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Formation of the *N,N*-Bidentate Chelates of 2-(2-Pyridylazo)phenolic Ligands with Nickel(II) in Nonaqueous Solvents

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The formation of *N,N*-bidentate 1:2 complexes of nickel(II) with various *N,N,O*-terdentate 2-(2-pyridylazo)phenolic ligands was detected spectrophotometrically in ethyl acetate and was examined with respect to the influences of Brønsted bases, the counter anions in the nickel(II) salts employed, solvent basicity, and the steric requirements around the donor nitrogen atoms in the ligand in the 1:2 complex. It is concluded that the stability of the *N,N*-bidentate complex species in solutions predominantly depends on the basicity of the counter anions X in NiX_2 and of the solvent. In the case of 1-(2-pyridylazo)-2-naphthol, owing to a high steric hindrance of the naphthalene ring, the formation of the *N,N*-bidentate complex was not observed even in the solvent of low basicity such as dioxane.

It is well known that in aqueous solutions nickel(II) ions react with *N,N,O*-terdentate 2-(2-pyridylazo)phenolic ligands such as 4-(2-pyridylazo)resorcinol (PAR) to form *N,N,O*-terdentate complexes.[1] Recently, we first reported the formation of an *N,N*-bidentate complex of an *N,N,O*-terdentate ligand, 4-(4-methyl-2-pyridylazo)resorcinol (4-MePAR), with nickel(II) perchlorate in an aprotic solvent, 1,4-dioxane.[2] The *N,N*-bidentate complex was isolated from neat dioxane solution and identified to be in a distorted planar configuration in which four nitrogen atoms of the two ligand molecules are coordinated to the nickel(II) atom (Fig. 1). Upon addition of a Brønsted base such as imidazole to the dioxane solution of the *N,N*-bidentate species, an *N,N,O*-terdentate complex was formed.[2] This fact indicates that weak Brønsted bases can promote the release of the intramolecularly hydrogen-bonded proton, N···H–O, in the *N,N*-bidentate complex.

In the present paper, we discuss the conditions required for the formation of the *N,N*-bidentate complexes of *N,N,O*-terdentate 2-(2-pyridylazo)phenolic ligands with a number of nickel(II) salts in various nonaqueous solvents.

Experimental

Materials. Ethyl acetate (Wako) was dried with anhydrous magnesium sulfate (Nakarai) or Molecular Sieves 4A (Wako) and distilled under argon atmosphere immediately before use. Ethanol and pyridine were dried with Molecular Sieves 3A or 4A and distilled under argon atmosphere. 1,4-Dioxane was purified as reported in the previous paper.[2] The purified solvents were stored under argon atmosphere. Other solvents used here were of specially-prepared reagent grade (Nakarai) or of guaranteed reagent grade (Wako).

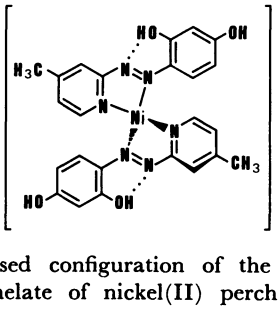

Fig. 1. Proposed configuration of the isolated *N,N*-bidentate chelate of nickel(II) perchlorate with 4-MePAR.[2]

Nickel(II) perchlorate dihydrate was prepared as described in the previous work.[2] Other nickel(II) salts were of reagent grade unless otherwise specified. The perchlorates of zinc(II), manganese(II), and lanthanum(III) were prepared by the same method as in the synthesis of nickel(II) perchlorate. The contents of water in the metal salts were determined by Karl-Fischer titration. Found: $Ni(ClO_4)_2\cdot 2.4H_2O$ (dried by heating the hexahydrate in vacuo), $Ni(ClO_4)_2\cdot 6.1H_2O$, $NiCl_2\cdot 1.0H_2O$ (dried by heating the hexahydrate in vacuo), $NiCl_2\cdot 5.7H_2O$ (Wako, $NiCl_2\cdot 6H_2O$), $Zn(ClO_4)_2\cdot 6.1H_2O$, $Mn(ClO_4)_2\cdot 4.0H_2O$ (dried the hexahydrate in vacuo over P_2O_5 at room temperature).

The free ligands, 4-MePAR, 5-dimethylamino-2-(2-pyridylazo)phenol (DAPAP), and 4-(2-pyridylazo)phenol (*p*-PAP), were prepared as described in the previous paper.[2] Other ligands, PAR,[3] 4-(*x*-methyl-2-pyridylazo)resorcinol (*x*-MePAR, x=3, 5, and 6),[4] 4-(2-pyridylazo)orcinol (PAO),[5] and 2-(2-pyridylazo)-1-naphthol (α-PAN),[6] were prepared and purified according to the literature. 1-(2-Pyridylazo)-2-naphthol (β-PAN) was obtained from Dojindo Laboratories and used without further purification.

The *N,N,O*-terdentate complex of DAPAP employed here was synthesized as follows. The free ligand, DAPAP (172 mg, 0.71 mmol), was dissolved in 100 cm^3 of warm ethanol. Nickel(II) chloride (95 mg, 0.40 mmol) dissolved in 10 cm^3 of water was added to the deep red solution of DAPAP. A dark pink solution obtained was evaporated to ca. 2/3 volumes and allowed to stand for several days in the dark. The dark wine red crystals were filtered, washed with water, and dried overnight in vacuo over P_2O_5. Found: C, 57.64; H, 4.84; N, 20.74%. Calcd for $Ni(C_{13}H_{13}N_4O)_2$: C, 57.70; H, 4.84; N, 20.70%. The *N,N,O*-terdentate complexes of α- and β-PAN were obtained by the analogous method. Found: $[Ni(\alpha\text{-panH}_{-1})_2]^{0,\dagger}$: C, 64.67; H, 3.47; N, 13.47%.

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† α-panH$_{-1}$ denotes the mono-deprotonated anionic form resulting from the dissociation of the *o*-hydroxyl proton of α-PAN.

$[Ni(\beta\text{-panH}_{-1})_2]^0$: C, 64.80; H, 3.73; N, 15.14%. Calcd for $Ni(C_{15}H_{10}N_3O)_2$: C, 64.90; H, 3.63; N, 15.14%.

Measurements. Electronic spectra and pH* (pH-meter readings) of the sample solutions at 25 °C were measured using the procedure reported previously.[2] Karl-Fischer titrations were performed with the 10—40 mg sample dissolved in 25 cm^3 of dried methanol (Dassui-Yozai ML, Mitsubishi) using a Mitsubishi Kasei Karl-Fischer titrator Model MS-2.

Results and Discussion

Formation of an *N,N*-Bidentate Complex of Nickel(II) Perchlorate with 4-MePAR in Ethyl Acetate. Figure 2 shows a spectral change for the complex formation of nickel(II) perchlorate dihydrate with 4-MePAR in ethyl acetate. The spectrum of the free ligand, 4-MePAR, possesses an absorption maximum at 381 nm ($\varepsilon_{max}=2.07\times10^4\ mol^{-1}\ dm^3\ cm^{-1}$) (Curve 1). In the low concentrations of nickel(II) perchlorate, an orange solution was formed (Curve 3). On further addition of nickel(II) perchlorate ($[Ni(II)]_t/[4\text{-MePAR}]_t>0.4$) to the orange solution, the absorbance around 450 nm decreased with the increase of that around 430 nm; the color of the solution was yellow. The spectrum of the yellow solution has a single absorption maximum at 428 nm ($\varepsilon_{max}=4.62\times10^4\ mol^{-1}\ dm^3\ cm^{-1}$ at $[Ni(II)]_t/[4\text{-MePAR}]_t\simeq2$) (Curve 5). Two sets of isosbestic points were observed in the overall spectral change. Molar ratio method indicates that the metal to ligand ratio of the complex in the orange solution is 1:3. The metal to ligand ratio of the final complex in the yellow solution was found to be 1:2. The above reaction behavior in ethyl acetate was also reproduced by using a hexahydrate of nickel(II) perchlorate. This fact shows that the coordinated water in nickel(II) perchlorate specimen does not significantly affect the formation of the 1:2 complex of nickel(II) with 4-MePAR.[7]

Curve 1 in Fig. 3 shows a spectrum in ethyl acetate of an *N,N*-bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, which was isolated from dioxane solution.[2] The spectrum has a single absorption band at 431 nm ($\varepsilon_{max}=3.49\times10^4\ mol^{-1}\ dm^3\ cm^{-1}$).[8] The spectrum of the yellow ethyl acetate solution essentially coincides with that of the isolated bidentate complex. This fact indicates that the *N,N*-bidentate complex is also formed in ethyl acetate as in neat dioxane.

Reactions of the *N,N*-Bidentate Complex with Brønsted Bases in Ethyl Acetate. The color change from yellow to pink was observed upon addition of a Brønsted base such as *o*-chloroaniline, *m*-chloroaniline, 2,6-lutidine, and imidazole to the ethyl acetate solution of the isolated *N,N*-bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$. The spectral change of the bidentate complex on addition of 2,6-lutidine is shown in Fig. 3. The spectral change shows two distinct isosbestic points at 481 nm for the first step and at 503 nm for the second step. This fact implies that the reaction proceeds in two steps. Molar ratio method indicates that the ratio of the bidentate complex to the base in the overall reaction is 1:2. The spectrum in ethyl acetate of the final complex with λ_{max}'s at 400 ($\varepsilon_{max}=3.5\times10^4$) and 546 nm ($\varepsilon_{max}=3.2\times10^4\ mol^{-1}\ dm^3\ cm^{-1}$) essentially coincides with that of an *N,N,O*-terdentate complex, $[Ni(4\text{-meparH}_{-1})_2]^0$, isolated from aqueous solution.[2] From these results, the spectral change of the reaction between the bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, and 2,6-lutidine is attributed to the formation of the *N,N,O*-terdentate complex, $[Ni(4\text{-meparH}_{-1})_2]^0$, indicating the deprotonation of the two *ortho*-hydroxyl groups of the ligands in the bidentate complex.

The behavior of the reactions in ethyl acetate of

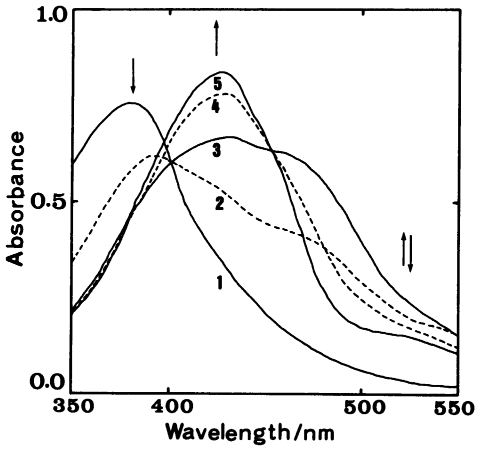


Fig. 2. Spectral change in the complex formation between nickel(II) perchlorate and 4-MePAR at 25 °C in ethyl acetate. $[4\text{-MePAR}]_t=3.57\times10^{-5}\ mol\ dm^{-3}$. $[Ni(II)]_t=0.00$ (1), 0.75 (2), 1.31 (3), 3.00 (4), and $7.49\times10^{-5}\ mol\ dm^{-3}$ (5).

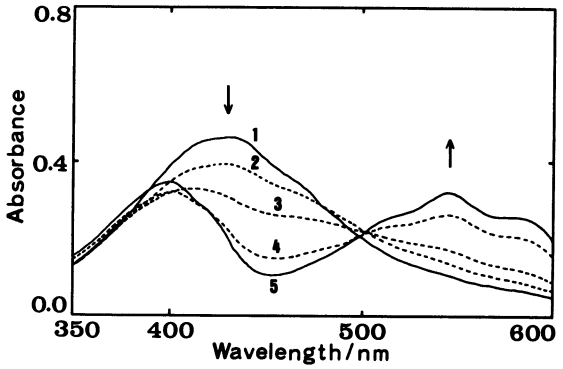


Fig. 3. Spectral change upon addition of 2,6-lutidine to the ethyl acetate solution of the isolated bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, at 25 °C. $[Ni\text{-}(4\text{-mepar})_2(ClO_4)_2]_t=9.89\times10^{-6}\ mol\ dm^{-3}$. $[2,6\text{-Lutidine}]_t=0.00$ (1), 0.70 (2), 1.41 (3), 2.10 (4), and $4.66\times10^{-5}\ mol\ dm^{-3}$ (5).

nickel(II) perchlorate with 4-MePAR and that of the bidentate complex with the base was identical with the behavior in neat dioxane.[2] This fact suggests that the effects of the solvation by ethyl acetate molecule on the reactions of $Ni(ClO_4)_2$ with 4-MePAR and of the Brønsted base with the bidentate complex are similar to the effects of the solvation by dioxane molecule.

Spectral Assignments of the Free Ligand 4-MePAR and Its Nickel(II) Complexes. In general, the bathochromic shift (red shift) of the absorption band in solution of azobenzene derivatives is caused by the following factors: Introduction of the auxochromic functional group such as OH and $N(CH_3)_2$ into the *para*-position of azo group, presence of the intramolecular hydrogen bond, N···H–O, bonding of cation such as proton to the azo nitrogens, and deprotonation of hydroxyl group.[9–13a,b] The absorption spectra of azobenzene derivatives with an auxochromic group have an absorption band in the range of 310—450 nm with relatively larger extinction coefficient ($\simeq 10^4\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$) in aqueous solutions and in organic solvents.[9–14] These bands are ascribed to the π-π^* (conjugation) transition of the azo chromophore.[9–12,15]

The absorption spectrum of 4-MePAR (Curve 1 in Fig. 2) is expected to show a large bathochromic shift compared with that of azobenzene, since 4-MePAR involves three functional groups, *p*-OH, *o*-OH, and CH_3, and the strong intramolecular hydrogen bonding. The main band of 4-MePAR shifted to longer wavelength (see below), owing to the interaction of transition dipole with highly polarizable solvents.[14] From the above results, the main band of the free ligand, 4-MePAR, could be assigned to that of π-π^* transition of the azo chromophore.

The *N*,*N*-bidentate chelate of nickel(II) with 4-MePAR has two five-membered chelate rings between nickel(II) and the two coordinated nitrogens in the ligand, namely, pyridyl and azo nitrogens (see Fig. 1). If the nickel(II) ions electrostatically act to the azo nitrogen in the same manner as proton, then the band of π-π^* transition of the free ligand should show a shift to longer wavelength by the formation of the Ni(II)–N(azo) bonds.[9,11] This assumption is consistent with the observed bathochromic shift of the *N*,*N*-bidentate complex. Thus, the main band at 431 nm of the *N*,*N*-bidentate chelate of nickel(II) (Curve 1 in Fig. 3) could probably be ascribed to a band of π-π^* transition. The absorption spectrum of the *N*,*N*,*O*-terdentate chelate of 4-MePAR in ethyl acetate (Curve 5 in Fig. 3) shows two characteristic bands at 400 and 546 nm with large molar extinction coefficients ($\simeq 3\times10^4\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$). The bands may be ascribed to those of π-π^* transition due to the deprotonation and/or the coordination of *o*-hydroxyl groups.[9]

The main bands of PAR, its methyl derivatives, and their nickel(II) complexes would also be assigned in a similar manner.

Spectral Features for Nickel(II) Complexes of 2-(2-Pyridylazo)phenolic Ligands. The absorption spectra of the free ligands generally show large red shifts by complex formation with metal ions in various solvent systems.[1,16,17] For example, Florence et al. have reported that in aqueous solution the *N*,*N*,*O*-terdentate complexes of M(II) ions with DAPAP derivatives have two absorption maxima in the range of 500 to 560 nm.[17] The similar spectral feature was observed in the complexes of other 2-(2-pyridylazo)phenolic ligands.[1,16] Table 1 summarizes the values of the red shift, $\Delta\lambda_{\max}=\lambda_{\max}(\text{complex})-\lambda_{\max}(\text{free ligand})$,[18] for the complexes of nickel(II) with 2-(2-pyridylazo)phenolic ligands in some nonaqueous solvents together with the color of the solution of the complexes. The complexes, $[\mathrm{Ni(pap)_2}]^{2+}$,[19] and $[\mathrm{Ni(4\text{-}mepar)_2}]^{2+}$, have the *N*,*N*-bidentate structure both in dioxane[2] and in ethyl acetate. Other nickel(II) complexes, $[\mathrm{Ni(4\text{-}meparH_{-1})_2}]^0$, $[\mathrm{Ni(\alpha\text{-}panH_{-1})_2}]^0$, $[\mathrm{Ni(\beta\text{-}panH_{-1})_2}]^0$, and $[\mathrm{Ni(dapapH_{-1})_2}]^0$, which were isolated from aqueous solution, are in the *N*,*N*,*O*-terdentate structure.[1,2,17] The values of $\Delta\lambda_{\max}$ for the *N*,*N*-bidentate and those for the *N*,*N*,*O*-terdentate complexes are remarkably different. The values of $\Delta\lambda_{\max}$ for the *N*,*N*-bidentate complexes were in the range of 45 to 77 nm, while those for the *N*,*N*,*O*-terdentate complexes in the range of 102 to 165 nm regardless of the kind of solvent used here;

Table 1. The Values of Red Shift ($\Delta\lambda_{\max}$) and the Color of the Solution of the *N*,*N*-Bidentate and the *N*,*N*,*O*-Terdentate Complexes of Nickel(II)

Species	$\Delta\lambda_{\max}$[a]/nm	Color	Solvent[b]
$[\mathrm{Ni(pap)_2}]^{2+}$,[c]	77	Yellow	AcOEt
	73	Yellow	Dioxane[f]
$[\mathrm{Ni(4\text{-}mepar)_2}]^{2+}$,[c]	48	Yellow	AcOEt
	49	Yellow	Dioxane[f]
$[\mathrm{Ni(4\text{-}mepar)_2}](\mathrm{ClO_4})_2$[c]	50[e]	Yellow	AcOEt
	45[e]	Yellow	Dioxane[f]
$[\mathrm{Ni(4\text{-}meparH_{-1})_2}]^0$,[d]	165	Pink	AcOEt
	161	Pink	Dioxane[f]
	134	Red	EtOH
	134[e]	Red	EtOH
	102, 122(sh)[e]	Red	DMF
$[\mathrm{Ni(dapapH_{-1})_2}]^0$,[d]	114	Pink	AcOEt
	>100[e]	Red	EtOH
$[\mathrm{Ni(\alpha\text{-}panH_{-1})_2}]^0$,[d]	118[e]	Purple	Dioxane
$[\mathrm{Ni(\beta\text{-}panH_{-1})_2}]^0$,[d]	111[e]	Pink	Dioxane

a) $\Delta\lambda_{\max}=\lambda_{\max}(\text{complex})-\lambda_{\max}(\text{free ligand})$. b) AcOEt denotes ethyl acetate. c) *N*,*N*-Bidentate structure. d) *N*,*N*,*O*-Terdentate structure. e) Synthesized complex. f) Ref. 2.

the values of the red shifts for the formations of the *N,N,O*-terdentate complexes are much larger than those of the *N,N*-bidentate complexes.

These results suggest that the coordination mode of the ligand in nickel(II) complexes can be distinguished by the magnitude of the red shifts of the absorption bands in the complex formation. The colors of the complexes of nickel(II) with 2-(2-pyridylazo)phenolic ligands are also quite different depending on the coordination mode, namely, yellowish color of the solutions is ascribed to the *N,N*-bidentate species and reddish color to the *N,N,O*-terdentate species (Table 1).

Effects of the Counter Anions in Nickel(II) Salts on the Formation of the *N,N*-Bidentate Complex. The spectral data of the 4-MePAR complexes of various nickel(II) salts in dioxane and in ethyl acetate are listed in Table 2 together with the pK_a values of the corresponding conjugate acids of the counter anions in the nickel(II) salts, metal to ligand ratio in the complex, and the colors of the solutions of the complexes. From the values of $\Delta\lambda_{max}$ and the color of the solution, the formation of the *N,N*-bidentate complex is confirmed also in the reaction of nickel(II) bromide with 4-MePAR (Curve B in Fig. 4). The spectra for the complexes of 4-MePAR with other nickel(II) salts such as chloride, nitrate, and acetate do not show the single band characteristic of the *N,N*-bidentate complexes but show that of the *N,N,O*-terdentate complexes as depicted by the two characteristic bands in the visible region (Curve C in Fig. 4). The spectrum of the 4-MePAR complex of a nickel(II) salt with counter anions of higher pK_a value shows a larger red shift, indicating the formation of an *N,N,O*-terdentate complex. These results reveal that the counter anions, Cl^-, NO_3^-, and CH_3COO^-, act as an acceptor on the *o*-hydroxyl protons of the *N,N*-bidentate complex.[2)]

Effects of Solvents on the Formation of the Bidentate Complex of Nickel(II) Perchlorate with 4-MePAR. Table 3 shows the absorption spectral data, metal to ligand ratios in the overall reaction, the color of the solution of the Ni(II)-4-MePAR complexes in thirteen solvents together with their properties, donor number (DN) and dielectric constants. The donor number is generally used as an empirical parameter of the solvent basicity; a high value of DN corresponds to the high basicity of solvent molecules.[20)] The larger red shifts ($\Delta\lambda_{max} \simeq 130$ nm) were observed for the reactions in the solvents of high DN, indicating only the formation of the *N,N,O*-terdentate complexes. In the solvents of lower DN such as nitromethane, the smaller red shifts, $\Delta\lambda_{max}$, were observed in the complex formation, showing the formation of the *N,N*-bidentate complexes. The addition of imidazole to the final

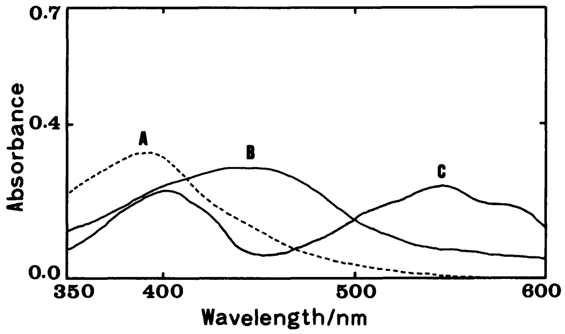


Fig. 4. Electronic spectra of the free ligand 4-MePAR, the *N,N*-bidentate, and the *N,N,O*-terdentate complexes at 25 °C in ethyl acetate. (A) Free ligand: $[\text{4-MePAR}]_t = 1.58 \times 10^{-5}$ mol dm^{-3}; (B) *N,N*-bidentate complex of nickel(II) bromide with 4-MePAR: $[\text{4-MePAR}]_t = 1.58 \times 10^{-5}$ mol dm^{-3}, $[\text{Ni(II)}]_t = 1.3 \times 10^{-5}$ mol dm^{-3}; (C) *N,N,O*-terdentate complex of nickel(II) nitrate with 4-MePAR: $[\text{4-MePAR}]_t = 1.35 \times 10^{-5}$ mol dm^{-3}, $[\text{Ni(II)}]_t = 1.0 \times 10^{-5}$ mol dm^{-3}.

Table 2. Spectral Data for the Complexes of Various Nickel(II) Salts with 4-MePAR

Nickel(II) salts	pK_a[a)]	λ_{max}[b)]/nm(ε_{max}/10^4 mol^{-1} dm^3 cm^{-1})	M : L[c)]	Color[d)]
$Ni(OAc)_2 \cdot 4H_2O$	4.7[e)]	402 (1.68), 544 (1.76)	1 : 1	Pink[g,h)]
$Ni(NO_3)_2 \cdot 6H_2O$	−1.64[f)]	403 (3.36), 544 (3.50)	1 : 2	Pink[i)]
				Pink[g,h)]
$NiCl_2 \cdot H_2O$	−7,[f)] −4[e)]	406 (3.2), 543 (2.7)	1 : 2	Pink[g,h)]
$NiCl_2 \cdot 6H_2O$				Pink[g)]
$Ni(ClO_4)_2 \cdot 2.4H_2O$	−8[f)]	428 (4.62)	1 : 2	Yellow[i)]
		426 (3.90)[j)]	1 : 2	Yellow[g,h)]
$Ni(ClO_4)_2 \cdot 6.1H_2O$		429 (4.69)	1 : 2	Yellow[i)]
		430		Yellow[g)]
$NiBr_2$	−9,[f)] −7[e)]	431 (>3.6)	1 : 2	Yellow[i)]

a) pK_a values of the conjugate acids of the counter anions in nickel(II) salts. b) At $[\text{Ni(II)}]_t/[\text{4-MePAR}]_t = 1$—2. c) Determined by molar ratio method. d) Color of the solution of the final complex. e) Ref. 23a. f) Ref. 23b. g) In neat dioxane. h) Ref. 2. i) In ethyl acetate. j) Synthesized complex.

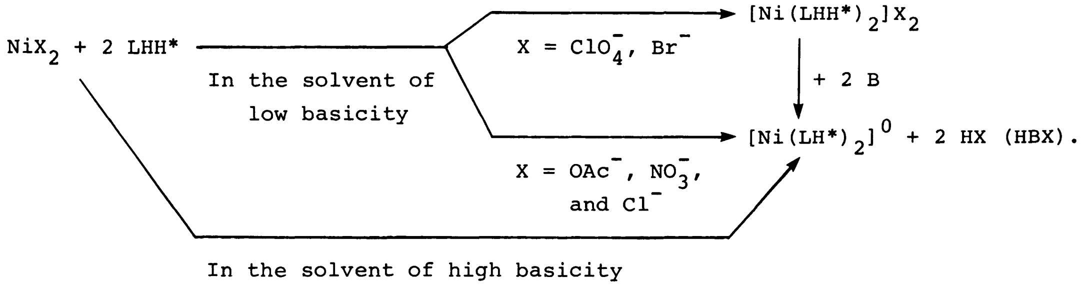
Ni(II)-4-MePAR complex in nitromethane caused a further red shift of about 60 nm in the visible region. The color of the nitromethane solution was changed from orange to pink. These facts strongly support the conversion of the *N,N*-bidentate complex to the *N,N,O*-terdentate complex in nitromethane. The contribution of the dielectric effect of the solvents to the formation of the *N,N*-bidentate complex was not obvious (Table 3).

The above results indicate that the stability in the solution of the *N,N*-bidentate species is strongly influenced by the basicities of the solvents, the counter anions, and the bases, B, added.

The reaction behavior of the Ni(II)-4-MePAR system is summarized in Scheme 1, where the ligand 4-MePAR is represented by LHH*; H and H* denote the *ortho*- and the *para*-hydroxyl protons, respectively.

Reactions between Nickel(II) Perchlorate and Various 2-(2-Pyridylazo)phenolic Ligands in Dioxane and Ethyl Acetate. Table 4 shows the spectral data of various 2-(2-pyridylazo)phenolic ligands and their metal complexes in dioxane and in ethyl acetate. All ligands except for *β*-PAN reacted with nickel(II) perchlorate to form the *N,N*-bidentate complexes as deduced from the smaller values of the red shift, $\Delta\lambda_{max}$, and the color of the solution. Upon addition of a Brønsted base, the formation of the *N,N,O*-terdentate complexes was observed for all ligands except for *p*-PAP having no coordinating *o*-hydroxyl group.

The spectra of the yellow solutions of the Ni(II)-DAPAP complexes in dioxane and ethyl acetate showed negative $\Delta\lambda_{max}$. Upon addition of a Brønsted base to the yellow solution of the



Scheme 1.

Table 3. Spectral Data for the Complex Formation of Nickel(II) Perchlorate with 4-MePAR in Various Solvents

Solvent	DN[a]	Dielectric constant[b]	λ_{max}/nm(ε_{max}/10^4 mol^{-1} dm^3 cm^{-1})		M : L[d]	Color[e]
			Ligand	Complex[c]		
$MeNO_2$	2.7	35.94	381 (1.92)	469 (1.60)	1 : 1	Orange
$PhNO_2$	4.4	34.82				Yellow
Dioxane	14.8	2.2	381 (2.10)	426 (3.90)[f]	1 : 2	Yellow[g]
Acetone	17.0	20.7				Pink
AcOEt	17.1	6.11 (20 °C)	381 (2.07)	428 (4.62)	1 : 2	Yellow
H_2O	18.0	78.54	389 (1.89)	401 (2.78), 511 (2.82)	1 : 2	Red[g,h]
MeOH	19	32.6				Red
EtOH	20	24.3	388 (2.24)	406 (2.74), 522 (3.15)	1 : 2	Red
DMF	26.6	36.71	398 (2.73)	513 (3.0)	1 : 1	Red
DMSO	29.8	46.6	390 (2.34)	405 (3.32), 537 (3.63)	1 : 2	Pink
Pyridine	33.1	12.01	391 (2.26)	413 (1.50), 528 (1.98)	1 : 1	Pink
$PhNH_2$		6.73				Pink
$CHCl_3$		4.724	386	440		Yellow

a) Donor number. b) The values at 25 °C. c) At $[Ni(II)]_t/[4\text{-MePAR}]_t \simeq 2$. d) Determined by molar ratio method. e) Color of the solution of the final complex. f) Synthesized complex. g) Ref. 2. h) In 10% (v/v) dioxane-water at pH* 4.2, $I = 0.1$ mol dm^{-3} ($NaClO_4$).

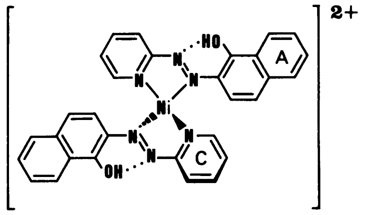
Table 4. Spectral Data for the Complex Formation of Metal Perchlorates with Various 2-(2-Pyridylazo)phenolic Ligands

Species	λ_{max}/nm(ε_{max}/ 10^4 mol^{-1} dm^3 cm^{-1})	Color	Solvent
PAR	382 (2.05)	Yellow	Dioxane
$[Ni(par)_2]^{2+}$	433 (4.60)	Yellow	
$[Ni(parH_{-1})_2]^0$	407 (3.41), 547 (3.35)	Pink[a)]	
3-MePAR	382 (1.88)	Yellow	AcOEt
$[Ni(3\text{-mepar})_2]^{2+}$	449 (4.84)	Yellow	
$[Ni(3\text{-meparH}_{-1})_2]^0$	413 (2.10), 529 (4.50)	Pink[b)]	
5-MePAR	384 (2.23)	Yellow	AcOEt
$[Ni(5\text{-mepar})_2]^{2+}$	437 (4.84)	Yellow	
$[Ni(5\text{-meparH}_{-1})_2]^0$	407 (2.18), 534 (4.08)	Pink[b)]	
6-MePAR	383 (2.06)	Yellow	AcOEt
$[Ni(6\text{-mepar})_2]^{2+}$	435 (4.76)	Yellow	
$[Ni(6\text{-meparH}_{-1})_2]^0$	—	Pink[a)]	
6-MePAR	384 (2.03)	Yellow	Dioxane
$[Ni(6\text{-mepar})_2]^{2+}$	439 (4.32)	Yellow	
$[Ni(6\text{-meparH}_{-1})_2]^0$	—	Pink[a)]	
PAO	378 (2.43)	Yellow	AcOEt
$[Ni(pao)_2]^{2+}$	425 (5.02)	Yellow	
$[Ni(paoH_{-1})_2]^0$	405 (3—4), 548 (2—3)	Pink[a)]	
DAPAP	443 (3.51—3.65)	Yellow	AcOEt
$[Ni(dapap)_2]^{2+}$	426 (5.3)	Yellow	
$[Ni(dapapH_{-1})_2]^0$	529 (sh, 7.10), 557 (7.55)	Pink[a)]	
DAPAP	444 (3.46)	Yellow	Dioxane[c)]
$[Ni(dapap)_2]^{2+}$	420 (4.6)	Yellow	
$[Ni(dapapH_{-1})_2]^0$	511 (9.10), 542 (9.08)	Pink[d)]	
p-PAP	347 (2.34)	Yellow	AcOEt
$[Ni(pap)_2]^{2+}$	424 (4.19)	Yellow	
p-PAP	347 (2.18)	Yellow	Dioxane[c)]
$[Ni(pap)_2]^{2+}$	420 (3.7)	Yellow	
α-PAN	358 (1.20), 485 (1.91)	Orange	Dioxane
$[Ni(\alpha\text{-pan})_2]^{2+}$	400 (2.14), 512 (3.24)	Red	
$[Ni(\alpha\text{-panH}_{-1})_2]^0$	561 (2.9), 603 (2.7)[e)]	Purple	
β-PAN	463 (1.82)	Yellow	Dioxane
$[Ni(\beta\text{-panH}_{-1})_2]^0$	396 (1.6), 533 (4.5), 574 (5.3)[e)]	Pink	
$[Zn(4\text{-mepar})_2]^{2+}$	420 (3.94)	Yellow	AcOEt
$[Zn(4\text{-meparH}_{-1})_2]^0$	—	Pink[a)]	
$[Zn(6\text{-mepar})_2]^{2+}$	440 (4.52)	Yellow	
$[Zn(6\text{-meparH}_{-1})_2]^0$	—	Pink[a)]	
$[La(6\text{-mepar})]^{3+}$	392 (1.6), 478 (1.3)	Orange	
$[La(6\text{-meparH}_{-1})]^{2+}$	548—558 (—)	Pink[a)]	

a) Color of the solution after the addition of a small excess of imidazole to the solution of the *N*,*N*-bidentate complex. b) In 1%(v/v) 2,6-lutidine-AcOEt. c) Ref. 2. d) In 30%(v/v) dioxane-water, pH* = 4.59, and I = 0.1 mol dm^{-3} ($NaClO_4$). e) Synthesized complex.

Ni(II)-DAPAP complexes, the color of the solution turned pink, showing the formation of the *N*,*N*,*O*-terdentate complex. The complex in the yellow solution has been isolated as $[Ni(dapap)_2](ClO_4)_2 \cdot H_2O$[21] from the dioxane solution.[2] The amount of proton liberated in the reaction, $[Ni(dapap)_2]^{2+} + 2H_2O \rightarrow [Ni(dapapH_{-1})_2]^0 + 2H_3O^+$, was found to be almost twice that of the complex dissolved in 30%(v/v) dioxane-water.[2] The spectral feature of the *N*,*N*-bidentate complex in ethyl acetate was similar to that in dioxane. From these results, the Ni(II)-DAPAP complex, yellow in ethyl acetate, was confirmed to be in the *N*,*N*-bidentate structure.

α-PAN, an isomer of β-PAN, reacted with nickel(II) perchlorate to form the *N*,*N*-bidentate complex (Curves 1 and 2 in Fig. 5). Upon addition of imidazole in neat dioxane the bidentate complex converted to the *N*,*N*,*O*-terdentate complex (Curve 3 in Fig. 5). β-PAN, however, did not form the *N*,*N*-bidentate complex. The difference in the reaction behavior between α-PAN and β-PAN with nickel(II) may be due to a steric hindrance of the bulky naphthalene ring in β-PAN. The configuration of the *N*,*N*-bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, isolated from dioxane solution, has been reported to be a distorted planar around the nickel(II) atom (see Fig. 1).[2,22] If the *N*,*N*-bidentate 1:2 nickel(II) complex of α-PAN and β-PAN in dioxane solution



$[Ni(\alpha\text{-pan})_2]^{2+}$

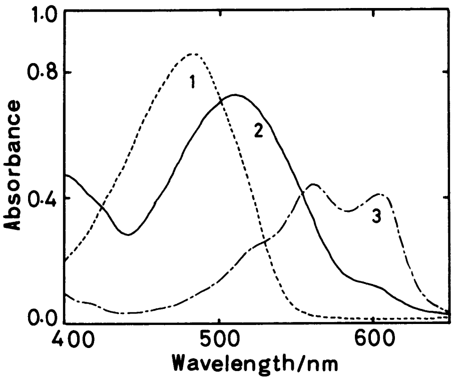
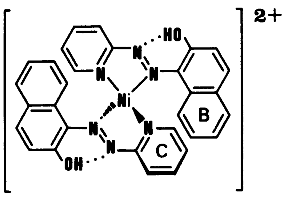


Fig. 5. Spectral features of the free ligand α-PAN and its nickel(II) complexes at 25 °C in neat dioxane. (1) Free ligand: $[\alpha\text{-PAN}]_t = 4.48 \times 10^{-5}$ mol dm^{-3}; (2) *N*,*N*-bidentate complex: $[\alpha\text{-PAN}]_t = 4.48 \times 10^{-5}$ mol dm^{-3}, $[Ni(II)]_t = 1.25 \times 10^{-4}$ mol dm^{-3}; (3) *N*,*N*,*O*-terdentate complex: $[\alpha\text{-PAN}]_t = 1.74 \times 10^{-5}$ mol dm^{-3}, $[Ni(II)]_t = 1.9 \times 10^{-5}$ mol dm^{-3}, and in the presence of an excess of imidazole.

are in the same configuration as that of the isolated bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, then the *N,N*-bidentate 1:2 nickel(II) complex of *β*-PAN is



$[Ni(\beta\text{-pan})_2]^{2+}$

presumed to have a large steric hindrance caused by the pyridyl ring (Ring C) in one ligand molecule and the bulky naphthalene ring (Ring B) in another ligand molecule. The naphthalene ring in the isomer *α*-PAN is expected to show no steric hindrance on the coordination of the donor nitrogen atoms because the ring A in the bidentate complex of *α*-PAN should occupy an opposite position compared with the ring B in the possible *N,N*-bidentate complex of *β*-PAN. In the coordination of the donor nitrogens in the 1:2 complexes of nickel(II) with 6-MePAR or PAO, the steric hindrance of the *ortho*-methyl group in pyridine ring or benzene ring was not obviously observed, though the configuration of the *N,N*-bidentate 1:2 complexes of these ligands is considered to be highly strained.

Complex Formation of the Other Metal Ions with Methyl-PAR Derivatives. The reaction behavior of zinc(II) perchlorate with 4-MePAR or 6-MePAR in ethyl acetate suggests the formation of the similar *N,N*-bidentate complex to that of nickel(II) in ethyl acetate (Table 4). The same results were also obtained in the reactions of manganese(II) perchlorate or lanthanum(III) perchlorate with 6-MePAR in ethyl acetate (Table 4). The formation of the *N,N*-bidentate complex of cobalt(II) bromide with 4-MePAR was also detected spectrophotometrically in dioxane.

Enhanced Acidity of the *ortho*-Hydroxyl Group in the Ligand 4-MePAR as a Sequence of *N,N*-Coordination to Nickel(II). The pK_a values in aqueous solution of the conjugate acids of the Brønsted bases are increased in the orders of $Br^-(-9)<ClO_4^-(-8)<Cl^-(-7)<NO_3^-(-1.64)<AcO^-(4.756)$ for the anionic bases[23b)] and DMF(0.0)<*o*-chloroaniline(2.6)<*m*-chloroaniline(3.5)<aniline(4.6)<pyridine(5.2)<2,6-lutidine(6.75)<imidazole(7.4) for the neutral bases.[23c)] In the solvents of lower basicity, the *N,N*-bidentate complex is formed in the reactions between 4-MePAR and nickel(II) salts, in which the counter anion of the nickel(II) is perchlorate or bromide. The other nickel(II) salts form only the *N,N,O*-terdentate complex. These facts indicate that the perchlorate and bromide ions behave as a weaker base than the other counter anions even in ethyl acetate and dioxane.

From the above results, an average pK_a value to be estimated in aqueous solution for the *ortho*-hydroxyl group of the ligand 4-MePAR in the *N,N*-bidentate nickel(II) complex may be evaluated to be ca. −7. The pK_a value of the *ortho*-hydroxyl group of the free ligand 4-MePAR in aqueous solution was reported to be ca. 11.[4)] Namely, owing to the *N,N*-coordination to nickel(II), the *ortho*-hydroxyl group of the ligand 4-MePAR behaves as such a strong acid in aqueous media as HCl and $HClO_4$.

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References

1) S. Shibata, "2-Pyridylazo Compounds in Analytical Chemistry," in "Chelates in Analytical Chemistry," ed by H. A. Flaschka and A. J. Barnard, Jr., Vol. 4, Marcel Dekker, Inc., New York, N. Y. (1972), p. 1; H. Kawamoto, T. Takenouchi, and H. Akaiwa, *Nippon Kagaku Kaishi*, **1983**, 358; H. Hoshino and T. Yotsuyanagi, *Bull. Chem. Soc. Jpn.*, **58**, 1037 (1985).

2) Y. Kudo, N. Yoshida, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **57**, 3099 (1984).

3) F. H. Pollard, P. Hanson, and W. J. Geary, *Anal. Chim. Acta*, **20**, 26 (1959).

4) W. J. Geary and F. Bottomley, *Talanta*, **14**, 537 (1967).

5) M. Hniličková and L. Sommer, *Fresenius' Z. Anal. Chem.*, **177**, 425 (1960).

6) R. G. Anderson and G. Nickless, *Analyst*, **93**, 13 (1968).

7) In 3%(v/v) water-dioxane, only the formation of the *N,N,O*-terdentate complex was observed in the reaction of nickel(II) perchlorate with 4-MePAR.

8) Upon further addition of nickel(II) perchlorate to the ethyl acetate solution of the isolated *N,N*-bidentate complex, $[Ni(4\text{-mepar})_2](ClO_4)_2$, the absorbance around 430 nm increases by 10—15%. This result suggests that in the presence of a small excess of nickel(II) perchlorate ($[Ni(II)]_t/[4\text{-MePAR}]_t$=0.5—1.0) the reaction, $Ni^{2+}+2$ 4-MePAR$\rightleftarrows[Ni(4\text{-mepar})_2]^{2+}$, could not sufficiently proceed to the right.

9) J. P. Hart and W. F. Smyth, *Spectrochim. Acta, Part A*, **36**, 279 (1980).

10) S. Yamamoto, N. Nishimura, and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, **44**, 2018 (1971).

11) F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, **45**, 42 (1962).

12) I. M. Issa, R. M. Issa, M. R. Mahmoud, and Y. M. Temerik, *Z. Phys. Chem. (Leipzig)*, **253**, 289 (1973).

13) a) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, **1953**, 2156; b) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952); c) N. Nishimura, T. Sueyoshi, H. Yamanaka, E. Imai, S. Yamamoto, and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, **49**, 1381 (1976).

14) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

15) Since the intensity of π-π^* transitions of azobenzene derivatives is larger than that of n-π^* transitions by a factor

of about 100 under usual conditions,[9–12] we would not discuss the n-π^* transitions of 4-MePAR and its nickel(II) complexes.

16) S. Shibata, M. Furukawa, and K. Tôei, *Anal. Chim. Acta,* **66**, 397 (1973); K. Mochizuki and M. Fujimoto, *Bull. Chem. Soc. Jpn.,* **58**, 1520 (1985); K. Mochizuki, T. Imamura, T. Ito, and M. Fujimoto, ibid., **51**, 1743 (1978).

17) D. A. Johnson and T. M. Florence, *Talanta,* **22**, 253 (1975).

18) We adopt the value of the longest λ_{max}, when two or more absorption bands are observed in the visible region. Though the physical meaning of $\Delta\lambda_{max}$ is not yet clear, this value is useful for the discrimination of the *N,N*-bidentate and the *N,N,O*-terdentate species in solution.

19) The ligand *p*-PAP reacts with metal ions to form only the *N,N*-bidentate complexes in solution, since *p*-PAP possesses no coordinating *o*-hydroxyl group. See, R. G. Anderson and G. Nickless, *Anal. Chim. Acta,* **39**, 469 (1967); Ref. 2.

20) V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions," Plenum Press, New York, N. Y. (1978), p. 17.

21) The *N,N*-bidentate 1:2 complex of nickel(II) with DAPAP was identified to be a monohydrate (Found: $0.93H_2O$) by Karl-Fischer titration. Found: C, 39.78; H, 3.62; N, 14.36; Cl, 9.20%. Calcd for $Ni(C_{13}H_{14}N_4O)_2(ClO_4)_2\cdot H_2O$: C, 41.08; H, 3.98; N, 14.74; Cl, 9.33%.

22) In ethyl acetate, nickel(II) perchlorate hexahydrate was found to be in a six-coordinated structure with λ_{max} (ε_{max})=725 (2.2), 1163 (2.4), 1213 (2.5), 1450 (2.0), and 1938 nm (6.9 mol^{-1} dm^3 cm^{-1}). It has been reported that in aqueous solution the spectrum of the $[Ni(H_2O)_6](ClO_4)_2$ has absorption maxima at 396 (ε_{max}=4.9), 663 (1.8), 729 (2.1), and 1176 nm (2.1 mol^{-1} dm^3 cm^{-1}) (see, H. Ito, *Nippon Kagaku Zasshi,* **77**, 1383 (1956)). Since the wavelength for the d-d transition of the divalent nickel did not remarkably change upon addition of the free ligand 4-MePAR to the light green solution of nickel(II) perchlorate, the configuration of the bidentate nickel(II) complex in ethyl acetate solution may be considered to be an octahedral involving the coordination of water and/or solvent molecules.

23) a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y. (1967), p. 140; b) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases. A Laboratory Manual," 1st ed, Methuen & Co., Ltd., London (1962); c) M. Tanaka, "San to Enki (Acids and Bases)," 4th ed, Shōkabo, Tokyo (1977), p. 177.