# Bivalent and Tervalent Cobalt Complexes of 4-(2-Pyridylazo)resorcinol, 1-(2-Pyridylazo)-2-naphthol, and their Thiazolyl Analogs in Aqueous and Aqueous Dioxane Media. Rapid-scan Spectral and Kinetic Studies*

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The reactions of Co$^{2+}$ with 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN), and their thiazolyl analogs TAR and TAN in aqueous or aqueous dioxane media are followed by a rapid-scan spectroscopic method combined with stopped-flow technique. The step of the fast formation of cobalt(II) complexes is clearly discriminated from the subsequent slower step of oxidation to the cobalt(III) state. Formation and redissolution of transient insoluble intermediates are observed in the stopped-flow signals for the light scattered by the reaction mixture. The metal-to-ligand ratio in the short-lived intermediate cobalt(II) complex of PAR and PAN is determined to be 1 : 2 by applying the method of continuous variation to the fast change in stopped-flow signals. The rate constants $k_1$ and $k_2$ for the step of formation of 1 : 1 cobalt(II) complex with the species LHH* and LH$^-$ of PAR in aqueous solution and with the species LH$_2^+$ and LH of PAN in 5%(v/v) dioxane–water are determined to be $k_1=4.8\times10^4$ and $k_2=9.8\times10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, and $k_1<10^3$ and $k_2=4.6\times10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively.

Some *ortho*-hydroxy azo compounds shown in Fig. 1 are reported to behave as terdentate ligands[1,2] forming colored chelates with many metal ions.[3] PAN and PAR have been used as sensitive analytical reagents for the spectrophotometric determination of cobalt.[4,5]

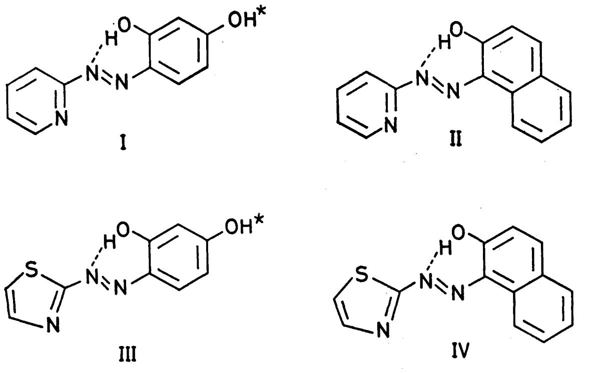

Fig. 1. Structural formulae of the ligands. I: 4-(2-pyridylazo)resorcinol (PAR), II: 1-(2-pyridylazo)-2-naphthol (PAN), III: 4-(2-thiazolylazo)resorcinol (TAR), IV: 1-(2-thiazolylazo)-2-naphthol (TAN).

As regards the cobalt chelates of PAN and PAR, a number of data have been reported on the composition and the stability constants.[3,6,7] On the basis of the measurements of magnetic susceptibility, Iwamoto and Fujimoto provided an evidence for the formation of cobalt(III) complexes in a solution prepared from Co$^{2+}$ and PAR or PAN.[8] This result has been supported by the studies on the substitution reaction with EDTA[5,9] and also by the proton magnetic resonance studies of the isolated complex.[10,11] Although the cobalt(III) complexes of these heterocyclic *ortho*-hydroxy azo compounds have been well characterized, no studies on cobalt(II) chelates have been reported so far.

In the present study, we have confirmed the formation of transient intermediate cobalt(II) complexes in the course of the reaction between Co$^{2+}$ and the ligands I—IV using a rapid-scan spectrophotometer equipped with a stopped-flow cell. The formation and redissolution of hardly visible fine precipitates in the course of the reaction between Co$^{2+}$ and PAN or TAN were also revealed by applying the stopped-flow technique to the measurements of the change in intensity of the scattered light.[12] The metal-to-ligand ratio in the transient cobalt(II) complexes, the mechanisms and the kinetic data for the step of formation of 1 : 1 cobalt(II) complexes, and some results on the cobalt(III) complexes are discussed.

## Experimental

*Materials.* Deionized water was distilled. Reagent grade materials were used unless otherwise specified.

The cobalt(II) perchlorate solution was prepared by heating cobalt(II) chloride with a small excess of perchloric acid until no trace of chloride ion was detected. The solution was standardized titrimetrically with EDTA using Xylenol Orange as an indicator.

PAR was synthesized by the usual method,[13] and recrystallized several times from 1 : 1(v/v) ethanol–water to yield reddish yellow needles of the monohydrate of the monosodium salt. Found: C, 51.34; H, 3.97; N, 16.26%. Calcd for $C_{11}H_8N_3O_2Na\cdot H_2O$: C, 51.77; H, 3.95; N, 16.47%. The concentration of PAR in the aqueous stock solution (*ca.* $10^{-4}$ mol dm$^{-3}$) was calculated from its weight.

Commercial PAN, TAR, and TAN (Dojindo, Kumamoto) were used without further purification. The purity was confirmed by elemental analyses. Stock solutions of these compounds ($1\times10^{-4}$ mol dm$^{-3}$) were prepared by dissolving the reagent in 50%(v/v) dioxane–water. The concentrations were calculated from the weighed amount.

A neutral 1 : 2 cobalt(III) complex of PAR, [Co$^{\text{III}}$L(LH*)] was prepared as follows, where LH* stands for the ligand with an undissociated *para*-hydroxyl group.† The stoichio-

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† Hereafter "PAR" stands for L$^{2-}$, LH$^-$, LH*$^-$, and/or LHH*, where H* denotes the proton of the *para*-hydroxyl group (Fig. 1).

metric amounts of cobalt(II) perchlorate and PAR were slowly mixed with vigorous stirring at pH 6.0—6.5. Precipitates formed gradually. Then the pH of the solution was lowered to 4.0 by adding dropwise dilute perchloric acid in order to complete the precipitation. The solution was allowed to stand for 24 h. Precipitates were filtered off, washed thoroughly with water and ethanol, and dried at 80 °C. The content of cobalt was determined titrimetrically with EDTA using Cu–PAN as an indicator after decomposition of the complex by heating with hydrogen peroxide and sulfuric acid. Found: C, 52.87; H, 3.66; N, 16.58; Co, 11.38%. Calcd for $C_{22}H_{15}N_6O_4Co \cdot H_2O$: C, 52.39; H, 3.20; N, 16.66; Co, 11.69%.

A pale-colored anion-exchange resin QAE-Sephadex A-25 in the Cl-form and a pale-colored cation exchanger SP-Sephadex C-25 in the Na-form were used in order to discern the sign of the net charge on the final cobalt(III)–PAR species formed in the reaction at various pH by the sensitive coloration on the resin grains.

*Measurements.* The absorption spectra were measured with a Hitachi recording spectrophotometer model EPS-3T. Fast changes in the absorption spectra and the rate of complex formation were measured with a Union Giken rapid-scan spectrophotometer model RA-1300 equipped with a stopped-flow cell.

The stopped-flow signal for the scattered light[12] was also observed with this apparatus.

All measurements were carried out at 25.0±0.2 °C. The ionic strength was maintained at 0.1 mol dm$^{-3}$ with sodium perchlorate. The pH of the solution was adjusted with acetate or hexamine buffers and measured with a Radiometer pH-meter 4d (Copenhagen) equipped with a glass electrode type G 202B and a reference calomel electrode type 401. The pH-meter readings for the 5 or 10%(v/v) dioxane–water solutions were used without correction.[14]

## Results and Discussion

*I. Rapid-scan Spectral Studies. Cobalt–PAR. Rapid-scan Spectra*: Figure 2(a) shows a typical example of the spectral change for the reaction of Co$^{2+}$ and PAR in aqueous solution at pH 5.46. Each spectrum was rapidly scanned at appropriate time intervals after the solution containing cobalt(II) perchlorate in excess was rapidly mixed with a PAR solution by the stopped-flow technique. The figure clearly indicates that two steps are involved in the reaction.

At the initial stage, the spectrum of the reaction mixture changed rapidly with an isosbestic point at 450 nm. The absorption around 400 nm due to the free ligand PAR decreased with the increase of a new absorption around 500 nm due to the complex. The rapid spectral change ceased in *ca.* 40—50 ms after mixing. Then a relatively slow spectral change occurred with other isosbestic points at 330 and 435 nm. The final equilibrium was attained in *ca.* 3 min under the given conditions.

The change in the rapid-scan spectra for the reaction of Co$^{2+}$ and PAR at pH 2.72 (Fig. 2(b)) differs from that at pH 5.46 (Fig. 2(a)), but it is still evident that two steps with two sets of isosbestic points are involved in the reaction.

In each case, the final spectrum coincides with the spectrum of [Co$^{III}$(par)$_2$], which was obtained under the same conditions either with an equilibrated solution prepared by mixing Co$^{2+}$ and PAR in the molar ratio of 1 : 2 or with an aqueous solution of the isolated 1 : 2 cobalt(III) complex [Co$^{III}$L(LH*)] (Fig. 7).

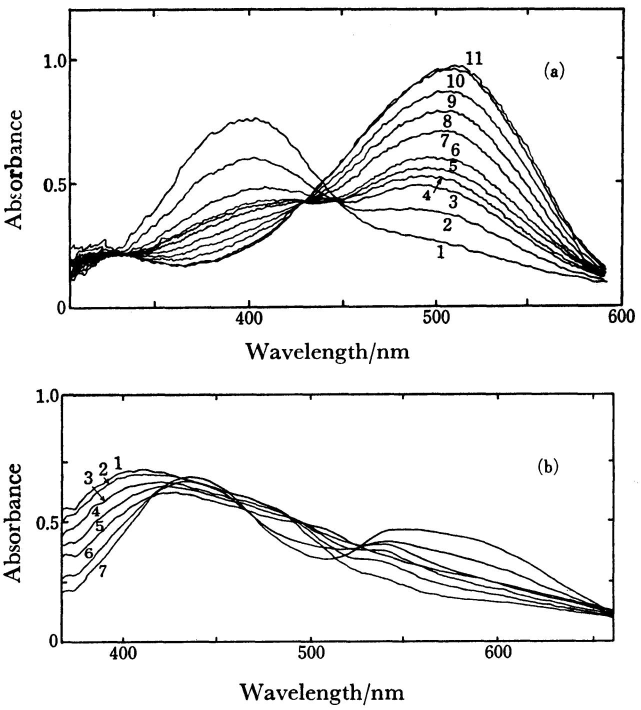


Fig. 2. (a) Rapid-scan spectra for the reaction of 7.64 × 10$^{-4}$ mol dm$^{-3}$ cobalt(II) perchlorate and 3.31 × 10$^{-5}$ mol dm$^{-3}$ PAR at pH 5.46, $I$=0.1 (NaClO$_4$), and 23 °C, measured at 0 (1), 10 (2), 25 (3), 50 (4), 100 ms (5), 0.5 (6), 5 (7), 20 s (8), 1 (9), 2 (10), and 3 min (11) after mixing. Scan rate: 300 nm/5 ms.

(b) Rapid-scan spectra for the reaction of 1.53 × 10$^{-3}$ mol dm$^{-3}$ cobalt(II) perchlorate and 3.57 × 10$^{-5}$ mol dm$^{-3}$ PAR at pH 2.72, $I$=0.1 (NaClO$_4$), and 25 °C, measured at 0 (1), 10 (2), 25 (3), 50 (4), 100 ms (5), 1 s (6), and 3 min (7) after mixing. Scan rate: 300 nm/5 ms.

*Stopped-flow Signal*: Figure 3 shows the change in absorbance with time at 510 nm in the course of the reaction under the same conditions as in Fig. 2(a). The stopped-flow signal also discriminates the fast reaction from the slower one. The rate of the first step

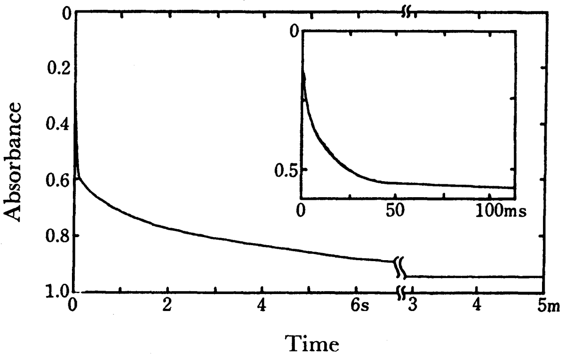
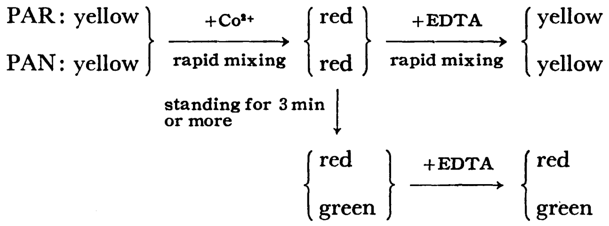


Fig. 3. Stopped-flow signal at 510 nm for the reaction of Co$^{2+}$ and PAR. The experimental conditions are the same as those for Fig. 2(a). Inset shows an expanded signal for the initial stage of the reaction.

was found to be enhanced under the same conditions with the increase in the initial concentration of $Co^{2+}$ ion (*vide infra*). This result indicates that the first step is the complex formation process. On the other hand, the effects of hydrogen peroxide on the reaction between $Co^{2+}$ and PAR reveal that the second step involves the oxidation of cobalt(II)-PAR complex. When the solution of PAR containing 6% $H_2O_2$ was mixed with a $Co^{2+}$ solution under the same conditions as in Fig. 3, only the second step was accelerated several-fold, leaving the first step essentially unaffected.

*Substitution Reaction with EDTA*: The results on the substitution reaction of cobalt-PAR complexes with EDTA also provide a further evidence for the presence of the Co(II) state in the initial stage of the present reaction and of the Co(III) state in the final stage. The solution containing $Co^{2+}$ ion in excess was rapidly mixed with a yellow PAR solution at pH 5 with a microsyringe. The red color of the solution thus formed turned orange by the subsequent rapid addition of EDTA. The color change indicates the liberation of yellow ligand PAR, suggesting the presence of labile Co(II) state immediately after the rapid mixing of $Co^{2+}$ and PAR.[15]

However, when once the final equilibrium is attained, the red color of the solution never changes on addition of even a large excess of EDTA. This fact suggests the formation of inert cobalt(III)-PAR complexes and the absence of labile cobalt(II)-PAR complexes in this stage of the reaction. The observed color changes are summarized in Scheme 1 together with those for the cobalt-PAN system.



Scheme 1. Color change at pH *ca.* 5.

*Ion-exchange Behavior of the Final Products*: The nature of the final products was also proved by their ion-exchange behavior. The final product obtained at pH 2.72 was strongly adsorbed on the cation-exchange resin but not on the anion-exchange resin. On the other hand, the final product at pH 5.46 was strongly adsorbed on the anion-exchange resin but not on the cation-exchange resin. These facts lead to the conclusion that the final product is a tervalent cobalt complex with two ligand molecules having dissociated or undissociated *para*-hydroxyl groups with respect to the azo group; the final products at pH 2.72 and 5.46 are a cationic species $[Co^{III}(LH^*)_2]^+$ and an anionic species $[Co^{III}L_2]^-$, respectively. The net charge on the final product is supported by the $pK_a$ value of the *para*-hydroxyl group of the ligand in $[Co(par)_2]$ (*vide infra*). It should be noted that 1 : 2 complexes are finally formed even though a large excess of $Co^{2+}$ reacts with the ligand PAR.

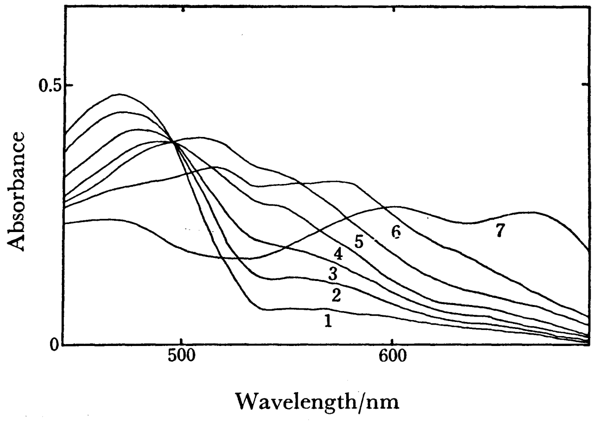


Fig. 4. Rapid-scan spectra for the reaction of $7.65 \times 10^{-4}$ mol $dm^{-3}$ cobalt(II) perchlorate and $2.99 \times 10^{-5}$ mol $dm^{-3}$ PAN in 5%(v/v) dioxane-water mixture at pH 4.72, $I=0.1$ ($NaClO_4$), and 25 °C, measured at 0 (1), 0.04 (2), 0.1 (3), 0.2 (4), 0.4 (5), 4 s (6), and 4 min (7) after mixing. Scan rate: 300 nm/20 ms.

*Cobalt-PAN.* *Rapid-scan Spectra*: Figure 4 shows the change of rapid-scan spectra for the reaction of $Co^{2+}$ ion and PAN at pH 4.72. The experiments were carried out in 5%(v/v) dioxane-water solutions because of the very low water-solubility of PAN. At the initial stage, the spectrum of the reaction mixture changes rapidly with an isosbestic point at 490 nm. The absorption around 470 nm due to the free ligand PAN decreases in 400 ms with the increase of a new absorption around 540 nm due to a red-colored complex. This absorption in turn decreases in a few minutes with the increase of an absorption around 650 nm due to the formation of a green-colored complex.

The lability of the cobalt in the red and the green complex was confirmed by means of the substitution reaction with EDTA. The results shown in Scheme 1 indicate the formation of a red-colored labile cobalt(II) complex immediately after the rapid mixing of $Co^{2+}$ and PAN and the subsequent slow formation of a green-colored inert cobalt(III) complex. These observations, together with the results of the kinetic study, indicate that the two-step reaction in Fig. 4 corresponds to the fast formation of cobalt(II)-PAN complex and the subsequent slow oxidation to a cobalt(III)-PAN complex $[Co^{III}(pan)_2]$.

However, no isosbestic point was observed for the oxidation step in contrast to the observation for the corresponding step of the cobalt-PAR system. For the reaction of $Co^{2+}$ with PAN the formation of a neutral insoluble intermediate $[Co^{II}(pan)_2]^0$ was expected, as observed for the $Ni^{2+}$-PAN system.[12] In order to confirm this expectation, the stopped-flow signal of the scattered light was measured for the reaction of the $Co^{2+}$-PAN system.

*Stopped-flow Signals for Scattered Light*: Figure 5 shows the change in intensity of scattered light in the course of the reaction. The intensity increases after a short induction period and then decreases gradually. The feature is essentially independent of the wavelength of the incident monochromatic light in the range 400—600 nm. The induction period appearing at the initial

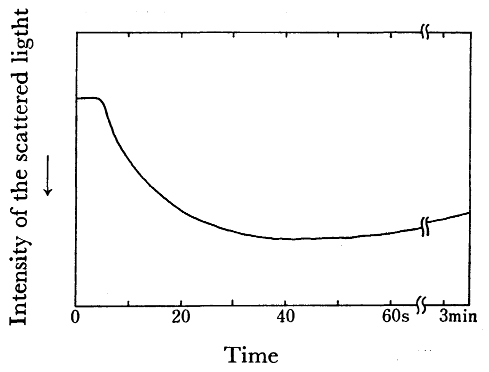


Fig. 5. Stopped-flow signal of the scattered light for the reaction of $1.91 \times 10^{-5}$ mol dm$^{-3}$ cobalt(II) perchlorate and $2.99 \times 10^{-5}$ mol dm$^{-3}$ PAN in 5%(v/v) dioxane-water mixture at pH 4.72, $I=0.1$ ($NaClO_4$) and 25 °C.

stage of the reaction corresponds to the formation of the cobalt(II)–PAN complex prior to the crystal growth. The subsequent increase in the intensity of the scattered light is due to the formation and the growth of the insoluble crystals of $[Co^{II}(pan)_2]^0$. The final decreasing portion of the signal indicates the process of redissolution of the insoluble intermediate. This corresponds to the step of oxidation of $[Co^{II}(pan)_2]^0$ forming a more soluble $[Co^{III}(pan)_2]^+$ complex. The lack of an isosbestic point in the spectra for the second step of the present reaction shown in Fig. 4 is due to the formation of an insoluble intermediate $[Co^{II}(pan)_2]^0$.

*Cobalt–TAR and Cobalt–TAN.* Similar spectral changes were observed for the reactions of $Co^{2+}$–TAR and –TAN. The ligands TAR and TAN, which have a thiazolyl group instead of pyridyl group in PAR and PAN, are insoluble in water. The experiments were, therefore, carried out in a 5 or 10%(v/v) dioxane–water solution. The spectral change for these systems also consists of a fast and a subsequent slower step. Two sets of distinct isosbestic points were observed in the spectra for the reaction of $Co^{2+}$ and TAR, while no isosbestic point was observed for the second step of the $Co^{2+}$–TAN system.

Experiments on the substitution reactions of the intermediates and the final products with EDTA were carried out for both the cobalt–TAR and the cobalt–TAN system in the same way as described for the PAR and the PAN system. Stopped-flow signals for the scattered light similar to the signal shown in Fig. 5 were observed for the $Co^{2+}$–TAN reaction.

It is concluded that the reactions of $Co^{2+}$–TAR and –TAN proceed by the same mechanism as for the $Co^{2+}$–PAR and –PAN systems, respectively. In each system, the first and the second step correspond to the formation of cobalt(II) complex and subsequent oxidation, respectively. The reaction of cobalt(II) with TAN involves the formation of insoluble intermediate, $[Co^{II}(tan)_2]^0$.

*Effect of Oxygen on the Oxidation of Cobalt(II) Complexes.* In order to ascertain if the cobalt(II) complexes are stable in deoxygenated media, we carried out spectrophotometric measurements for the cobalt(II)–PAN and the cobalt(II)–PAR system with a device connected to a vacuum system (Fig. 6). In this device the solutions of $Co^{2+}$ and the ligand were separately degassed beforehand by freezing several times. Then the solutions were mixed and introduced into the optical cell *in vacuo*. This approach succeeded in detection of the cobalt(II)–PAN and the cobalt(II)–PAR complex even with an ordinary spectrophotometer, since in the measurements with this device the rate of oxidation was lowered by 50—60 times for both systems as compared with that in undegassed solutions. Spectra thus obtained were identical with those of the cobalt(II) complexes observed transiently by the rapid-scan spectrophotometer. It is concluded that $[Co^{II}(pan)_2]$ and $[Co^{II}(par)_2]$ complexes are oxidized by oxygen in the solution and that even a trace amount of oxygen takes part in the oxidation to cobalt(III) complexes.

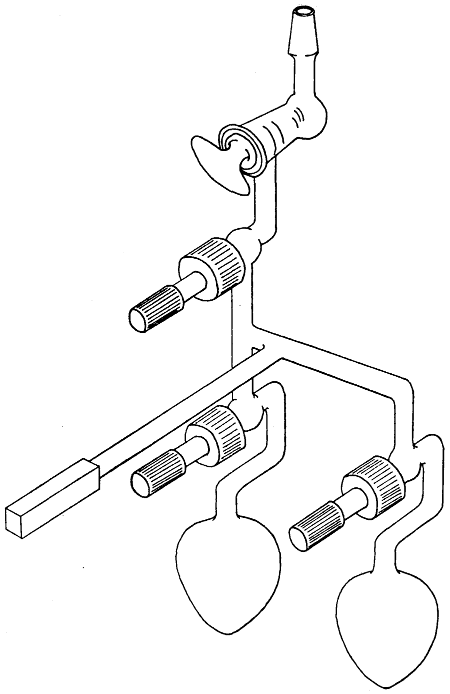


Fig. 6. Evacuable mixing device for measurements of absorption spectra in deoxygenated systems.

*II. Equilibrium and Kinetic Studies. Composition of the Cobalt–PAR and –PAN Complexes.* The Composition of the short-lived intermediate cobalt(II) complexes was determined to be 1 : 2 by applying the method of continuous variation to the first rapid change of the stopped-flow signals as shown in the inset of Fig. 3. The composition of the cobalt(III) complexes of PAR and PAN in the aqueous and the 50%(v/v) dioxane–water solutions, respectively, was determined also to be 1 : 2 by the usual continuous variation method.

*Protonation-Deprotonation of $[Co^{III}(par)_2]$.* Figure 7 shows the pH-dependence of the spectrum of an aqueous solution of the isolated cobalt(III)–PAR complex $[Co^{III}L(LH^*)]$. The same pH-dependence of the spectrum was also observed with an equilibrated solution prepared from $Co^{2+}$ and PAR in a molar ratio of 1 : 2. It is attributed to the protonation-deprotonation of the *para*-hydroxyl group of the coordinated

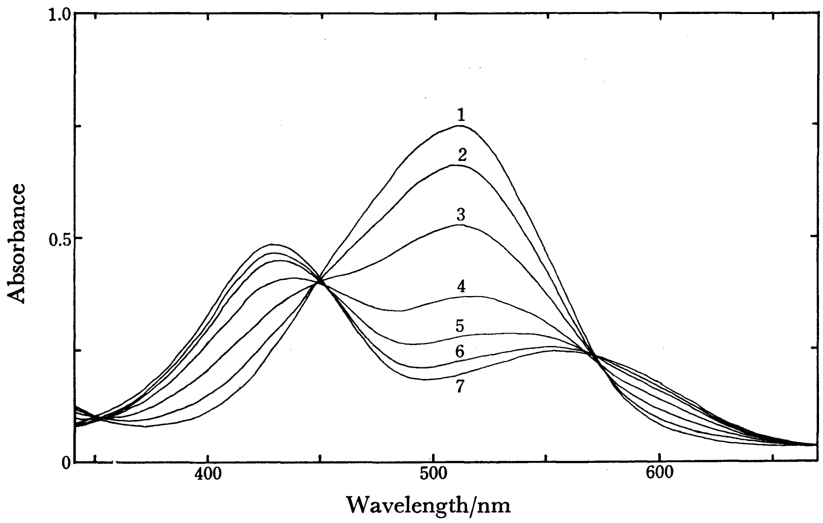


Fig. 7. Absorption spectra of the aqueous solution of $[\mathrm{Co^{III}(par)_2}]$ as a function of pH at 25 °C and $I$=0.1 ($\mathrm{NaClO_4}$). $[\mathrm{Co^{III}(par)_2}] = 1.26\times10^{-5}\ \mathrm{mol\ dm^{-3}}$. pH=9.29 (1), 5.05 (2), 4.39 (3), 3.73 (4), 3.26 (5), 2.77 (6), and 1.88 (7).

PAR in the inert cobalt(III) complex.

Acid-dissociation constants for

$$[\mathrm{Co^{III}(LH^*)_2}]^+ \xrightleftharpoons{K_{a1}} [\mathrm{Co^{III}L(LH^*)}] + \mathrm{H^+}$$

and

$$[\mathrm{Co^{III}L(LH^*)}] \xrightleftharpoons{K_{a2}} [\mathrm{Co^{III}L_2}]^- + \mathrm{H^+}$$

were determined from the result shown in Fig. 7. The plots of absorbance *vs.* pH at 420, 510, and 600 nm indicate that the values of $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ are not quite different from each other, the average value being 4.1.[16)]

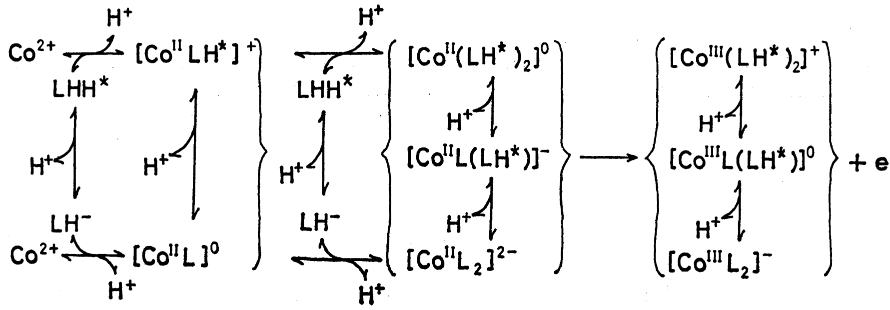
From these results and the ion-exchange behavior the cobalt(III)–PAR complexes are found to be in the form of an anionic $[\mathrm{Co^{III}L_2}]^-$ ($\lambda_{\max}$=510 nm, $\varepsilon_{\max}$=57000) at pH 6 or higher, and a cationic $[\mathrm{Co^{III}(LH^*)_2}]^+$ ($\lambda_{\max}$=430 nm, $\varepsilon_{\max}$=37500; $\lambda_{\max}$=558 nm, $\varepsilon_{\max}$=18300) at pH 2 or lower. Features of the spectral change depicted in Fig. 7 suggest the formation of a neutral species $[\mathrm{Co^{III}L(LH^*)}]^0$, since two sets of isosbestic points are observed at 452 and 568, and 448 and 574 nm.[17)]

*Overall Reaction Mechanisms for the Formation of Cobalt(III) Complexes.* On the basis of the results given above the overall reaction mechanisms for the formation of 1 : 2 cobalt(III) complexes with the ligands PAR and PAN are summarized in Schemes 2 and 3, respectively. It should be noted that cobalt(II) complexes are oxidized only *via* formation of 1 : 2 complexes, $[\mathrm{Co^{II}(par)_2}]$ or $[\mathrm{Co^{II}(pan)_2}]$.

*Kinetics on the Formation of Cobalt(II) Complexes.* Kinetic measurements were carried out under the conditions of $\mathrm{Co^{2+}}$ ion in large excess over the ligand. For the calculation of rate constants, the first rapid change in the stopped-flow signal was analyzed after subtracting the part of slower oxidation step involved in the signal. The stopped-flow signals were followed at the absorption maxima for the 1 : 2 cobalt(II) complexes and for the free ligands PAR or PAN as well. Both signals for the fast complex formation gave a single exponential curve characterized by the same pseudo-first-order rate constant, $k_{\mathrm{obsd}}$. The result and the values of $k_{\mathrm{obsd}}$ suggest that the coordination of the first ligand is the rate-determining step, the coordination of the second ligand molecule proceeding very fast.

*Cobalt(II)–PAR*: The rate of formation of cobalt(II)–PAR complex was determined in aqueous solution at pH 3—6 with 10—100 fold excess of $\mathrm{Co^{2+}}$ ion over the ligand. The absorbance change at 510 nm was used for the calculation of rate constants. The pseudo-first-order rate constant $k_{\mathrm{obsd}}$ showed first-order dependence on the total concentration of $\mathrm{Co^{2+}}$, [Co], at constant pH as shown by

$$k_{\mathrm{obsd}} = k_{\mathrm{f}}[\mathrm{Co}] + k_{\mathrm{d}}. \qquad (1)$$

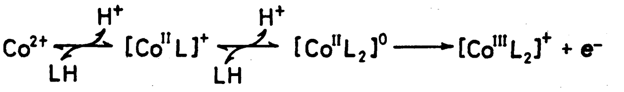


Scheme 2. Overall reaction mechanism for the formation of $[\mathrm{Co^{III}(par)_2}]$.

Table 1. Kinetic data[a)] for the formation of cobalt(II) complexes at 25 °C and $I=0.1$ ($NaClO_4$)

| Ligand | $\frac{[Co]}{10^{-3}\ mol\ dm^{-3}}$ | Rate constant $k_{obsd}/s^{-1}$ |  |  |  |  | Ligand | $\frac{[Co]}{10^{-3}\ mol\ dm^{-3}}$ | Rate constant $k_{obsd}/s^{-1}$ at pH 4.7 |
|---|---|---|---|---|---|---|---|---|---|
|  | at pH | 3.03 | 4.10 | 4.62 | 4.95 | 5.60 |  |  |  |
| PAR[b)] | 0.38 | 7.0 | 28 | 37 | 38 | 39 | TAR[c)] | 0.38 | 44 |
|  | 0.77 | 23 | 44 | 59 | 60 | 72 |  | 0.77 | 68 |
|  | 1.53 | 45 | 83 | 110 | 120 | 130 |  | 1.53 | 110 |
|  | 2.30 | 67 | 120 | 140 | 160 | 200 |  | 2.30 | 150 |
|  | 3.06 | 83 | — | 180 | 210 | 240 |  | 3.06 | 210 |
| $k_f/10^4\ dm^3\ mol^{-1}\ s^{-1}$ |  | 2.8 | 4.7 | 5.4 | 6.1 | 7.7 | $k_f/10^4\ dm^3\ mol^{-1}\ s^{-1}$ |  | 6.1 |
| $k_d/s^{-1}$ [e)] |  | 3.0 | 15 | 19 | 22 | 23 | $k_d/s^{-1}$ [e)] |  | 20 |
|  | at pH | 3.83 | 4.45 | 4.72 | 5.03 |  |  |  | at pH 4.7 |
| PAN[c)] | 0.38 | 1.7 | 1.7 | 2.3 | 2.2 |  | TAN[d)] | 0.38 | 4.0 |
|  | 0.77 | 3.4 | 3.7 | 4.5 | 4.3 |  |  | 0.77 | 6.4 |
|  | 1.53 | 6.8 | 6.6 | 8.3 | 9.9 |  |  | 1.53 | 12 |
|  | 2.30 | 9.9 | 9.8 | 11 | 12 |  |  | 2.30 | 14 |
|  | 3.06 | 12 | 14 | 14 | 15 |  |  | 3.06 | 19 |
| $k_f/10^3\ dm^3\ mol^{-1}\ s^{-1}$ |  | 4.1 | 4.4 | 4.5 | 4.8 |  | $k_f/10^3\ dm^3\ mol^{-1}\ s^{-1}$ |  | 5.6 |
| $k_d/s^{-1}$ [e)] |  | 0.3 | 0.2 | 0.5 | 0.5 |  | $k_d/s^{-1}$ [e)] |  | 2 |

a) Experimental error ± 15%. Value of pH kept within ±0.05. Concentration of the ligands in the range (2—4) × $10^{-5}$ mol dm$^{-3}$. b) Measured in water. c) Measured in 5% (v/v) dioxane–water. d) Measured in 10% (v/v) dioxane–water. e) Ref. 20.



Scheme 3. Overall reaction mechanism for the formation of $[Co^{III}(pan)_2]$.

Forward and backward rate constants, $k_f$ and $k_d$, were evaluated from the slope and the intercept of the linear plot of $k_{obsd}$ against [Co] (Table 1). Under the experimental conditions the mechanism for the step of formation of 1 : 1 cobalt(II)–PAR complex was postulated as follows, the hydrolysis of $Co^{2+}$ being neglected.[18)]

$$\begin{tikzcd}
Co^{2+} + LHH^* \arrow[r, shift left, "k_1"] \arrow[d, shift right, "K_a"'] & CoLH^{*+} + H^+ \arrow[l, shift left, "k_{-1}"] \arrow[d, shift right, "K_G"'] \\
Co^{2+} + LH^- + H^+ \arrow[r, shift left, "k_2"] \arrow[u, shift right] & CoL + 2H^+ \arrow[l, shift left, "k_{-2}"] \arrow[u, shift right]
\end{tikzcd}$$

According to this mechanism, the overall formation rate constant $k_f$ is expressed by

$$k_f = \frac{k_1[H] + k_2K_a}{[H] + K_a} \tag{2}$$

or

$$k_f(1 + K_a[H]^{-1}) = k_1 + k_2K_a[H]^{-1}, \tag{3}$$

where $K_a$ denotes the acid-dissociation constant of *para*-hydroxyl proton of PAR. The plot of $k_f(1+K_a[H]^{-1})$ against $[H]^{-1}$ gives a straight line. The rate constants $k_1$ and $k_2$ were determined from the intercept and the slope to be $4.8 \times 10^4$ and $9.8 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively, using the value $pK_a = 5.6$.[7)]

*Cobalt(II)–PAN:* The rate of formation of the cobalt(II)–PAN complex was measured with 5% (v/v) dioxane–water solutions at pH 3—5 with 10—100 fold excess of $Co^{2+}$ ion over the ligand. For the calculation of rate constants, the stopped-flow signal at 540 nm, the absorption maximum of the 1 : 2 complex, was used. The pseudo-first-order rate constant, $k_{obsd}$, at constant pH showed first-order dependence on [Co], as shown by Eq. 1 (see Table 1). The $k_f$ values obtained from the linear plot show a slight dependence of [H]. The pH-dependence of $k_{obsd}$ is interpreted by the following reaction scheme.

$$\begin{tikzcd}
Co^{2+} + LH_2^+ \arrow[r, shift left, "k_1"] \arrow[d, shift right, "K_a'"'] & Co^{II}L^+ + 2H^+, \arrow[l, shift left, "k_{-1}"] \arrow[dl, shift left, "k_{-2}"] \\
Co^{2+} + LH + H^+ \arrow[u, shift right] \arrow[ur, shift left, "k_2"] &
\end{tikzcd}$$

where $LH_2^+$ denotes a unipositive species of PAN protonated on the pyridyl nitrogen having $K_a' = 10^{-2.9}$.[19)] According to this mechanism the overall formation rate constant $k_f$ is expressed by

$$k_f = \frac{k_1[H] + k_2K_a'}{[H] + K_a'} \tag{4}$$

or

$$k_f(1 + K_a'[H]^{-1}) = k_1 + k_2K_a'[H]^{-1}. \tag{5}$$

The plot of $k_f(1+K_a'[H]^{-1})$ against $[H]^{-1}$ gives a straight line. The rate constants $k_1$ and $k_2$ were determined from the intercept and the slope to be $< 10^3$ and $4.6 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively.

The rate constants $k_f$ and $k_d$ were also evaluated for the TAR and the TAN complex. The data obtained for the cobalt(II)–TAR and –TAN systems would be explained by the mechanisms for the PAR and the PAN complex, respectively.

The rate constants are summarized in Tables 1 and 2. It is noticeable in Table 2 that the protonated cationic species of PAN is inert for the complex formation of $Co^{2+}$ as was found in the reaction of $Ni^{2+}$ and PAR,[21)] suggesting that the first coordinating group in PAR and PAN is the pyridyl group in the ligands.

Wilkins reported the kinetic data on the reactions of a neutral ligand 4-(2-pyridylazo)-*N*,*N*-dimethylaniline

Table 2. Rate constants for the formation of cobalt(II) complexes at 25 °C and $I=0.1$ ($NaClO_4$)

| Ligand | | Rate constant | |
|---|---|---|---|
| PAR | $LH_2$ | $k_1/dm^3\ mol^{-1}\ s^{-1}$ | $4.8\times10^4$ |
| | $LH^-$ | $k_2/dm^3\ mol^{-1}\ s^{-1}$ | $9.8\times10^4$ |
| PAN | $LH_2^+$ | $k_1/dm^3\ mol^{-1}\ s^{-1}$ | $<10^3$ |
| | LH | $k_2/dm^3\ mol^{-1}\ s^{-1}$ | $4.6\times10^3$ |
| PAD[a)] | | $k_f/dm^3\ mol^{-1}\ s^{-1}$ | $4.0\times10^4$ |
| $H_2O$[b)] | | $k_{H_2O}/s^{-1}$ | $1.1\times10^6$ |

a) Ref. 22. b) Ref. 27.

(PAD) with $Co^{2+}$ or $Ni^{2+}$ ion.[22] PAD is a bidentate ligand having a structure similar to that of PAR except for the absence of intramolecular hydrogen-bond. In his paper, the values of the formation constant of the outer-sphere complex for the neutral ligand species, $K_{OS}$,[23] and the distance of closest approach of the reactant molecules, $a$, are estimated to be 0.1 $dm^3\ mol^{-1}$ and 5 Å, respectively. Since the rate constants reported for the reactions of $Co^{2+}$ and PAD are in the same order of magnitude as the rate constants for the reactions of $Co^{2+}$ and the neutral species of PAR, $LH_2$ (see Table 2), it would be reasonable to assume that the reaction of PAR and $Co^{2+}$ also proceeds by the same mechanism as in the case of PAD and that the internal rotation of the resorcinol moiety around the C–N axis in PAR preceded by the rupture of the stable intramolecular hydrogen-bond does not eventually lower the overall rate of complex formation.

However, in the reaction of $Co^{2+}$ and PAN the formation rate constant is smaller by one order of magnitude than that of the corresponding reaction of PAR. This difference observed in similar ligands might be explained by the following: (a) the difference in values of $K_{OS}$[23] for the two systems, (b) the effect of small amounts of dioxane added in the case of PAN on the rate constants, (c) retardation of complex formation by the relative slowness of the internal rotation of the bulky naphthol moiety in PAN for the formation of the terdentate complex,[1] and (d) steric hindrance caused by the shape of a bulky ligand PAN on the first coordination site in the ligand.

As regards (a), if the relatively small rate constants for the $Co^{2+}$–PAN system as compared with the case of $Co^{2+}$–PAR were attributed to the lower values of $K_{OS}$, the reaction distance $a$ for the complex formation of PAN would be evaluated to be 2—3 Å.[25] This is about a half of the value of $a$ estimated by Funahashi and Tanaka for the $Ni^{2+}$–PAR system,[25] and would be too small as the reaction distance for the $Co^{2+}$–PAN system. The second possibility (b) is also not essential, since the rate constant of complex formation of a similar ligand TAR is in the same order of magnitude even in dioxane–water media as that of PAR observed in aqueous media. Therefore, it would be reasonable to infer that the intervening step of internal rotation of the bulky naphthol moiety around the C–N axis (c) and a steric hindrance caused by the particular shape of the bulky PAN molecule on the site of the first coordination at the pyridyl nitrogen atom (d) would essentially be responsible for the retardation of the overall reaction in PAN. The smaller rate constants observed for the reaction of $Ni^{2+}$ and PAN as compared with those of $Ni^{2+}$ and PAR would also be attributed to the difference in character of these ligands.[26]

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