# Proton Magnetic Resonance Studies of 4-(2-Pyridylazo)resorcinol (PAR) and Its Cobalt(III) Complexes†

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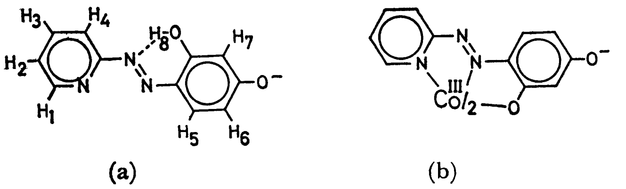
The $^1$H NMR spectra of PAR, $[Co^{III}(par)_2]^-$, and $[Co^{III}(par)(dien)]^+$ were measured in $D_2O$ solutions. The signals were assigned. The deuteration of $H_7$ was observed in $D_2O$ solutions of free ligand PAR around pD 9—10, where PAR exists in the form of $LH^-$ having an intramolecular hydrogen-bond. The significant up-field shift for the resonance of $H_1$ was observed in $[Co^{III}(par)_2]^-$ but not in $[Co^{III}(par)(dien)]^+$. The shift was interpreted in terms of the magnetic anisotropy due to the $\pi$-electron system of the neighboring PAR molecule in the complex. The down-field shift for the resonance of the $H_5$ signal of the cobalt(III) complexes reflects the structural change of PAR upon chelate-ring formation. PAR coordinates to cobalt(III) ion in planar terdentate fashion, *viz.*, in a *mer* configuration.

4-(2-Pyridylazo)resorcinol (PAR, Fig. 1(a)) has widely been used as a metallochromic indicator.[1] A number of data on the compositions and the stability constants of the PAR-chelates have been reported.[1–5] In a previous paper,[6] we confirmed in the course of the reactions between $Co^{2+}$ and PAR and its analogs the fast formation of a transient intermediate cobalt(II) complex and the subsequent slower oxidation to cobalt(III) complex. The measurements of magnetic susceptibility have also confirmed the formation of cobalt(III) complex in the solution prepared from $Co^{2+}$ and PAR.[7]



(a) (b)

Fig. 1. Structural formulae of (a) PAR with numbering of the protons and (b) its cobalt(III) complex.

As a part of serial studies on the metal chelates of PAR and its analogs,[6–8] the $^1$H NMR spectra of PAR and its cobalt(III) complexes were studied in the present paper. Figure 1 shows the suggested structures of a free ligand PAR and the metal complexes of PAR. A form with an intramolecular hydrogen-bond (Fig. 1(a)) has been suggested for a free ligand PAR in solutions.[1,9] On the other hand, no direct evidence on the structures of the PAR chelates has been reported so far. The crystal structures of $[Cu(pan)(OH_2)]ClO_4$,[10] $[Ni(tan)_2]$,[11] $[Fe(tan)_2]$,[12] $[PdCl(tan)]$,[13] $[Co(tan)_2]ClO_4$,[14] and $[Cu(tan)(OH_2)_2]ClO_4$[15] have been reported, where pan and tan denote 1-(2-pyridylazo)-2-naphthol and 1-(2-thiazolylazo)-2-naphthol, respectively. The results of the X-ray analyses of these complexes suggest that the cobalt–PAR complex has the structure shown in Fig. 1(b), since PAN and TAN, as well as PAR, are *o*-hydroxy azo compounds and the PAR complexes can have the same chelate structure as the PAN and TAN complexes. Therefore, a structural change of the ligand PAR occurs upon coordination; breaking of the intramolecular hydrogen-bond and subsequent internal rotation of the resorcinol ring around the C–N bond by 180°. The main interest of the present work is to elucidate the structures of PAR and its cobalt(III) complexes in solutions by $^1$H NMR measurements.

## Experimental

*Materials.* PAR and $[Co^{III}(par)_2]$ were prepared as reported in the previous paper.[6] Deuterium oxide (99.7%), DMSO-$d_6$ (99.5%), and *ca.* 40% NaOD in $D_2O$ were purchased from E. Merck, Ltd. Reagent grade materials were used unless otherwise specified.

A new complex $[Co^{III}(par)(dien)]Cl \cdot NaCl$ was prepared from $[Co^{III}Cl_3(dien)]$ after the synthetic route described for the preparation of $[Co^{III}(ida)(dien)]$ from $[Co^{III}Cl_3 \cdot (dien)]$[16] (ida=iminodiacetate ion). Two grams of the monosodium salt of PAR in 75 ml $H_2O$ were added to 50 ml of suspended aqueous solution containing 2.1 g of $[Co^{III}Cl_3(dien)]$ and 0.6 g of charcoal at 50 °C with stirring. The addition of 20 ml of 20% aqueous solution of $AgNO_3$ produced a deep red solution. The reaction mixture was stirred for 2 h at 50 °C and cooled. After the further addition of 0.3 g of NaCl, the solution was filtered. The pH of the filtrate was adjusted to 7—8 with NaOH and the solution was diluted to 400 ml with water. One hundred milliliters of this solution were passed through a column of a cation-exchange resin SP-Sephadex C-25 in the Na-form (400 mm × 30 mm i.d.) and eluted with a 0.1 mol dm$^{-3}$ aqueous solution of NaCl at pH 7—8 (NaOH). The eluates from the main band were collected and evaporated to a small volume at 40—50 °C. The precipitated sodium chloride was filtered off and the filtrate was evaporated to dryness. A small amount of ethanol was added to the residue. The extract was filtered to remove sodium chloride. Successive filtration and extraction yield *ca.* 30 mg of deep red black crystals with golden luster. The yield was very low because of the high solubilities of the product in $H_2O$ and ethanol. Found: C, 38.44; H, 4.74; N, 17.96%. Calcd for $C_{15}H_{21}N_6O_2Cl_2CoNa$: C, 38.40; H, 4.30; N, 17.91%. The elemental analysis shows that the isolated complex contains one mole of sodium chloride.

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[$Pd^{II}Cl(par)$] was synthesized by the reaction between monosodium salt of PAR and palladium(II) chloride in an aqueous solution at pH 1—2 (HCl). The precipitate which formed upon mixing of the stoichiometric amounts of the reagents was filtered off, washed with water, and dried in a desiccator over silica gel. Found: C, 36.09; H, 2.65; N, 11.43%. Calcd for $C_{11}H_8N_3O_2ClPd \cdot 0.5H_2O$: C, 36.19; H, 2.49; N, 11.51%.

*Measurements.* 100 MHz $^1H$ NMR spectra were measured with a JEOL PS-100 spectrometer. Tetramethylsilane (TMS) and sodium trimethylsilylpropanesulfonate (DSS) were used as internal standards in DMSO-$d_6$ and $D_2O$ solutions, respectively. The pD (pH-meter reading +0.40)[17] of the $D_2O$ solutions was adjusted with NaOD and measured in nitrogen atmosphere with a Horiba pH-meter model M-7 equipped with a small glass electrode type 1826 05T and a reference electrode type 2410.

The $^1H$ NMR spectra of [$Co^{III}(par)_2$] and [$Co^{III}$(par)-(dien)] in $D_2O$ solutions were measured at pD *ca.* 10, where the coordinated PAR in [$Co^{III}(par)_2$] and [$Co^{III}$(par)-(dien)] exists in the same chemical form (*vide infra*) and the solubilities of the complexes were enough for the $^1H$ NMR measurements.

The $^1H$ NMR spectra of the 1:1 PAR-complexes, [$La^{III}$-(par)] and [$Zn^{II}$(par)], were measured with the alkaline-DMSO-$d_6$–$D_2O$ solutions. The mixture of the monosodium salt of PAR and about fifty-fold excess of anhydrous La-$(NO_3)_3$ or anhydrous $ZnCl_2$ was dissolved as much as possible in 50%(v/v) DMSO-$d_6$–$D_2O$. One drop of 10% $D_2O$ solution of NaOD was added. The solution was filtered. The red filtrate was subjected to the measurements.[18]

The $^1H$ NMR spectrum of [$Pd^{II}Cl(par)$] was measured with a red DMSO-$d_6$–$D_2O$ solution, which was prepared by adding a small amount of 10% $D_2O$ solution of NaOD to a green solution of the complex in 50%(v/v) DMSO-$d_6$–$D_2O$.[21]

Absorption spectra were measured at 25 °C and $I=0.1$ ($NaClO_4$) with a Hitachi recording spectrophotometer Model EPS-3T. The pH of the aqueous solution of [$Co^{III}$(par)-(dien)]Cl was measured with a Radiometer pH-meter 4d (Copenhagen) equipped with a glass electrode type G 202B and a reference electrode type 410.

## Results and Discussion

*$^1H$ NMR Spectra of the Free Ligand.* The 100 MHz spectrum of the monosodium salt of PAR in DMSO-$d_6$ at 90 °C is given in Fig. 2. Under these conditions the spectrum was highly resolved. Since the observed signals were well-separated from each other as compared with the coupling constants, the first-order analysis of the spin-spin coupling constants and the values of the chemical shifts allowed the assignments of the signals. The assignments were further confirmed by applying the method of double irradiation at the resonance frequencies for the protons, $H_1$, $H_2$, $H_3$, $H_4$, and $H_6$. In Table 1 are listed the values of the chemical shifts measured for band centers or maxima and the coupling constants evaluated from the spacings of the split signals (for numbering of the protons, see Fig. 1(a)). The significant difference in the values of $J_{12}$ and $J_{23}$ permitted the unambiguous assignments of $H_2$ and $H_3$. Though no direct evidence has been reported so far, the following facts suggest the presence of intramolecular hydrogen-bond for the free ligand PAR (Fig. 1(a)) in solutions: The p$K_a$ value of the *o*-hydroxyl group (12.31) is much higher than that of the *p*-hydroxyl group (5.6)[1] and also higher than the value of p$K_{a2}$ for resorcinol (11.06);[22] the proton-transfer reaction of the *o*-hydroxyl group of PAR proceeds slowly;[9] the IR spectrum of 4-(phenylazo)resorcinol in $CCl_4$ shows a broad band due to an intramolecular hydrogen-bond -OH···N= around 2860 $cm^{-1}$.[23] Furthermore, we observed the following facts: The resonance for the $H_8$, the proton of the *o*-hydroxyl group, appeared at very low field at 25 °C (see Table 1); The chemical shift of this resonance was not affected on dilution; The resonance disappeared by addition of one portion of

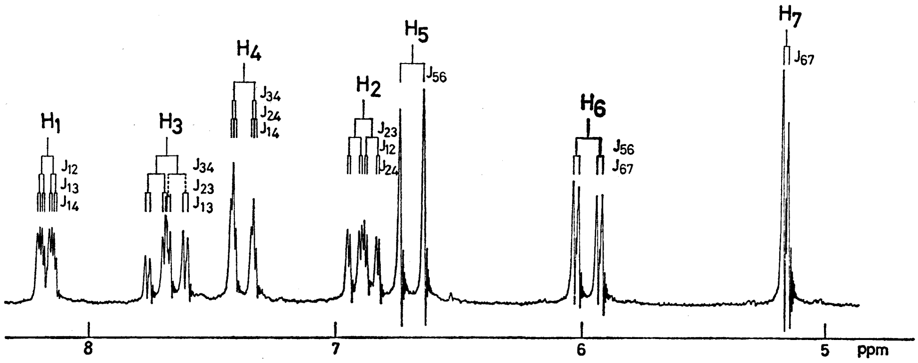

Fig. 2. 100 MHz $^1H$ NMR spectrum of the monosodium salt of PAR in DMSO-$d_6$ at 90 °C.

Table 1. $^1H$ NMR spectral data of the free ligand PAR[a)]

| | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ | $H_8$ | |
|---|---|---|---|---|---|---|---|---|---|
| Chemical shift[b)] | 8.17 | 6.90 | 7.68 | 7.38 | 6.69 | 5.99 | 5.18 | 16.59[d)] | |
| | $J_{12}$ | $J_{23}$ | $J_{34}$ | $J_{56}$ | $J_{13}$ | $J_{24}$ | $J_{67}$ | $J_{14}$ | $J_{57}$ |
| Coupling constant[c)] | 4.9 | 7.0 | 8.4 | 9.7 | 2.0 | 1.4 | 2.3 | 1.1 | ≃0 |

a) Data for the monosodium salt in DMSO-$d_6$ at 90 °C. b) In ppm referred to TMS. c) In Hz. d) At 25 °C. The resonance for $H_8$ diminished at 90 °C.

$D_2O$. These results directly show the presence of an intramolecular hydrogen-bond in the free PAR.[24]

$^1H$ NMR spectra of PAR in $D_2O$ solutions were measured in the range of pD 9—14, where PAR exists in the form of $LD^-$ and $L^{2-}$ as revealed in the electronic absorption spectra.[1]††† In the pD range, where two species of PAR are in equilibrium, only the averaged $^1H$ NMR spectrum of $LD^-$ and $L^{2-}$ was observed instead of the simple sum of each spectrum. The chemical shifts of the protons $H_1$, $H_5$, and $H_7$ moved to lower field with increasing concentration of NaOD, while that of $H_6$ was almost invariable with varying pD. Figure 3 shows the plots of the chemical shifts of $H_5$ and $H_7$ *vs.* pD. From these plots, the p$K_a$ value for the acid-dissociation of the *o*-hydroxyl group in $D_2O$

$$LD^- \xrightleftharpoons{K_a} L^{2-} + D^+$$

was determined to be 12.8±0.3, which is reasonable compared with the literature value 12.31 determined spectrophotometrically in $H_2O$.[1] Figure 4(a) shows the $^1H$ NMR spectrum of the free ligand PAR in $D_2O$ solution at pD 9.3, which corresponds to the spectrum of $LD^-$ as is clear from Fig. 3.

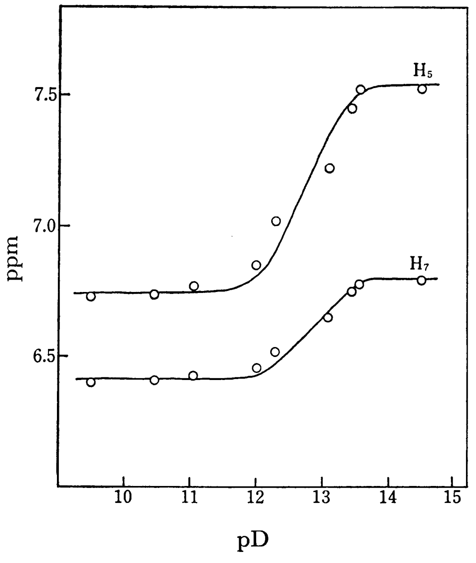

Fig. 3. Plots of the chemical shifts corresponding to $H_5$ and $H_7$ *vs.* pD.

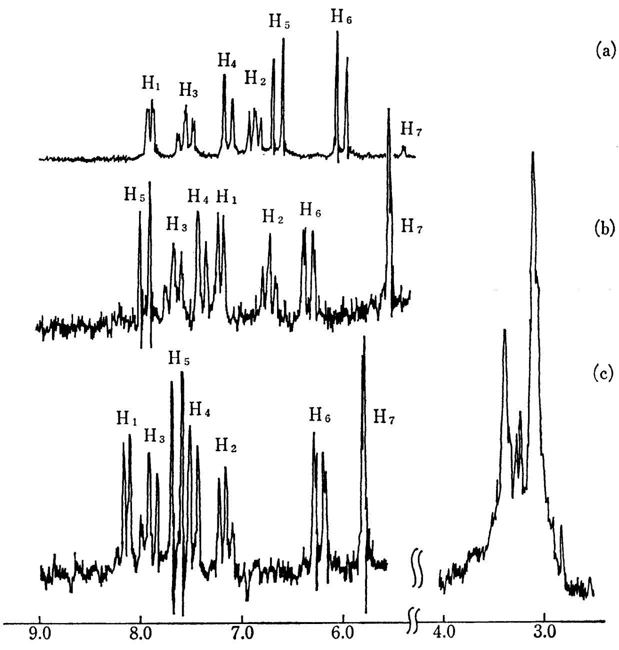

Fig. 4. $^1H$ NMR spectra in $D_2O$ solution of (a) PAR at pD 9.3, (b) $[Co^{III}(par)_2]$, and (c) $[Co^{III}(par)(dien)]$ at pD *ca.* 10.

In the course of the experiments on the pD-dependency of the $^1H$ NMR spectra, it was found that the proton $H_7$ was deuterated in $D_2O$ solutions. The intensity of the signal for $H_7$ decreased with the lapse of time. At the same time, the signal shape of the $H_6$ resonance changed gradually. The rate of the deuteration depended strongly on the pD of the solution. The deuteration of $H_7$ can be distinctly observed in Fig. 4(a). The integrated intensity for the signal of $H_7$ in the spectrum (a) is considerably less than that for one proton. In addition the $H_6$–$H_7$ coupling observed in the resonance for $H_6$ has almost disappeared (see the signal shape of the $H_6$ resonance in Fig. 2). The plot of the integrated intensity of the $H_7$ signal *vs.* time allowed the kinetic measurements of the deuteration. The half-times of the deuteration at room temperature at pD 9.3 and *ca.* 14 were found to be 80 min and 2.5 day, respectively. The deuteration proceeds much faster in $LD^-$ than in $L^{2-}$. The $LD^-$ species of PAR has an intramolecular hydrogen-bond, which may affect the electronic state of the carbon atom bonded to $H_7$ so as to facilitate the H–D exchange in $D_2O$. In fact, no corresponding deuteration was observed in $L^{2-}$, $[Co^{III}(par)_2]$, and $[Co^{III}(par)(dien)]$ containing no intramolecular hydrogen-bond.

*$^1H$ NMR Spectra of the Cobalt(III) Complexes.* Figure 4(b) shows the $^1H$ NMR spectrum of $[Co^{III}(par)_2]$ in $D_2O$ solution at pD *ca.* 10. Under this condition $[Co^{III}(par)_2]$ exists in the form of $[Co^{III}L_2]^-$.[6] The spectrum indicates that two ligand molecules in $[Co^{III}L_2]^-$ are magnetically and chemically equivalent. The $^1H$ NMR spectrum of $[Co^{III}(par)(dien)]$ at pD *ca.* 10 is shown in Fig. 4(c). The integrated intensities of the signals showed the presence of seven aromatic protons and six methylene protons (complex multiplet centered at *ca.* 3.2 ppm) corresponding to the coordinated ligands PAR and dien, respectively. As will be described later, $[Co^{III}(par)(dien)]$ exists in the form of $[Co^{III}L(dien)]^+$ at pD *ca.* 10.

Small couplings were not clearly observed in the spectra of $[Co^{III}L_2]^-$ and $[Co^{III}L(dien)]^+$ because of the low solubilities of the complexes in $D_2O$. However, comparison of the spectrum of the free ligand with those of the cobalt(III) complexes revealed that the spin-spin couplings in PAR remained essentially unchanged upon coordination, though the chemical shifts of some protons changed considerably. All the

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††† Hereafter, "PAR" stands for $L^{2-}$, $LH^-$, $LH^{*-}$, $LHH^*$, and/or $LD^-$, where $H^*$ denotes the proton of the *p*-hydroxyl group.

signals of $[Co^{III}L_2]^-$ and $[Co^{III}L(dien)]^+$ were unambiguously assigned by the analysis of the coupling constants. The coupling constant $J_{12}$ is smaller than $J_{23}$ in the cobalt(III) complexes as well. The assignments are given in Table 2.

Table 2. $^1H$ NMR chemical shifts of $LH^-$, $[Co^{III}L_2]^-$, and $[Co^{III}L(dien)]^+$ [a)]

| | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ |
|---|---|---|---|---|---|---|---|
| $LH^-$ [b)] | 7.90 | 6.86 | 7.56 | 7.13 | 6.63 | 6.00 | 5.40 |
| $[Co^{III}L_2]^-$ [c)] | 7.23 | 6.75 | 7.70 | 7.41 | 7.98 | 6.37 | 5.56 |
| $[Co^{III}L(dien)]^+$ [d)] | 8.14 | 7.16 | 7.92 | 7.48 | 7.64 | 6.23 | 5.78 |

a) In $D_2O$. Chemical shifts in ppm referred to DSS.
b) Monosodium salt. At pD 9.3. c) At pD *ca.* 10.
d) Chloride. At pD *ca.* 10.

The resonance of $H_1$ in $[Co^{III}L_2]^-$ shows a definite up-field shift compared with that in free PAR. On the other hand, such an up-field shift was not observed for the $H_1$ resonance of $[Co^{III}L(dien)]^+$ (see Table 2). In order to clarify whether the difference in chemical shift of $H_1$ is caused by the number of PAR molecules in the complex, we measured $^1H$ NMR spectra of the PAR chelates of other metal ions containing only one PAR ligand, $[Pd^{II}ClL]^-$, $[La^{III}L]^+$, and $[Zn^{II}L]^0$, in 50%(v/v) DMSO-$d_6$–$D_2O$ mixed solvents containing one drop of *ca.* 10% NaOD.[18,21] No up-field shift of the $H_1$ signal was observed for these complexes. Spectral pattern of these complexes was very similar to that of $[Co^{III}L(dien)]^+$ but not to that of $[Co^{III}L_2]^-$. A careful inspection of molecular models reveals a plausible explanation for the up-field shift of the $H_1$ signal of $[Co^{III}(par)_2]$. The proton $H_1$ of one PAR molecule in $[Co^{III}(par)_2]$ is disposed close to and above the azo group of the other PAR molecule, only when two PAR molecules coordinate to cobalt(III) ion in planar fashion as terdentate ligands. In view of this fact and the above-mentioned observations, the large up-field shift can reasonably be explained as being caused by the magnetic anisotropy due to the $\pi$-electron system of the azo group in the neighboring ligand PAR. The up-field shift of the $H_1$ signal would not be expected for free PAR, $[Co^{III}L(dien)]^+$, $[Pd^{II}ClL]^-$, $[La^{III}L]^+$, and $[Zn^{II}L]$, since the proton $H_1$ in these compounds cannot experience the chemical environment as described above.

Similar up-field shifts have been observed for the *ortho*-protons of pyridyl nitrogen in $[M(phen)_3]^{n+}$ [25] (M=Fe(II), Ru(II), Zn(II), and Co(III)), in $[Co^{III}(phen)_2(en)]^{3+}$,[26] and in $[Fe^{II}(bipy)_3]^{2+}$.[27] One of the $\beta$-methylene protons in tris-($N,N'$-dibutyl-2,3-butanediimine)iron(II) complex has been also reported to show similar large up-field shifts.[28] The up-field shifts observed in these complexes have been interpreted in terms of the ring current of the neighboring aromatic ligands[26,27] or in terms of the magnetic anisotropy due to the imine bonds of the neighboring ligands.[28]

Another remarkable feature found in the $^1H$ NMR spectra of cobalt(III)–PAR complexes in comparison with that of the free PAR is a large difference in the chemical shift of the proton $H_5$. The $H_5$ signal appears at 6.63 ppm in the free ligand at pD 9.3, while the corresponding signal appears at 7.98 ppm in $[Co^{III}L_2]^-$ and 7.64 ppm in $[Co^{III}L(dien)]^+$ at pD *ca.* 10. As was discussed before, around pD 10 the free ligand PAR and the cobalt(III) complexes have the structures shown in Figs. 1(a) and 1(b), respectively. The terdentate and planar coordination of PAR molecule is accompanied by an internal rotation of resorcinol ring moiety around C–N axis by 180°. The molecular model suggests that the coordination of PAR causes a fairly strong strain in the complexes especially for the bond angle around cobalt(III) ion. The bond angles, N(pyridine)–Co–N(azo) and N(azo)–Co–O, are expected to be significantly smaller than 90°. As a result, a fairly close contact appears between the proton $H_5$ and the azo group. The proton $H_5$ in such a chemical environment would be susceptible to the effect of the magnetic anisotropy due to the $\pi$-electron system of the azo group in addition to the effect of the ring current of the resorcinol ring. The location of the proton $H_5$ in such an environment causes a down-field shift when the complexes are in the magnetic field.

Very similar situation has been found in the crystal structure of $[Co^{III}(tan)_2]$.[14] The X-ray analysis of $[Co^{III}(tan)_2]$ shows that the bond angles around the cobalt atom within the chelate ring are compressed to 84.9 and 81.6° and that the coordinated TAN is deformed due to the in-plane close contact around the azo group. The significant down-field shift of the $H_5$ signal observed for the cobalt(III) complexes of PAR can be ascribed to the structural change of PAR upon chelate-ring formation.

On the basis of the $^1H$ NMR studies, it is concluded that PAR coordinates to cobalt(III) ion in planar fashion as a terdentate ligand, namely, in the *mer* configuration.

*Acid-Base Behavior of* $[Co^{III}(par)(dien)]$. In order to confirm the chemical species of $[Co^{III}(par)(dien)]$ present under the conditions of the $^1H$ NMR measurements, the absorption spectra were measured in aqueous solutions at various pH. Figure 5 shows the pH-

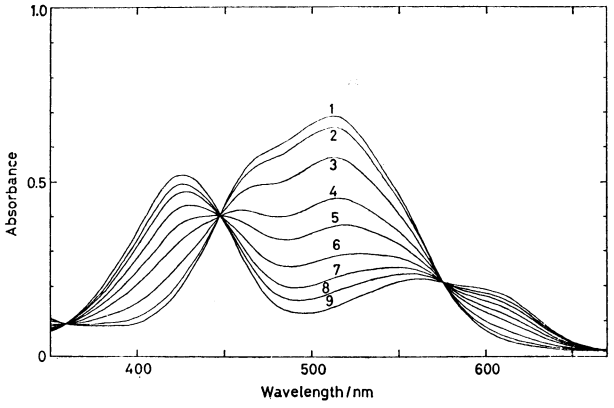

Fig. 5. Absorption spectra of the aqueous solution of $[Co^{III}(par)(dien)]$ as a function of pH at 25 °C and $I$=0.1 ($NaClO_4$). pH=8.88 (1), 5.79 (2), 5.06 (3), 4.60 (4), 4.33 (5), 4.01 (6), 3.67 (7), 3.34 (8), and 2.36 (9).

dependence of the absorption spectrum of [Co$^{III}$(par)(dien)]. Well-defined isosbestic points were observed at 359, 447, and 576 nm, which demonstrate the presence of a simple equilibrium. The spectral change with varying pH was fully reversible. In view of the inertness of the cobalt(III) complexes against the ligand dissociation, the pH-dependence of the spectrum can be attributed to the protonation-deprotonation equilibrium of a *p*-hydroxyl group of the coordinated PAR in [Co$^{III}$(par)(dien)]. From the plot of absorbance at 500 nm *vs*. pH, the value of p$K_a$ for the acid-dissociation

$$[\mathrm{Co^{III}LH^*(dien)}]^{2+} \xrightleftharpoons{K_a} [\mathrm{Co^{III}L(dien)}]^+ + \mathrm{H}^+$$

was determined to be 4.52±0.03. The average value of the acid-dissociation constants for p$K_{a1}$([Co$^{III}$(LH*)$_2$]$^+$) and p$K_{a2}$([Co$^{III}$L(LH*)]) has been reported to be 4.1.[6] Around pH 10, where the $^1$H NMR measurements were carried out, [Co$^{III}$(par)(dien)] exists only in the form of [Co$^{III}$L(dien)]$^+$.

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18) The stability constants and the acid-dissocation constants for the present systems in aqueous media have been reported to be $K_{\mathrm{La(par)}} = 10^{9.2}$,[19] $K_{\mathrm{Zn(par)}} = 10^{11.9\pm0.1}$,[20] $K_{\mathrm{Zn(par)_2}} = 10^{10.3\pm0.2}$,[20] and $K(\mathrm{ZnL^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{ZnLH^*}) = 10^{5.90\pm0.05}$.[20] Though the value of $K(\mathrm{LaL^-} + \mathrm{H^+} \rightleftharpoons \mathrm{LaLH^*})$ has not been reported so far, it is expected to be in the order of magnitude *ca.* $10^6$ from the corresponding values of $K$ for other lanthanide(III)–PAR systems.[19] These values suggest that in the sample solutions used for the $^1$H NMR measurements the complexes are predominantly present as 1 : 1 complexes with the dissociated *p*-hydroxyl group of the coordinated PAR.

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