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Acid-Dissociation Behavior of *para*-Hydroxyl Group in the *N,N,O*-Terdentate Ligand, 4-(4-Methyl-2-pyridylazo)resorcinol, Coordinated to a Transition Metal Ion

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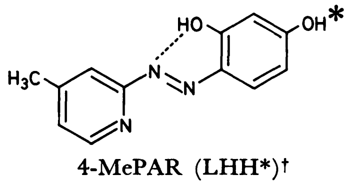
The acid-dissociation behavior of 1:1 and 1:2 complexes of transition metals with an *N,N,O*-terdentate ligand, 4-(4-methyl-2-pyridylazo)resorcinol (4-MePAR), is spectrophotometrically studied in ethanol at 25 °C. The values of apparent pK_a of the *p*-hydroxyl group of the ligand in the metal complexes are found to be in the order, Pd(II)<Co(III)<Ni(II)<Mn(II). The electronic structures of the *p*-hydroxyl oxygen atoms in the solid complexes of Mn(II), Ni(II), Pd(II), and Co(III) are examined on the basis of the data of X-ray photoelectron spectroscopy (XPS). The decrease in the electron density on the *p*-hydroxyl oxygen atom caused by the inductive effect through the azo nitrogen and the benzene ring of the coordination of the ligand to the central metal atom is larger in the Pd(II) and Co(III) complexes compared with that in the Ni(II) and Mn(II) complexes.

It is well-known that the reactivity and the electronic structure of organic compounds are affected by the coordination to the metal atom.[1,2] Corsini et al. potentiometrically pointed out that in aqueous dioxane solution the acid dissociation of *p*-hydroxyl group in an *N,N,O*-terdentate ligand, 4-(2-pyridylazo)resorcinol (PAR), is accelerated by the coordination to the transition metal ions.[3] However, despite the importance of the ligand PAR in the field of analytical chemistry and of coordination chemistry, no work on the electronic structures of PAR and its metal chelates has been reported so far. Recently, we found out, by the application of X-ray photoelectron spectroscopy (XPS), the characteristics of the chemical bonding of bivalent metal ions with donor atoms in analogous complexes of an *N,N,O*-terdentate ligand.[4] It is of interest to obtain the detailed information on the electronic structures of multidentate complexes in order to understand the reaction behavior of the complexes in solutions.

In the present paper, we report the acid-dissociation behavior of the metal chelates of an *N,N,O*-terdentate ligand, 4-(4-methyl-2-pyridylazo)resorcinol (4-MePAR), in ethanol; the electronic structures of the isolated complexes are discussed on the basis of XPS measurements. The results of XPS measurements are correlated to the acid-dissociation behavior in ethanol of the *p*-hydroxyl groups in the metal–4-MePAR complexes.



4-MePAR (LHH*)†

Experimental

Materials. Ethanol was dried with Molecular Sieves 3A or 4A for several days and distilled under argon atmosphere immediately before use. The ligand 4-MePAR (LHH*), its Ni(II) complex, $[\mathrm{Ni(LH^*)_2}]^0$, and a terdentate Pd(II) complex of 5-dimethylamino-2-(2-pyridylazo)phenol (DAPAP) were prepared according to the literature.[4–6] The *N,N,O*-terdentate complexes of other bivalent or tervalent metal ions with 4-MePAR were prepared by the analogous method as described in the previous papers.[7,8] $[\mathrm{Pd(LH^*)Cl}]^0$: Color: dark green. Found: C, 37.11; H, 3.05; N, 10.75; Cl, 8.97%. Calcd for $\mathrm{Pd(C_{12}H_{10}N_3O_2)Cl\cdot H_2O}$: C, 37.14; H, 3.12; N, 10.83; Cl, 9.13%. The configuration around Pd(II) in the complex, $[\mathrm{Pd(LH^*)Cl}]^0\cdot\mathrm{H_2O}$, was identified to be essentially four-coordinated form by the XPS measurements: The $\mathrm{Pd(3d_{5/2})}$ binding energy of the Pd(II)–4-MePAR complex, 338.6 eV, was almost equal to that of the corresponding four-coordinated complex of Pd(II) with DAPAP, $[\mathrm{Pd(dapapH_{-1})Cl}]^0$, 338.0 eV.[9] $[\mathrm{Mn(LH^*)_2}]^0$: Color: dark wine red. Found: C, 52.78; H, 3.87; N, 15.34%. Calcd for $\mathrm{Mn(C_{12}H_{10}N_3O_2)_2\cdot 0.6\,NaCl}$: C, 52.75; H, 3.69; N, 15.38%. $[\mathrm{Co^{III}L(LH^*)}]^0$: Color: dark wine red. Found: C, 53.13; H, 3.37; N, 15.97%. Calcd for $\mathrm{Co^{III}C_{24}H_{19}N_6O_4\cdot 0.5\,NaCl}$: C, 53.03; H, 3.52; N, 15.46%. Bases employed here were of guaranteed reagent grade (Wako or Tokyo Kasei).

Measurements. Samples for XPS measurements were prepared in the form of a thin layer mounted on a nickel substrate covered with a fine gold mesh and dried overnight under 10^{-5}—10^{-7} Pa. XPS spectra of the samples were measured on a VG ESCA 3 spectrometer employing Mg $K\alpha$ (1253.6 eV) radiation under ca. 10^{-7} Pa at room temperature. In order to compensate for the charging of the insulating samples during the photoelectron ejection process, we referenced the spectra of all elements in each sample to the photoelectron line of C(1s). All raw binding energies were corrected to C(1s) value, 285.0 eV, of a

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† The ligand 4-MePAR is abbreviated to be LHH*, where H and H* denote the *ortho*- and the *para*-hydroxyl protons, respectively.

hydrocarbon.[6] The O(1s) peak in each complex was deconvoluted using two or three symmetric Gaussian curves.[4]

Visible absorption spectra of the samples in absolute ethanol were measured at 25.0±0.3 °C with a Hitachi EPS-3T spectrometer equipped with a 1 cm quartz cell. The preparations of the ethanol solutions for the measurements of visible spectra were carried out in a glove bag filled with argon. The concentrations of the solutions of the free ligand and the complexes were calculated from the weighed amount or the absorbance of the solution.

Results and Discussion

Reactions between Brønsted Bases and Metal-4-MePAR Complexes in Ethanol. Figure 1 shows the spectral change in the reaction of the *N,N,O*-terdentate chelate of Pd(II) with 4-MePAR with a Brønsted base, 2,6-lutidine, in ethanol. 2,6-Lutidine behaves exclusively as a Brønsted base; a very weak coordinating property of this base could be neglected. The spectrum of the Pd(II) complex has two absorption maxima in visible region at 442 ($\varepsilon_{max}=1.54\times10^4$) and around 590 nm ($\varepsilon_{max}=0.78\times10^4$ mol^{-1} dm^3 cm^{-1}) (Curve 1). Upon addition of a Brønsted base, 2,6-lutidine (pK_a in water (pK_a^W)=6.75), the absorbance around 440 nm decreased with the increase of that around 530 nm. The color of the solution changes from green to pink.[10] A set of isosbestic points for the spectral change was observed at 470 and 596 nm. This result shows the simple equilibrium for the reaction between the Pd(II)-4-MePAR complex and 2,6-lutidine. The final spectrum of the Pd(II) complex (Curve 4) possesses an absorption maximum at 535 nm ($\varepsilon_{max}=3.34\times10^4$ mol^{-1} dm^3 cm^{-1}). The reaction of $[Pd(LH^*)Cl]^0$ is similar to the deprotonation in ethanol of the Mn(II)-4-MePAR complex or the Ni(II)-4-MePAR complex by triethylamine (pK_a^W=10.9), $[M(LH^*)_2]^0 \rightleftarrows [ML(LH^*)]^- + H^+ \rightleftarrows [ML_2]^{2-} + 2H^+$ (Fig. 2a).[11] The reaction of the Mn(II) and/or Ni(II) complexes with 2,6-lutidine showed no spectral change. On the other hand, a reaction of 2,6-lutidine with the Pd(II)-DAPAP complex, $[Pd(dapapH_{-1})Cl]^0$, which has no dissociable hydroxyl group, did not indicate a large spectral change in the visible region. The above results exhibit that the large spectral change observed in the reaction of the Pd(II) complex, $[Pd(LH^*)Cl]^0$, with 2,6-lutidine is attributed to the deprotonation of *p*-hydroxyl group, $[Pd(LH^*)Cl]^0 \rightleftarrows [PdLCl]^- + H^+$ (Fig. 1). The reaction of the Co(III) complex, $[Co^{III}L(LH^*)]^0$, with 2,6-lutidine was interpreted in the same manner (Fig. 2b).[8]

The order of the values of the pK_a's of uni-positive conjugate acids does not show appreciable change with respect to the change in medium from water to ethanol.[12,13] Therefore, the values of acid-dissociation constants of the ligand 4-MePAR and its com-

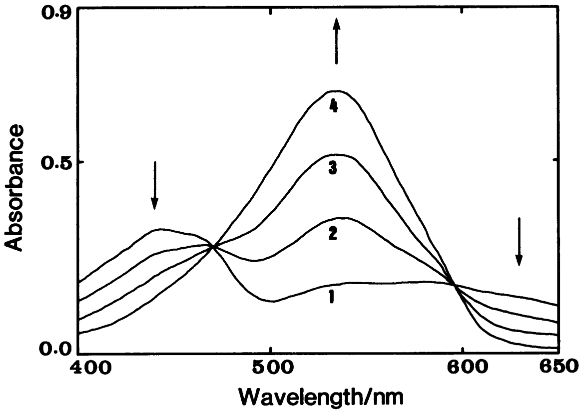

Fig. 1. Spectral change in the reaction between the Pd(II)-4-MePAR complex, $[Pd(LH^*)Cl]^0$, and 2,6-lutidine in ethanol at 25 °C.
$[Pd(LH^*)Cl]_t=2.04\times10^{-5}$ mol dm^{-3}. $[2,6\text{-lutidine}]_t=0.00$ (1), 1.66×10^{-4} (2), 6.14×10^{-4} (3), 0.0858 mol dm^{-3} (4).

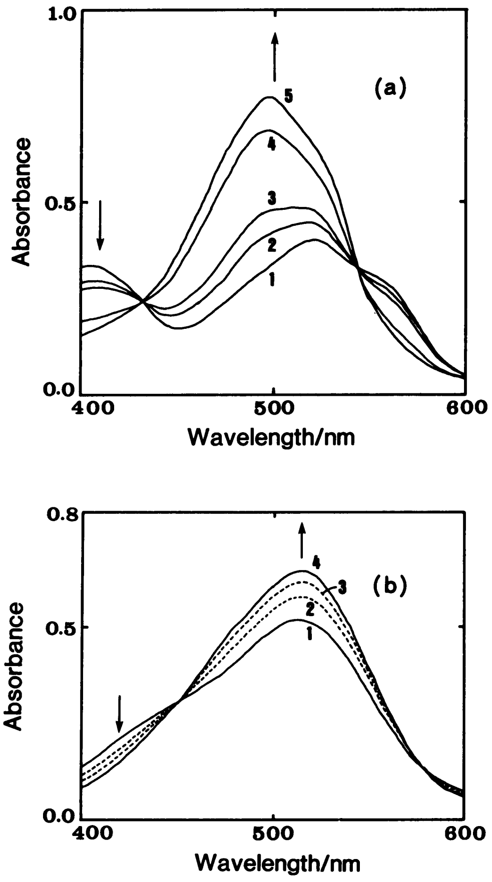

Fig. 2. Spectral changes upon additions of Brønsted bases to the ethanol solutions of the *N,N,O*-terdentate complexes of 4-MePAR at 25 °C.
(a) Ni(II)-4-MePAR complex-triethylamine. $[Ni(LH^*)_2]_t=1.31\times10^{-5}$ mol dm^{-3}. $[\text{triethylamine}]_t=0.00$ (1), 1.39×10^{-4} (2), 4.92×10^{-4} (3), 2.16×10^{-2} (4), 0.144 mol dm^{-3} (5).
(b) Co(III)-4-MePAR complex-2,6-lutidine. $[Co^{III}L(LH^*)]_t=1.01\times10^{-5}$ mol dm^{-3}. $[2,6\text{-lutidine}]_t=0.00$ (1), 8.24×10^{-3} (2), 3.09×10^{-2} (3), 0.172 mol dm^{-3} (4).

plexes in water and in ethanol can be estimated by the spectral change in the reactions of these species with a Brønsted base of known pK_a value in two solvents. Figure 3 shows the plot of the absorbance of the Co(III) complex of 4-MePAR at 420 and 510 nm against the values of pK_a^{EtOH} of the added bases. From Fig. 3, the value of apparent pK_a of the Co(III) complex in ethanol was obtained; 6.4 for the reaction, $[Co^{III}L(LH^*)]^0 \rightleftarrows [Co^{III}L_2]^- + H^+$, 5.6 for $[Pd(LH^*)Cl]^0 \rightleftarrows [PdLCl]^- + H^+$, 7.3 for $LHH^* \rightleftarrows LH^- + H^+$.[14] The values of (p$K_{a1}^{EtOH}$+p$K_{a2}^{EtOH}$)/2 for the reactions, $[M(LH^*)_2]^0 \rightleftarrows [ML(LH^*)]^- + H^+$, p$K_{a1}^{EtOH}$, and $[ML(LH^*)]^- \rightleftarrows [ML_2]^{2-} + H^+$, p$K_{a2}^{EtOH}$, were determined to be 9.3 and 10.1 for M=Ni(II) and Mn(II), respectively.[14] The order of the value of pK_a of the *p*-hydroxyl group of 4-MePAR and its complexes in ethanol was found to be Pd(II)<Co(III)<4-MePAR<Ni(II)<Mn(II). The order of acid-dissociation constants in the metal-4-MePAR system in ethanol was in good agreement with the corresponding order for the metal-PAR system in 50% aqueous dioxane solution, Pd(II) (5.38)<Cu(II) (5.5)<Co(III) (6.0)<PAR (7.0)<Ni(II) (pK_{a1}=7.7, pK_{a2}=9.2)≃Zn(II) (7.7, 9.3)<Mn(II) (8.8, 10.3).[3,15]

Possible Structures of the Species Formed in the Reactions of 4-MePAR or Its Complexes with Brønsted Bases in Ethanol. Ethanol is classified to a solvent of relatively low dielectric constant (24.3 at 25 °C).[16] The reaction equilibria, $AH + B \rightleftarrows A^- \cdot HB^+ \rightleftarrows A^- + HB^+$, would be present in ethanol, where AH and B denote a Brønsted acid and a Lewis base, respectively.[17] If an ion-pair species mainly formed under the experimental conditions,[18] then the association constant for the above reaction is approximately expressed by the equation, $K_A(B) = [A^- \cdot HB^+]/([AH][B])$. The absorbance A at wavelength λ (nm) of a mixed solution of the acid AH and the base B with initial concentrations $[AH]_0$ and $[B]_0$ (mol dm^{-3}) respectively is related to $K_A(B)$ as in the equation, $\log\{[B]_0 - (A - A_1)/\Delta\varepsilon\} = \log\{(A - A_1)/(A_2 - A)\} - \log K_A(B)$, where $A_1 = \varepsilon_1[AH]_0$, $A_2 = \varepsilon_2[A^- \cdot HB^+] \simeq \varepsilon_2[AH]_0$, $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$, and ε_1 and ε_2 are the molar absorption coefficients (mol^{-1} dm^3 cm^{-1}) at λ of the acid, AH, and the ion pair, $A^- \cdot HB^+$, respectively.[18] If the above approximation is appropriate in ethanol, then the plot of $\log\{[B]_0 - (A - A_1)/\Delta\varepsilon\}$ (=log [B]) against $\log\{(A - A_1)/(A_2 - A)\}$ (=$\log\{[A^- \cdot HB^+]/[AH]\}$) should give a straight line with a slope=1 and an intercept=log K_A(B). The plot of log [B] vs. log $\{[A^- \cdot HB^+]/[AH]\}$ for the Co(III) complex in ethanol gave a straight line with a slope of 1.0. The similar results were obtained as for the plots for the Pd(II) complex (slope=0.9) and the free ligand 4-MePAR (1.3). The logarithms of the association constants, log K_A(B), are listed in Table 1 together with the spectral data. The order in log K_A(B) reflected the order of the acid-dissociation constants in ethanol of the *p*-hydroxyl group of the free ligand and its complexes. Further studies are necessary to clarify the structures of these ion-pair species in ethanol.

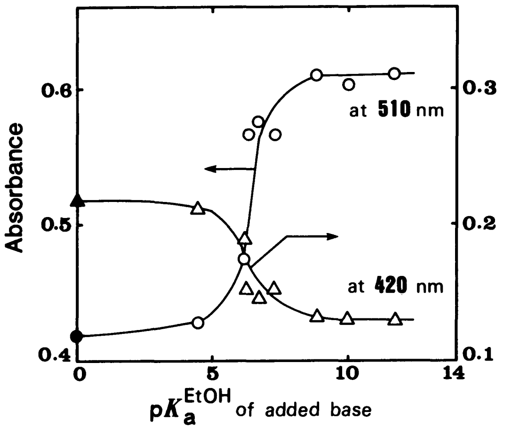

Fig. 3. Change of absorbance of the Co(III)–4-MePAR complex upon addition of a large excess of various Brønsted bases in ethanol at 25 °C. $[Co^{III}L(LH^*)]_t = 9.30 \times 10^{-6}$ mol dm^{-3}. $[base]_t/[Co^{III}L(LH^*)]_t = 10^3$—$10^4$. Added base: *m*-chloroaniline (pK_a^{EtOH}=4.5), *p*-toluidine (6.24), 2,6-lutidine (≃6.8), imidazole (6.30, 7.3), triethanolamine (8.9), diethanolamine (10.0), triethylamine (11.9).[12,13] Full circle and triangle indicate the absorbance of the Co(III) complex in the absence of the Brønsted base.

XPS Evidence for the Increased Acid Dissociation of the *para*-Hydroxyl Group in Metal Complexes of 4-MePAR. Table 2 lists the XPS data for 4-MePAR and its metal complexes investigated here together with the electronegativities of the central metal atoms. The higher value of the core electron binding energy (BE) of the donor atom generally corresponds to the lower electron density on the donor atom.[4,19] Namely, the higher BE's of the N(1s) and the O(1s) in the *N,N,O*-terdentate complexes of 4-MePAR are attributed to the decrease in the electron densities on the donor atoms due to the formation of coordination bond. In general, the relative order of the O(1s) BE in a series of the same type of compounds is $O^{\delta-}$<M-O<M-OH.[20] From this fact, the highest peak of deconvoluted O(1s) BE was assigned to the peak of the *p*-hydroxyl oxygen in the *N,N,O*-terdentate complexes of 4-MePAR.[21] The ratio of the intensity of the deconvoluted O(1s) BE of the coordinated and the non-coordinated phenolic oxygen atoms was found to be almost 1:1 for the Ni(II) and the Mn(II) complexes. On the other hand, the ratio of the intensity in the deconvoluted O(1s) BE's for the Co(III) complex was found to be 1:2:1 from the lower BE to the higher BE, where the largest intensity ratio does indicate the presence of two atoms of the coordinated phenolic oxygen (see Table 2).

On the basis of the above assignments, the order of the values of BE of the *p*-hydroxyl oxygen atom in the 4-MePAR complexes was obtained to be Pd(II)[22]≃Co(III)>Ni(II)≃Mn(II). The above order seems to reflect the acid-dissociation constants of the *p*-hydroxyl group in the complexes. The results of the O(1s) BE's deconvoluted show at least that the electron densities on the *p*-hydroxyl oxygen atoms in the Pd(II) and the Co(III) complexes are lower than those in the Ni(II) and the Mn(II) complexes.

The N(1s) BE's are directly affected by the electron-withdrawing effect of the central metal atom due to the formation of the M–N (azo and pyridyl) bonds, whereas the O(1s) BE's of the coordinated *o*-hydroxyl oxygen atoms in the resorcinol ring are not largely influenced by the coordination to the metal atom.[4] Therefore, the difference between the raw O(1s) and the raw N(1s) BE's, O(1s)−N(1s), in each complex appears to be the characteristic parameter for the extent of electron-withdrawing effect of the azo group on the *p*-hydroxyl group. The above discussion was supported by the linear correlation between the differences of BE's and the electronegativities of the central metal atoms: the lower value of O(1s)−N(1s) corresponds to the higher electron-withdrawing effect of the central metal atom. The plot of the difference of BE's, O(1s)−N(1s), against the apparent $\mathrm{p}K_\mathrm{a}^\mathrm{EtOH}$ of the *p*-hydroxyl group in the metal-4-MePAR com-

Table 1. Visible Absorption Spectral and Equilibrium Data for the Free Ligand 4-MePAR and Its Metal Complexes in Ethanol at 25 °C

Compounds	$\lambda_\mathrm{max}/\mathrm{nm}(\varepsilon_\mathrm{max})$[a]		Added base[b]	$\log K_\mathrm{A}(\mathrm{B})$[c]
	AH	AH+B		
LHH*	388 (2.24)	406 (3.44)	$\mathrm{NEt_3}$	4.02±0.18
		407 (3.52)	$\mathrm{HN(CH_2CH_2OH)_2}$	3.88±0.16
		406 (3.44)	$\mathrm{N(CH_2CH_2OH)_3}$	3.00±0.16
		—[d]	2,6-Lutidine	
$[\mathrm{Co^{III}L(LH^*)}]^0$	514 (4.73)	514 (6.32)	$\mathrm{NEt_3}$	≃6
		515 (6.52)	$\mathrm{HN(CH_2CH_2OH)_2}$	5.74±0.13
		514 (6.58)	$\mathrm{N(CH_2CH_2OH)_3}$	
		514 (6.12)	2,6-Lutidine	2.11±0.06
$[\mathrm{Pd(LH^*)Cl}]^0$	442 (1.54) ≃590 (0.78)	535 (3.34)	2,6-Lutidine	3.48±0.14

a) $\varepsilon_\mathrm{max}/10^4\,\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$. b) $\mathrm{p}K_\mathrm{a}^\mathrm{w}$: $\mathrm{NEt_3}$, 10.9; $\mathrm{HN(CH_2CH_2OH)_2}$, 9.0; $\mathrm{N(CH_2CH_2OH)_3}$, 7.9; 2.6-lutidine, 6.75. See Ref. 12. c) $K_\mathrm{A}(\mathrm{B})/\mathrm{mol^{-1}\,dm^3}$. d) No reaction was observed.

Table 2. Core Electron Binding Energies of O(1s) and N(1s) Levels[a] in the Ligand 4-MePAR and Its Metal Complexes

Compounds	Binding Energy/eV					χ_M[b]
	O(1s)			N(1s)	O(1s)−N(1s)	
	Raw	Deconvolution[c]	Assignment[d]			
LHH*[e]	528 531.3			395 398.3		
$[\mathrm{Mn(LH^*)_2}]^0$	531.8	530.1 (0.42) 532.6 (0.58)	Mn-O H-O	399.1	132.7	1.5
$[\mathrm{Ni(LH^*)_2}]^0$	531.9	529.7 (0.44) 532.7(0.56)	Ni-O H-O	399.8	132.1[f]	1.8
$[\mathrm{Co^{III}L(LH^*)}]^0$	531.3	527.1 (0.34) 531.1 (0.46) 533.1 (0.20)	$\mathrm{O^{\delta-}}$ Co-O H-O	399.8	131.5	>1.8
$[\mathrm{Pd(LH^*)Cl}]^0$	532.3	—[g]		401.3	131.0	2.2

a) All raw BE's were corrected to C(1s) value of the hydrocarbons, 285.0 eV.[6] b) Pauling's electronegativity value. c) Deconvoluted peaks with an error of ±0.5 eV and the value in parentheses shows the relative intensity of the peak. d) Assignments of the deconvoluted peaks. e) Ref. 6. f) The value was reported to be 131.8 eV in the previous work (see Ref. 6). g) Unable to deconvolute due to a very small O(1s) signal.

plexes is shown in Fig. 4. The acid dissociation of the *p*-hydroxyl group in the 4-MePAR complexes increased with the increase in the extent of the electron-withdrawing effect of the azo group coordinated to the central metal ions.

From XPS results, it is concluded that the coordination of the ligand 4-MePAR to the metal atom tends to decrease in the electron density on the *para*-hydroxyl oxygen atom in the ligand through inductive effect, thereby facilitating the acid dissociation of the *para*-hydroxyl group.

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9) The abbreviation dapapH$_{-1}$ denotes the monoanionic form of the free ligand, DAPAP, in the complex.

10) The color change of the Pd(II) complex, $[Pd(LH^*)Cl]^0$, from green at pH$\simeq$4 to pink at pH$\simeq$7 was observed in aqueous solution.

11) The spectral change in ethanol coincided with that observed in the pH titration of $[Ni(LH^*)_2]^0$ in 10%(v/v) dioxane-water. In the pH titration, the *N,N,O*-terdentate complex, $[Ni(LH^*)_2]^0$, was found to dissociate two *p*-hydroxyl protons in the ligand to form $[NiL_2]^{2-}$.6) From these results, the change observed upon addition of triethylamine is attributed to a liberation of two protons of *p*-hydroxyl groups in the terdentate 1:2 complex. The spectrum of the final complex, $[NiL_2]^{2-}$, showed a single absorption maximum at 498 nm ($\varepsilon_{max}=5.89\times10^4$ mol^{-1} dm^3 cm^{-1}) in absolute ethanol.

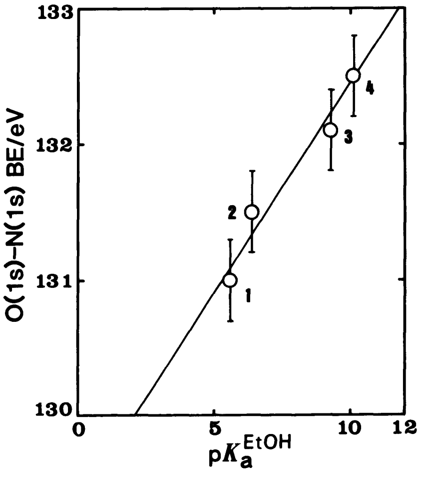

Fig. 4. Plot of the difference of BE's, O(ls) − N(1s), vs. the values of apparent pK_a in ethanol of the *N,N,O*-terdentate metal-4-MePAR complexes. Metal=Pd(II) (1), Co(III) (2), Ni(II) (3), and Mn(II) (4).

12) The correlation between the value of pK_a for the conjugate acid HB^+ ($\rightleftarrows H^+ + B$) in aqueous solution and that in absolute ethanol is generally expressed by the equation, pK_a in ethanol (pK_a^{EtOH})=pK_a^W +1.0. See, M. Tanaka, "San to Enki (Acids and Bases)," 4th ed, Syokabo, Tokyo (1977), p. 69.

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14) Values of apparent pK_a were obtained from the data at the half-neutralization, where [acid] = [conjugate base] and therefore the pK_a^{EtOH} of the added Brønsted base is equal to the pK_a of the Brønsted acid titrated. The values of pK_a^{EtOH} of the Mn(II) and Ni(II) complexes were obtained with average values for the pK_a^{EtOH}'s of the two *p*-hydroxyl groups.

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17) The species, $A^-\cdot HB^+$ and A^-, could not generally be distinguished by the spectroscopic measurements used in the present work, so one may write the apparent equilibrium constant as $K_A(B)=[A^-\cdot HB^+ + A^-]/([AH][B])$. See, N. Tokura, "Yōbaiwa (Solvation)," 1st ed, Kagaku Dōjin, Kyoto (1972), p. 23; O. D. Bonner and P. R. Prichard, *J. Solution Chem.*, **8**, 113 (1979).

18) It has been reported that, in nonaqueous solvents of relatively low dielectric constants ($D<30$), the salts of bulky ions predominantly form the ion-pairing species, i.e., *p*-nitrophenol-amine complexes or imidazolium picrate. See, R. Scott, D. De Palma, and S. Vinogradov, *J. Phys. Chem.*, **72**, 3192 (1968); H. Collaer, M. C. Haulait-Pirson, and P. Huyskens, *J. Solution Chem.*, **6**, 73 (1977); M. Nakahara and J. Osugi, *Kagaku (Chemistry)*, **25**, 1026 (1969).

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21) The intensity ratio of the peak of O(ls) BE's for *o*-hydroxypyridylazo compounds, represented by 4-MePAR, is complicated by the presence of keto-enol (hydrazone-azo) tautomers. See, T. Yoshida, *Bull. Chem. Soc. Jpn.*, **53**, 498 (1980). The fraction of keto tautomer of 4-MePAR was estimated to be 44% in solid state from the XPS measurements.

22) For the metal-4-MePAR and the M(II)-DAPAP systems, it was observed that the order of the deconvoluted N(ls) and O(ls) peaks with higher BE's between the complexes is nearly parallel to that of the raw N(ls) and O(ls) peaks. Y. Kudo, unpublished data. Therefore, it is suggested that the deconvoluted O(ls) BE of the *p*-hydroxyl group in the Pd(II) complex is higher than that in the Co(III) complex.