mol^{-1}}$ for pyridine and 8.4 for dimethyl sulfoxide.[10] Further, the K_{MWS} value increases in the order: 2-methylpyridine < pyridine < 4-methylpyridine < dimethyl sulfoxide. This apparently is contradictory to the expectation from the donor number concept because pyridine is a stronger donor solvent than dimethyl sulfoxide with respect to donor number.[4]

Recently, Maria et al.[18] investigated the nonprotogenic solvent effects on basicity-dependent properties and concluded that the electrostatic/charge-transfer ratio for hydrogen-bonding increases in the order: $-\Delta S^\circ < \Delta\nu_{\mathrm{OH}} < -\Delta H^\circ < -\Delta G^\circ$. This means that the electrostatic effect is a major contribution to ΔG° and a minor contribution to ΔS°. This conclusion is helpful in explaining the present results.

The dimethyl sulfoxide molecule has a trigonal pyramid structure in which the dipole lies almost along the S=O bond and is exposed,[19] and its dipole moment (3.9) is larger than that of pyridine (2.2). Therefore, it is likely that the larger K_{WS} value for dimethyl sulfoxide refers to the contribution from its large dipole moment, as compared with pyridine. The enthalpic parameter, donor number is much less electrostatic and can not always explain the order of hydrogen-bonding equilibria. The bonded O–H stretching wavenumber, which is more sensitive to the charge-transfer interaction than

Table 5. Equilibrium Constants in Nitrobenzene at 25 °C

In NB [a]	K_{WS}	K_{MS} [b]	K_{MWS}	$K_{\mathrm{MWS-S}}$	$K_{\mathrm{MWS-WS}}$	$K_{\mathrm{MWS-W}}$
DMSO[c]	1.5	4.2	24	12	(9)	(1.0)
Py[d]	1.0	0	6.5	1.3	(5)	(1.6)
2-MePy[e]	1.0	0	5.7	<0.1	(2)	(0.7)
4-MePy[f]	0.9	0	11.5	5.2	(11)	(1.2)

a) Nitrobenzene. b) The coordination constant of donor solvent. c) Dimethyl sulfoxide, Ref. 3. d) Pyridine. e) 2-Methylpyridine. f) 4-Methylpyridine. Either of values in parentheses for donor solvent should be considered.

ΔG°,[18] decreases in the order: dimethyl sulfoxide (3425 cm^{-1}) > pyridine (3360) > 4-methylpyridine (3325) > 2-methylpyridine (3320) in nitrobenzene and dimethyl sulfoxide (3441)[10]> pyridine (3393)[9]> 4-methylpyridine (3377)[9] in tetrachloromethane. This means that a stronger charge-transfer from the pyridines to the water molecule occurs and as a result the pyridines should give a larger K_{MWS}, as compared with dimethyl sulfoxide. However, the results obtained (Table 5) are not the case. The smaller K_{MWS} values for the pyridines may result from steric hindrance between the pyridine ring and the methyl groups in $[\mathrm{Ni(tmc)}]^{2+}$ and the more marked steric hindrance effect is seen for 2-methylpyridine where the K_{MWS} value is smaller than that for 4-methylpyridine although both donor solvents have similar $\mathrm{p}K_{\mathrm{a}}$ values[5] and the bonded O–H stretching wavenumbers.

Hydrogen-bonding donicity of water is also enhanced by the coordination of WS to $[\mathrm{Ni(tmc)}]^{2+}$. The $K_{\mathrm{MWS\text{-}S}}$ value increases in the order: 2-methylpyridine < pyridine < 4-methylpyridine < dimethyl sulfoxide. This order is the same as for K_{MWS}. For pyridine and 4-methylpyridine which are sterically similar to each other with respect to the coordination it is seen that stronger the coordinating ability of the 1 : 1 W–S complex to $[\mathrm{Ni(tmc)}]^{2+}$, the stronger the hydrogen-bonding donicity of the water coordinated.

The present results agree with a suggestion by Gutmann[4] that a first hydrogen bond involving a given site of a molecule or ion enhances the electron-donor or -acceptor power of the adjacent sites of opposite nature, whereas it weakens the reactivity of the neighboring sites of the same nature. Huyskens[20] also reported a similar effect of charge transfer: The basicity of phenol increases with increasing formation constant for hydrogen-bonding between phenol and nitrogen bases (tetramethylurea and triethylamine).

Conclusions

Coordinating ability of the water which is hydrogen-bonded to a donor solvent as a 1 : 1 complex (WS) is increased. Further, the hydrogen-bonding donicity of the residual hydrogen atom of the water is also increased by its coordination to the nickel complex. In the water–donor solvent complex, the charge-transfer to the water is more marked for pyridine than dimethyl sulfoxide but the coordination of the water–pyridine complex to $[\mathrm{Ni(tmc)}]^{2+}$ is sterically hindered. The hydrogen-bonding acceptor power of pyridine is weaker than that of dimethyl sulfoxide although donor number of pyridine is larger than that of dimethyl sulfoxide. This is because the electrostatic nature of hydrogen-bonding gives stronger hydrogen-bonding acceptor power for dimethyl sulfoxide which has a larger dipole moment, as compared with pyridine.

This work was supported by a Grant-in-Aid for Scientific Research No. 04640556 from the Ministry of Education, Science and Culture.

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