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Bivalent Cobalt Complexes with 1-(2-Pyridylazo)-2-naphthol and Analogous Ligands

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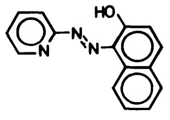
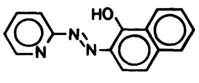
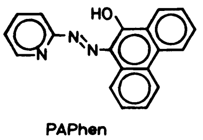
Bivalent cobalt complexes with the title ligands were synthesized, isolated, and characterized by absorption spectra and magnetic moments. It has been suggested that the cobalt(II) complexes have more flexible structures than the corresponding cobalt(III) complexes. The cobalt(II) complexes were found to be oxidized to the cobalt(III) complexes in DMSO in the presence of copper(II) ions. Cyclic voltammetry elucidated the reversible Co^{II}/Co^{III} couples of the cobalt complexes in acetonitrile. The values of $E_{1/2}$ for the Co^{II}/Co^{III} couples were found to depend on the coordinating ligands. The relation between $E_{1/2}$ and pK_a of the *ortho*-hydroxyl group in the ligands was discussed.

Some *o*-hydroxy azo compounds in the following structural formula[1)] are well known to behave as terdentate ligands,[2,3)] which form colored chelates with many metal ions.[4)] They have been used as sensitive analytical reagents for the spectrophotometric determination of cobalt,[5,6)] because they form very stable cobalt(III) complexes.[7)]


β-PAN


α-PAN


PAPhen

In the reactions between cobalt(II) ion and the title ligands in aqueous media, the cobalt(II) complexes formed are immediately oxidized by dissolved oxygen to the corresponding cobalt(III) complexes.[7)] Therefore it is difficult to isolate the cobalt(II) complexes and to investigate their characters, whereas the formation[7)] and the structures[8,9)] of the cobalt(III) complexes have been well characterized. In addition, some information about redox behavior of such cobalt complexes has been obtained: (1) The cobalt(II) complexes are easily oxidized in aqueous solution, but they are considerably stable in organic solvents,[5,10)] and (2) the cobalt(III) complex with β-PAN are reduced to the cobalt(II) complex by hyperoxide in dimethyl sulfoxide, DMSO,[11)] though details of the electrochemical data about the Co^{II}/Co^{III} couples, which enable us to predict what complex prefers the cobalt(III) state, have not been reported so far.

In the present paper,[10)] we report the synthesis, isolation, and characterization of the cobalt(II) complexes with the title ligands, as well as the electrochemical study of their cobalt complexes in acetonitrile solution by cyclic voltammetry.

Experimental

Measurements. Absorption spectra were recorded on Hitachi EPS-3T and 340 spectrophotometers. Magnetic susceptibilities were measured by Gouy method. The pH was measured with a TOA HM-20E pH-meter equipped with a composite electrode, type GST-155C.

Cyclic voltammograms were recorded at 25±0.3 °C with a Yanagimoto Polarographic Analyzer P-1100. The three-electrode system, consisting of a glassy carbon indicator electrode, GCE, (surface area: 7.1×10^{-2} cm^2), a platinum-wire auxiliary electrode, and a reference electrode, was employed. The reference electrode systems were as follows: (A) sample || salt bridge with saturated Et_4NClO_4 || saturated KCl || agar bridge of saturated KCl || SCE, and (B) sample || CH_3CN salt bridge containing 0.1 mol dm^{-3} Et_4NClO_4 || Ag–Ag$^+$(0.01 mol dm^{-3} $AgNO_3$) in acetonitrile. G4-sintered glasses were set between bridges and samples or reference electrodes. The difference in potentials observed for the above two systems, E(Ag/Ag$^+$)$-E$(SCE), was always constant, −0.315 V, in all our measurements.[12)] The potentials measured in (A) are listed in the text and tables. A glassy carbon electrode was polished up with diamond powder (Royal Diamond Compound 1-W-47) until the surface became a mirror before each run, so that sufficient reproducibilities could be obtained. Et_4NClO_4 was used as a supporting electrolyte.

Materials. Commercial grade acetonitrile dried over CaH_2 was twice distilled under nitrogen atmosphere. The purified solvent was stored under nitrogen atmosphere.

The cobalt complexes, [Co^{III}(β-pan)$_2$]Cl[11)] and [Co^{III}(β-pan)(dien)](ClO$_4$)$_2$,[9)] were reported previously.

The bivalent cobalt complex, [Co^{II}(β-tan)$_2$] was prepared from the stoichiometric amount of Co(ClO$_4$)$_2$·6H$_2$O and β-TAN in a similar way to [Co^{III}(β-pan)$_2$]Cl, and easily isolated. The composition (metal to ligand ratio=1 : 2) and the oxidation state of the cobalt were confirmed by UV spectra[15)] and elemental analysis. On the other hand, the bivalent cobalt complexes with β-PAN, α-PAN, and PAPhen could not be obtained by mixing the components. The syntheses of the cobalt(II) complexes were as follows:

1) Free acid form of β-PAN (1.0 g) and ascorbic acid (1.0 g) were completely dissolved in ethanol (500 cm^3) by heating under nitrogen atmosphere. To the solution, CoCl$_2$ (0.26 g) dissolved in a small amount of ethanol was added. The mixture was stirred and kept at 50 °C for 1.5 h. The green product formed was filtered, washed with ethanol, and dried *in vacuo* (yield 1.25 g). The green complex of a definite composition was always obtained

under the above conditions. Found: C, 54.51; H, 3.74; N, 10.86; Cl, 6.62%. Calcd for $C_{30}H_{20}N_6O_2Co \cdot C_6H_8O_6 \cdot (3/2)HCl$: C, 54.99; H, 3.78; N, 10.69, Cl, 6.76%. An analogous product was obtained for *α*-PAN. IR spectrum of the green complex shows the bands corresponding to ascorbic acid at around 1753 and 1650—1680 cm^{-1}. The magnetic moment μ_{eff} at 300 K is 1.94 BM. ESR spectra show no signals of organic radicals. Above data suggest that the green complex is a bivalent cobalt complex, though the state of ascorbic acid in the green complex and the structure of the green complex are not clear. A similar product was obtained for PAPhen by the analogous method. Found: C, 58.78; H, 3.87; N, 9.77%. Calcd for $C_{38}H_{24}N_6O_2Co \cdot C_6H_8O_6 \cdot 2HCl$: C, 57.29; H, 3.89; N, 9.54%.

2) To an ethanol solution (500 cm^3) of the green complex (1.0 g) with *β*-PAN, sodium metal (0.1 g) dissolved in ethanol (5 cm^3) was added. The solution turned red immediately. The red complex precipitated by evaporation was filtered, washed with ethanol thoroughly, recrystallized from ethanol–chloroform (1 : 1 v/v) several times, and dried *in vacuo* (yield *ca.* 60%). The red complex is more soluble in nonpolar solvents such as chloroform than in ethanol and insoluble in water, indicating itself acting as a noncharged complex. ESR spectra at 77 K showed the signal of cobalt(II) ion for the red complex, whereas no signal appeared for [Co^{III}(*β*-pan)$_2$]Cl. The red complexes, [Co^{II}(*α*-pan)$_2$] and [Co^{II}(paphen)$_2$], were also synthesized by the analogous method. [Co^{II}(*β*-pan)$_2$]: Color: deep reddish purple. Crystal form: too fine to be identified. Found: C, 63.52; H, 3.65; N, 14.39; Cl, 1.27%. Calcd for $C_{30}H_{20}N_6O_2Co \cdot (1/4)NaCl$: C, 63.21; H, 3.54; N, 14.74; Cl, 1.55%. [Co^{II}(*α*-pan)$_2$]: Color: dark purple. Tabular crystals. Found: C, 63.17; H, 3.65; N, 14.83%. Calcd for $C_{30}H_{20}N_6O_2Co \cdot (1/4)NaCl$: C, 63.21; H, 3.54; N, 14.74%. [Co^{II}(paphen)$_2$]: Color: deep red purple. Tabular crystals. Found: C, 68.04; H, 3.59; N, 12.87%. Calcd for $C_{38}H_{24}N_6O_2Co$: C, 69.62; H, 3.69; N, 12.82%.

Results and Discussion

Characterization of the Red Cobalt(II) Complexes. The data of absorption spectra in $CHCl_3$ and magnetic moments (solid) at room temperature for the red complexes are listed in Table 1. The absorption spectrum of [Co^{II}(*β*-pan)$_2$] is the same as that of the cobalt(II) complex observed in the rapid-scan spectral study of the reaction between Co^{2+} ion and *β*-PAN[7] and in the reduction product of [Co^{III}(*β*-pan)$_2$]Cl by O_2^- ion.[11] The data of elemental analysis and the absence of absorption bands assignable to cobalt(III) in the spectra measured in $CHCl_3$ indicate that the complexes do not contain cobalt(III) complexes. Though the absorption spectra of these complexes did not change in an aprotic solvent, DMSO, even bubbled with O_2 for *ca.* 30 min, the absorption spectra changed immediately to those corresponding to the cobalt(III) complexes, when a small amount of water (0.5 cm^3 H_2O to 3.5 cm^3 DMSO) was added.

Table 1. Data of absorption spectra and magnetic moments

Complex	λ_{max}/nm	$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}	μ_{eff}/BM at 297 K
[Co^{II}(*β*-pan)$_2$]	522	2.83	2.31
[Co^{II}(*α*-pan)$_2$]	322 545	2.80 3.44	2.16
[Co^{II}(paphen)$_2$]	310 520	3.38 3.74	2.52

Magnetic moments of the red complexes also show that these complexes are not cobalt(III) complexes but cobalt(II) complexes with more than one spin. It is well known that μ_{eff} of a cobalt(II) complex is variable depending on its spin-state, coordination number and geometry.[16] For example, the μ_{eff} values are expected to be 5.0—5.8, 1.80—1.85, and 2.2—2.9 BM, for octahedral high-spin, octahedral low-spin, and four-coordinated low-spin cobalt(II) complexes, respectively.[16] The μ_{eff} values listed in Table 1 are smaller than those for octahedral high-spin complexes and larger than those for octahedral low-spin complexes. The reason for this anomalous magnetic moment is interpreted as follows: 1) A mixture of high-spin cobalt(II) complexes and diamagnetic cobalt(III) complexes, 2) four-coordinated low-spin complexes, or 3) spin-state equilibrium between ^2E_g and $^4T_{1g}$ states. The possibility for 1) is excluded from results of absorption spectra and elemental analyses as mentioned above. From the results of temperature-dependence of the magnetic moment for $Co^{II}(paphen)_2 \cdot 4EtOH \cdot (1/3)CHCl_3$ (pink complex), Pandeya *et al.* took the spin-state equilibrium between ^2E_g and $^4T_{1g}$ into account.[17] Though the composition of their complex is different from that synthesized in the present study, the similarity of our data to theirs suggests that the case 3) is more probable for the other red complexes, [Co^{II}(*β*-pan)$_2$] and [Co^{II}(*α*-pan)$_2$]. Therefore, the structures of the cobalt(II) complexes are expected to be considerably flexible, whereas cobalt(III) complexes have rigid structures.[9]

These cobalt(II) complexes were found to react with copper(II) ions in DMSO. The red solutions of the cobalt(II) complexes in DMSO changed to green by the addition of copper(II) perchlorate; the same changes were observed for other copper(II) salts as well. The spectra of the final products corresponded to those for the cobalt(III) complexes. The effect of perchlorate ions was neglected, since no changes in the spectra of the cobalt(II) complexes were observed by the addition of perchlorates of other metals such as zinc(II). The oxidation by copper(II) ions should form copper(I) ions. The difference between the spectra of the final products with and without addition of 2,2′-biquinoline gave the spectrum of copper(I)-2,2′-biquinoline complex, indicating the presence of copper(I) ions in the solutions of final products. These observations reveal the oxidation of the cobalt(II) complexes to the corresponding cobalt(III) complexes by copper(II) ions in DMSO.

Cyclic Voltammetry on the Cobalt Complexes. Cyclic voltammetry was carried out between −0.5 and +0.7 V *vs.* SCE in the scan-speed range from 10 to 500 m V s^{-1}. $[\mathrm{Co^{III}}(\beta\text{-pan})_2]\mathrm{Cl}$ showed one peak in both cathodic and anodic runs in this potential range. The other cobalt complexes with analogous ligands also showed similar cyclic voltammograms in the same potential range. Figure 1 shows the typical cyclic voltammogram of $[\mathrm{Co^{III}}(\beta\text{-pan})_2]\mathrm{Cl}$ in acetonitrile.[18] The cyclic voltammograms observed on $[\mathrm{Co^{II}}(\beta\text{-pan})_2]$ and $[\mathrm{Co^{III}}(\beta\text{-pan})_2]\mathrm{ClO_4}$ were essentially the same to that of $[\mathrm{Co^{III}}(\beta\text{-pan})_2]\mathrm{Cl}$. The data for $[\mathrm{Co^{III}}(\beta\text{-pan})_2]^+$ are listed in Table 2. It was found that (1) the cathodic and anodic peak currents of the observed wave, $(i_p)_c$ and $(i_p)_a$, measured at various sweep rates, v, were propotional to $v^{1/2}$, (2) the difference between cathodic ($(E_p)_c$) and anodic ($(E_p)_a$) peak potentials, $\Delta E=(E_p)_c-(E_p)_a$ was always *ca.* 60 mV, (3) the values of $(E_p)_c$ and $(E_p)_a$ were independent of v, (4) $(i_p)_a/(i_p)_c=1$ for all v, and (5) the peak potentials were independent of the kinds of indicator electrodes: A very similar wave was obtained when a GCE was changed to a Pt-electrode. On the basis of these results, the wave observed can be regarded as a simple one-electron transfer reversible system, $\mathrm{A+e} \rightleftharpoons \mathrm{B}$.[19]

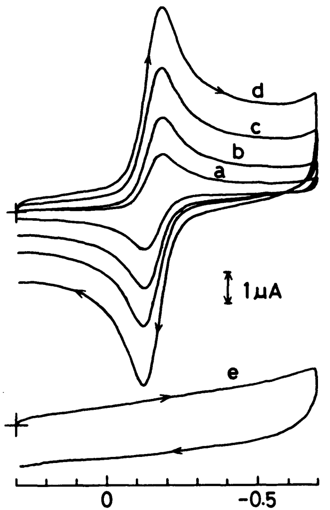


Fig. 1. Cyclic voltamograms of 2.0×10^{-4} mol dm^{-3} $[\mathrm{Co^{III}}(\beta\text{-pan})_2]^+$ in acetonitrile solution cotaining 0.1 mol dm^{-3} $\mathrm{Et_4NClO_4}$ at 25 °C. Sweep rate: **a**, 20; **b**, 50; **c**, 100; **d**, 200 mV s^{-1}. **e** is blank at sweep rate= 100 mV s^{-1}.

In order to elucidate the products of one-electron reduction of $[\mathrm{Co^{III}}(\beta\text{-pan})_2]^+$, the constant potential electrolysis of the cobalt(III) complex at −1.0 V *vs.* $\mathrm{Ag/Ag^+}$ (−0.68 V *vs.* SCE) was performed under the same conditions as in the measurement of the cyclic voltammogram. The absorption spectrum of the solution was observed during the electrolysis. As the absorption at 600 nm due to the cobalt(III) complex decreased gradually, a new band at about 520 nm due to the cobalt(II) complex appeared. Finally, the absorption spectrum almost coincided with that of $[\mathrm{Co^{II}}(\beta\text{-pan})_2]$. Therefore, the above mentioned one-electron reversible process can be assigned

Table 2. Data of cyclic voltammetry on $[\mathrm{Co^{III}}(\beta\text{-pan})_2]^+$ in acetonitrile[a)]

v/mV s^{-1}	$(i_p)_c/\mu A$	$(i_p)_a/\mu A$	$(i_p)_c/(i_p)_a$	$(E_p)_c/V^{b)}$	$(E_p)_a/V^{b)}$	ΔE_p/mV
10	1.3_2	1.2_3	1.0_7	-0.18_0	-0.12_0	~60
20	1.8_0	1.7_0	1.0_6			
50	2.8_6	2.7_5	1.0_4			
100	4.0_7	3.7_5	1.0_9			
200	5.7_1	5.2_8	1.0_8			
500	9.0_4	8.1_0	1.1_2			

a) $[\mathrm{Co^{III}}(\beta\text{-pan})_2]^+$: 2.0×10^{-4} mol dm^{-3}. $I=0.1$ ($\mathrm{Et_4NClO_4}$). $T=25$ °C. b) *vs.* SCE.

Table 3. Data of the waves assigned to the $\mathrm{Co^{II}/Co^{III}}$ couple[a)]

Complex	$(E_p)_c$/V	$(E_p)_a$/V	ΔE_p/V	$E_{1/2}/V^{b)}$	$pK_a{}^{c)}$
$[\mathrm{Co^{III}}(\beta\text{-pan})_2]^{+\,d)}$	-0.18_0	-0.12_0	0.06_0	-0.15_0	12.7
$[\mathrm{Co^{II}}(\beta\text{-pan})_2]^{e)}$	-0.18_0	-0.12_0	0.06_0	-0.15_0	
$[\mathrm{Co^{III}}(\beta\text{-pan})(\mathrm{dien})]^{2+\,d)}$	-0.32_6	-0.26_5	0.06_1	-0.29_6	
$[\mathrm{Co^{II}}(\alpha\text{-pan})_2]^{e)}$	-0.07_5	-0.01_0	0.06_5	-0.04_3	10.7
$[\mathrm{Co^{II}}(\mathrm{paphen})_2]^{e)}$	-0.20_0	-0.14_0	0.06_0	-0.17_0	13.5
$[\mathrm{Co^{II}}(\beta\text{-tan})_2]^{e)}$	$+0.02_0$	$+0.08_0$	0.06_0	$+0.05_0$	9.5

a) In acetonitrile. *vs.* SCE. $I=0.1$ ($\mathrm{Et_4NClO_4}$). $T=25$ °C. b) $E_{1/2}=((E_p)_c+(E_p)_a)/2$. c) 50% (v/v) dioxane-water media. $I=0.1$ (KCl). $T=25$ °C. d) The forward scan is to negative direction and the backward to positive. e) The forward scan is to positive direction and the backward to negative.

to the electron transfer, $[Co^{III}(\beta\text{-pan})_2]^+ + e \rightleftharpoons [Co^{II}(\beta\text{-pan})_2]$. The waves observed for the other cobalt complexes were also assignable to that for the Co^{II}/Co^{III} couples.

The data for the cobalt complexes with β-PAN and analogous ligands in acetonitrile are listed in Table 3 with the values of pK_a for the *ortho*-hydroxyl groups in the ligands. It is obvious that $E_{1/2}$ of the Co^{II}/Co^{III} couple is dependent on the coordinating ligands. Some features are as follows: $E_{1/2}$ of the Co^{II}/Co^{III} couple shifts to the more negative side in $[Co^{III}(\beta\text{-pan})(\text{dien})]^{2+}$ which has one β-PAN, than in $[Co^{III}(\beta\text{-pan})_2]^+$. The value of $E_{1/2}$ of $[Co^{II}(\beta\text{-pan})_2]$ is more negative than that of $[Co^{II}(\alpha\text{-pan})_2]$ where α-PAN is different from β-PAN in the position of the azo and *ortho*-hydroxyl groups attached to the naphthol moiety. From the comparison between $[Co^{II}(\beta\text{-pan})_2]$ and $[Co^{II}(\beta\text{-tan})_2]$, in which the ligands have the same moieties, 2-naphthols, $E_{1/2}$ of the complex with thiazolyl group is more positive than that of the complex with pyridyl group. Therefore, $[Co^{II}(\beta\text{-tan})_2]$ is expected to be more stable than $[Co^{II}(\beta\text{-pan})_2]$ against the oxidation by dissolved oxygen in aqueous solution (the half-wave potential for $O_2 \rightarrow O_2^-$, $E_{1/2} = -0.05$ V *vs.* SCE in aqueous neutral solution[20]). Indeed, the observations such as, the easy extraction of $[Co^{II}(\beta\text{-tan})_2]$ into organic phase[15] and the considerably easy isolation of the complex, support the above idea. For the cobalt complexes with these analogous ligands, there is a remarkable feature of the relation between $E_{1/2}$ and pK_a of the ligands. It can be seen that as the pK_a value of the *ortho*-hydroxyl group in the coordinating ligand increases, $E_{1/2}$ shifts to the more negative direction. This suggests that cobalt(III) state is more stabilized as the basicity of the coordinating ligand increases, *i.e.*, as the ligand can coordinate strongly to the cobalt ion.

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1) Ligand abbreviations: α-PAN=2-(2-pyridylazo)-1-naphthol; β-PAN=1-(2-pyridylazo)-2-naphthol: PAPhen=10-(2-pyridylazo)-9-phenanthrol; β-TAN=1-(2-thiazolylazo)-2-naphthol; dien=diethylenetriamine.

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