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Transition-metal Complexes of Pyrrole Pigments. XV. Coordination of Pyridine Bases to the Axial Sites of Cobalt Corroles[†]

Yukito Murakami,* Sunao Yamada, Yoshihisa Matsuda, and Kazunori Sakata**

Department of Organic Synthesis, Faculty of Engineering, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

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Cobalt(III) corroles exist predominantly as polymeric species in a concentration range above 5×10^{-3} M in chloroform at room temperature as confirmed by NMR measurements. The coordination behavior of pyridine bases at the axial sites of cobalt(III) corroles, in a concentration range where they are present exclusively in the monomeric species, has been investigated by measuring electronic spectra in acetone at 25.0±0.1 °C. Penta- and hexa-coordination processes were found to take place, and the stepwise formation constants were interpreted by means of the equations $\log K_i = a\cdot pK_a + b$ and $\log K_i/K_i{}^0 = \rho\sigma$. When the cobalt corrole was reduced at the nuclear cobalt from trivalent to bivalent state, only one pyridine molecule was coordinated at its axial sites, hexa-coordination being no longer possible as confirmed by ESR measurements. The axial ligation behavior of cobalt corroles is quite analogous in nature to that of cobalt corrinoid.

Axial-ligation equilibria for the corrinoid complexes have been studied rather extensively[1)] in order to clarify the metabolic functions of vitamin B_{12} systems. It is important, however, to characterize the corrinoid skeleton by referring to the axial ligation behavior of the cobalt complexes of analogous macrocyclic tetrapyrroles involving different numbers of π-electrons in their skeletons, in view of the increasing interest in the chemistry of vitamin B_{12}. The interaction of various organic bases with 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatocobalt(II) perchlorate (Co(II)–TDHC) has been investigated.[2)] The cobalt(II) complex of 1,19-disubstituted tetradehydrocorrin was found to take up one amine base in its axial position, but unable to yield the corresponding hexa-coordinated complex in which both axial positions were occupied by amines.

We have shown in this work that the axial coordination sites of cobalt(III) corroles are entirely occupied stepwise by amine bases. The equatorial ligand effect, exerted by the corrole skeleton on the axial coordination behavior, is effectively discussed in the light of vitamin B_{12} chemistry.

Experimental

Electronic spectra were taken on a Union Giken SM-401 high sensitive spectrophotometer. Acetone as a solvent for spectroscopic measurements was prepared by fractional distillation after being refluxed with potassium carbonate and kept over a molecular sieve (3A, 1/16; Ishizu Pharmaceutical Co., Ltd.). A Bruker WH-90 FT spectrometer was used to obtain NMR spectra in chloroform-*d* (>99.5%; E, Merck, Darmstadt) at room temperature. Chemical shifts are given in ppm from internal TMS and calibrated with a chloroform signal as the secondary external reference. ESR spectra were recorded on a JEOL JES-ME-3 X-band spectrometer equipped with a 100 kHz field modulation unit. The anionic cobalt(II) complex was prepared by reduction of the corresponding cobalt(III) corrole with sodium tetrahydroborate in *N,N*-dimethylformamide, and measured in the same solvent at 77 K, concentrations being maintained in the 10^{-2}—10^{-3} M range. The manganese ion diffused thermally into magnesium oxide was used to obtain the standard reference signals for measurements.

Commercial liquid amines (pyridine, 2-methyl-, 3-methyl-, 4-methyl-, and 3-acetylpyridine) were refluxed with potassium hydroxide and fractionally distilled. Commercial 4-cyanopyridine was recrystallized from aqueous ethanol. 4-Aminopyridine was prepared by ammonolysis of (4-pyridinio)pyridinium dichloride[3)] and recrystallized twice from benzene. 3-Hydroxypyridine was obtained from ammonium pyridine-3-sulfonate by treatment with potassium hydroxide at elevated temperature,[4)] and purified by sublimation *in vacuo.*

2-Acetoxymethyl-3,4-diethyl-5-ethoxycarbonylpyrrole. Into a solution of 2-methyl-3,4-diethyl-5-ethoxycarbonylpyrrole[5)–7)] (2.5 g) in dry acetic acid (60 ml) was added lead tetraacetate (5.3 g) in small portions at 15-min intervals with stirring at room temperature. The reaction mixture was further stirred at room temperature for 3 h, evaporated *in vacuo*, and the residue was poured into cold water (120 ml). The resulting orange precipitates were recovered by filtration and washed thoroughly with water. Recrystallization from acetone-water gave colorless plates; yield 2.5 g (78%), mp 88.2—89.0 °C. IR (Nujol mull): 3314 (N–H str.), 1741 (acetoxy C=O str.), and 1668 $\mathrm{cm^{-1}}$ (ester C=O str.). NMR (CCl_4, TMS): δ 1.19 (9H, overlapping t J=7.0 Hz, 3- and 4-$CH_2\underline{CH_3}$, and 5-$CO_2CH_2\underline{CH_3}$), 1.99 (3H, s, 2-$CH_2OCO\underline{CH_3}$), 2.54 (4H, overlapping q J=7.0 Hz, 3- and 4-$\underline{CH_2}CH_3$), 4.25 (2H, q J=7.0 Hz, 5-$CO_2\underline{CH_2}CH_3$), 4.96 (2H, s, 2-$\underline{CH_2}OCOCH_3$), and 9.80 (1H, broad s, NH).

3,3′,4,4′-Tetraethyl-5,5′-diethoxycarbonyldipyrromethane. A solution of 2-acetoxymethyl-3,4-diethyl-5-ethoxycarbonylpyrrole (3.5 g) in ethanol (70 ml) containing hydrochloric acid (37%, 2.6 ml) was refluxed for 5 h with stirring. The solution was concentrated gradually *in vacuo* until a small amount of crystalline precipitates started to appear. After being allowed to stand overnight in a refrigerator, the crystalline solid was recovered by filtration to give colorless prisms; yield 2.5 g (94%), mp 93.0—96.1 °C. IR (Nujol mull): 3320 (N–H str.), 1696 (free ester C=O str.), and 1657 $\mathrm{cm^{-1}}$ (bound ester C=O str.). NMR (CCl_4, TMS): δ 1.09 (18H, overlapping t J=7.0 Hz, 3,3′-$CH_2\underline{CH_3}$, 4,4′-$CH_2\underline{CH_3}$, and 5,5′-$CO_2CH_2\underline{CH_3}$), 2.51 (8H, overlapping q J=7.0 Hz, 3,3′-$\underline{CH_2}CH_3$ and 4,4′-$\underline{CH_2}CH_3$), 3.87 (2H, s, bridging CH_2), 4.16 (4H, q J=7.0 Hz, 5,5′-$CO_2\underline{CH_2}CH_3$), and 10.04 (2H, broad s, NH).

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* To whom correspondence should be addressed.

** Present address: Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804.

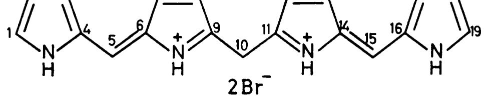
3,3′,4,4′-Tetraethyldipyrromethane-5,5′-dicarboxylic Acid. A mixture of 3,3′,4,4′-tetraethyl-5,5′-diethoxycarbonyldipyrromethane (2.0 g) and ethanol (35 ml) was refluxed with stirring for a short period. After addition of sodium hydroxide (1.0 g) dissolved in water (10 ml), the reaction mixture was refluxed for 2 h with stirring. A large portion of ethanol was removed *in vacuo* from the mixture, and water (50 ml) was then added to it. Acetic acid was added to adjust the pH of the solution to 4—5. White precipitates were recovered by filtration, washed thoroughly with water, and dried *in vacuo* to give white powder; yield 1.8 g (100%), mp 135—145 °C (dec). On being left to stand the color of the product gradually turned violet particularly when slightly wet. IR (Nujol mull): 3300 (N–H str.), 3210 (O–H str.), and 1661 cm^{-1} (C=O str.).

*1,19-Dideoxy-2,3,7,8,12,13,17,18-octaethylbiladiene-ac Dihydrobromide (**1**).* A mixture of 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid (2.7 g), 2-formyl-3,4-diethylpyrrole[7,8] (2.3 g), and ethanol (80 ml) was heated at 60 °C with occasional shaking. Vigorous reaction took place upon addition of 47% aqueous hydrobromic acid (16 ml) at one time to the hot reaction mixture. The mixture was refluxed for 3 min and allowed to stand overnight in a refrigerator. The glittering red crystals were recovered by filtration, washed with ethyl ether, and recrystallized from chloroform–methanol to give reddish brown prisms; yield 4.0 g (79%). $\lambda_{\max}$ ($CHCl_3$): 374, 433, 460, and 526 nm. IR (KBr disk): 1605 cm^{-1} (biladiene skeletal str.). NMR (CF_3CO_2H, TMS): δ 1.26 (24H, overlapping t $J=7.0$ Hz, $CH_2\underline{CH_3}$), 2.74 (16H, overlapping q $J=7.0$ Hz, $\underline{CH_2}CH_3$), 4.60 (2H, s, bridging $-CH_2-$), 7.55 (2H, s, bridging $-CH=$), and 7.77 (2H, d $J=3.5$ Hz, 1,19-H). Found: C, 61.13; H, 7.28; N, 7.90%. Calcd for $C_{35}H_{50}Br_2N_4$: C, 61.21; H, 7.35; N, 8.16%.

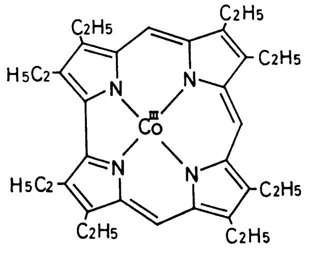
*1,19-Dideoxy-2,3,17,18-tetramethyl-7,8,12,13-tetraethylbiladiene-ac Dihydrobromide (**2**).* This was prepared from 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid (1.7 g) and 2-formyl-3,4-dimethylpyrrole[9] (1.05 g) in methanol (50 ml) and aqueous hydrobromic acid (47%, 9 ml) in the same manner as described above; reddish brown prisms, yield 2.4 g (73%). IR (KBr disk): 1608 cm^{-1} (biladiene skeletal str.).

*2,3,7,8,12,13,17,18-Octaethylcorrolatocobalt(III) (**3**).* To a mixture of biladiene-ac dihydrobromide **1** (200 mg) and *N,N*-dimethylformamide (25 ml) was added cobalt(II) acetate tetrahydrate (160 mg) dissolved in *N,N*-dimethylformamide (5 ml) with stirring. The reaction mixture was heated at 50 °C for 30 min with stirring and subsequently allowed to cool at 0 °C for 1 h. Recovered crystalline solid was recrystallized from chloroform–methanol as dark brown prisms; yield 90 mg (53%). The osmometric determination of molecular weight in carbon tetrachloride: 1125—1300 in the concentration range 2—4 × 10^{-3} M; calcd mol wt for $C_{35}H_{43}CoN_4$ (monomer) 578.68. This result indicates the existence of monomer–polymer equilibrium in concentrated solutions. Found: C, 72.67; H, 7.46; N, 9.69%. Calcd for $C_{35}H_{43}CoN_4$: C, 72.63; H, 7.50; N, 9.68%.

*Pyridine(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)cobalt(III) (**4**).* A mixture of cobalt(II) acetate tetrahydrate (800 mg) and pyridine (20 ml) was heated on an oil bath until it turned into a clear solution. Biladiene-ac dihydrobromide **2** (1.0 g) was added to the reaction mixture, which was subsequently heated at 70—75 °C for 20 min with stirring. After addition of hot methanol (70 ml), the mixture was allowed to stand in a refrigerator for 2 h. The crystalline solid was recovered by filtration, and recrystallized from chloroform-methanol-pyridine (3 : 1 : 1) to give glittering purple prisms; yield 720 mg (76%). IR (Nujol mull): 1602 cm^{-1} (pyridine skeletal str.). Found: C, 72.07; H, 6.56; N, 12.48%. Calcd for $C_{36}H_{40}CoN_5$: C, 71.85; H, 6.71; N, 11.64%.



1: $R_2=R_3=R_7=R_8=R_{12}=R_{13}=R_{17}=R_{18}=C_2H_5$
2: $R_2=R_3=R_{17}=R_{18}=CH_3$; $R_7=R_8=R_{12}=R_{13}=C_2H_5$



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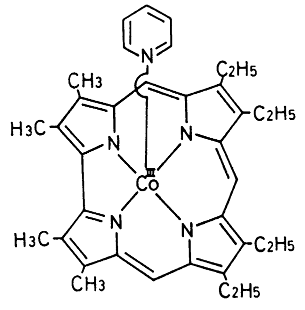

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Results

NMR Behavior of Cobalt(III) Corrole. The NMR spectra of cobalt(III) corrole **3** were measured for the 10^{-2}—10^{-4} M concentration range in chloroform-*d* at room temperature. The intensity of proton signals appearing in the −5—+3 ppm region highly depends on concentration of the cobalt chelate as shown in Fig. 1. Particular attention should be paid to proton signals due to methylenes of the ethyl groups placed at the peripheral positions. The intensity of the meth-

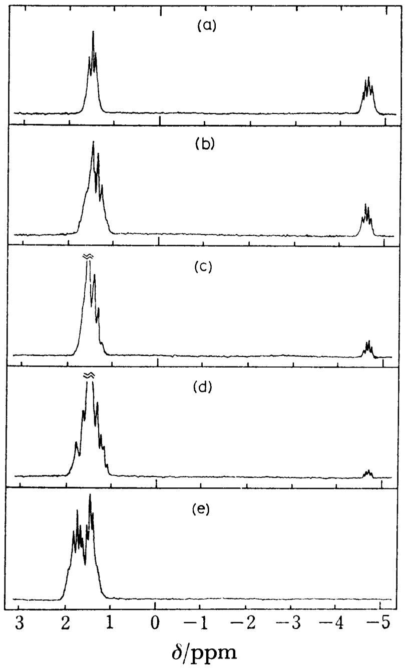


Fig. 1. NMR spectra of cobalt corrole **3** for the −5—+3 ppm range in chloroform-*d* at room temperature at various concentrations: (a), 3.04 × 10^{-2} M; (b), 8.64 × 10^{-3} M; (c), 2.94 × 10^{-3} M; (d), 8.64 × 10^{-4} M; (e), 8.64 × 10^{-3} M (pyridine was added, 1.40 × 10^{-2}M).

ylene-proton signal observed at −4.6 ppm in a relatively high concentration range (Fig. 1 (a)) diminishes with decrease in the concentration of the complex. The intensity decrease is counterbalanced with the intensity increase for signals appearing in the 1.5—2.0 ppm range. The high-field signal (−4.6 ppm) disappeared completely, and the new signals were observed in the 1.5—2.0 ppm range upon addition of a 1.5-fold amount of pyridine to the cobalt corrole in 8.64×10^{-3} M (Fig. 1 (e)). The spectral change indicates that the cobalt corrole which exists in polymeric species (D and P in Scheme 2) in a relatively high concentration range dissociates into the monomer form upon coordination of pyridine at the axial sites.

The NMR behavior of the cobalt corrole is in line with the osmometric data which indicate the presence of monomer–dimer–polymer equilibria in a relatively high concentration range. From these measurements, cobalt(III) corrole **3** can exist predominantly in a monomeric species in a concentration range below 10^{-4} M. Since some minor impurity involved in chloroform-*d* showed a proton signal at 1.5 ppm, we were not able to evaluate the equilibrium constant for dimer formation.

Interaction between Cobalt(III) Corrole and Pyridine Bases. The electronic spectra for cobalt corrole **3** were measured by changing the concentration of pyridine bases in a wider range (0.5—10^4-fold amounts relative to **3**), while the concentration of **3** was maintained constant ($\approx 7\times10^{-6}$ M). The spectral changes upon addition of pyridine are shown in Fig. 2, where isosbestic points are observed at 373, 400, 450, and 520 nm for the lower pyridine concentrations, and at 393, 460, and 532 nm for the higher concentrations (10^{-3}—10^{-1} M), while no distinct isosbestic points are present for the intermediate concentration range (10^{-4}—10^{-3} M). For the concentration range 10^{-1}—1 M, the electronic spectrum remains practically unchanged. This indicates that the axial sites of **3** are entirely occupied by pyridine molecules in this base-concentration range. As the pyridine concentration rises still higher, the spectral curves do not pass the isosbestic points most plausibly due to some solvent effect.

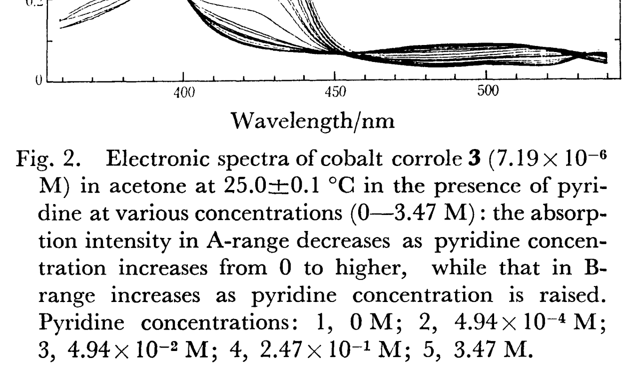


Fig. 2. Electronic spectra of cobalt corrole **3** (7.19×10^{-6} M) in acetone at 25.0±0.1 °C in the presence of pyridine at various concentrations (0—3.47 M): the absorption intensity in A-range decreases as pyridine concentration increases from 0 to higher, while that in B-range increases as pyridine concentration is raised. Pyridine concentrations: 1, 0 M; 2, 4.94×10^{-4} M; 3, 4.94×10^{-2} M; 4, 2.47×10^{-1} M; 5, 3.47 M.

The spectral behavior is in line with the following equilibria.

$$\text{Penta-coordination:}\quad \text{CoL} + \text{B} \rightleftharpoons \text{CoLB}$$

$$K_1 = \frac{[\text{CoLB}]}{[\text{CoL}][\text{B}]} \tag{1}$$

$$\text{Hexa-coordination:}\quad \text{CoLB} + \text{B} \rightleftharpoons \text{CoLB}_2$$

$$K_2 = \frac{[\text{CoLB}_2]}{[\text{CoLB}][\text{B}]} \tag{2}$$

where CoL and B stand for cobalt corrole **3** and a pyridine base, respectively. At relatively low levels of the base concentration where the first set of isosbestic points are observed, the following stoichiometric relations hold.

$$[\text{CoL}]_\text{T} = [\text{CoL}] + [\text{CoLB}] + [\text{CoLB}_2] \tag{3}$$

$$[\text{B}]_\text{T} = [\text{B}] + [\text{CoLB}] + 2[\text{CoLB}_2] \tag{4}$$

where $[\text{CoL}]_\text{T}$ and $[\text{B}]_\text{T}$ represent total concentrations of cobalt corrole **3** and a pyridine base, respectively. Since no hexa-coordinated complex exists in any significant concentration, the last term of each equation can be neglected. The equilibrium constant (K_1) for the first axial coordination is given by

$$K_1 = \frac{[\text{CoLB}]}{([\text{CoL}]_\text{T}-[\text{CoLB}])([\text{B}]_\text{T}-[\text{CoLB}])} \tag{5}$$

We employ here notations ε_i and A_i to represent molar extinction coefficient and optical density, respectively, for a cobalt corrole complex of coordination number i (i=4, 5, and 6), and A_obsd for observed optical density at various base concentrations while the concentration of cobalt complex was maintained constant. The following equation is derived for the first equilibrium step:

$$A_4 - A_\text{obsd} = (\varepsilon_4-\varepsilon_5)[\text{CoLB}]l = \Delta\varepsilon_\text{I}[\text{CoLB}]l \tag{6}$$

where l represents the length of light path.

For the higher base-concentration range where the second set of isosbestic points are observed, Eqs. 3 and 4 can be simplified as follows:

$$[\text{CoL}]_\text{T} = [\text{CoLB}] + [\text{CoLB}_2] \tag{7}$$

$$[\text{B}]_\text{T} = [\text{B}] \tag{8}$$

Since a pyridine base was present in a large excess relative to the cobalt complex, the contribution of [CoLB] and $[\text{CoLB}_2]$ to $[\text{B}]_\text{T}$ can be neglected. The corresponding equilibrium constant (K_2) is

$$K_2 = \frac{[\text{CoLB}_2]}{([\text{CoL}]_\text{T}-[\text{CoLB}_2])[\text{B}]} \tag{9}$$

and

$$A_\text{obsd} - A_6 = (\varepsilon_5-\varepsilon_6)[\text{CoLB}]l = \Delta\varepsilon_\text{II}[\text{CoLB}]l \tag{10}$$

Combination of Eqs. 7 through 10 gives

$$A_\text{obsd} = \frac{\Delta\varepsilon_\text{II}[\text{CoL}]_\text{T}}{1+K_2[\text{B}]_\text{T}}l + A_6 \tag{11}$$

or

$$\frac{[\text{CoL}]_\text{T}l}{A_\text{obsd}-A_6} = \frac{1}{\Delta\varepsilon_\text{II}} + \frac{K_2}{\Delta\varepsilon_\text{II}}[\text{B}]_\text{T} \tag{12}$$

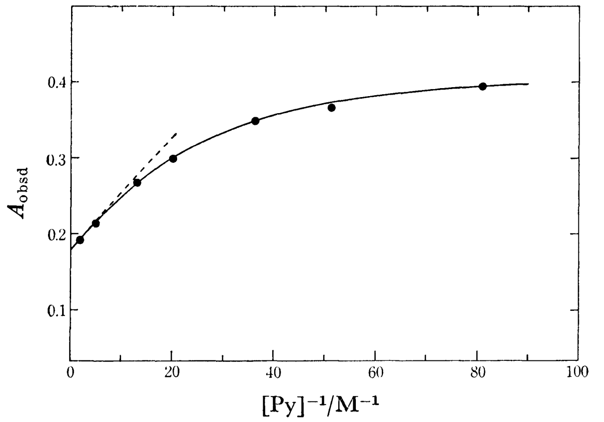


Fig. 3. Correlation of absorbance (at 380 nm) wtih pyridine concentration ([Py]) for the cobalt corrole (**3**)-pyridine system: [**3**] = 7.19 × 10^{-6} M in acetone at 25.0±0.1 °C.

The subsequent mathematical treatments were performed by referring to the absorption intensities observed at 380 nm. The A_6-values were evaluated by extrapolation of the A_{obsd}—[Pyridine base]$^{-1}$ correlation curve to [Pyridine base]$^{-1}$→0 on the basis of Eq. 11, as exemplified for the **3**–pyridine system in Fig. 3. Since all the cobalt species exist in the hexa-coordinated form at the pyridine-base concentrations of 0.1—1 M as judged from the corresponding spectral behavior (refer to Fig. 2), A_6-values can be evaluated directly from the corresponding spectra. The agreement between graphically and directly determined A_6-values was quite satisfactory; *e.g.*, 0.182 and 0.179, respectively, with pyridine at 7.19 × 10^{-6} M of **3**. The graphically determined A_6-values were used, however, for further computations for the sake of reliability. K_2 and $\Delta\varepsilon_{II}$ values were obtained by means of Eq. 12, as exemplified for the **3**–pyridine system in Fig. 4. From the analysis of spectral data for the second equilibrium step, ε_5 and ε_6 values were evaluated, which can be used for the analysis of the first equilibrium step by means of Eqs. 5 and 6.

The axial coordination behavior of penta-coordinated cobalt corrole **4** was also investigated in the presence of large excess of pyridine bases and the corresponding K_2-values were evaluated in the same way as described above. The equilibrium step for the **4**–pyridine base systems under investigation can be referred to process **5**$\rightleftharpoons$**6** shown in Scheme 1. We confirmed this by preparing the penta-coordinated 4-aminopyridine and 4-methylpyridine adducts of (tetramethyltetraethylcorrolato)cobalt(III) independently. In the presence of the same pyridine bases as used for the formation of these base adducts, the corresponding equilibrium constants were evaluated by means of Eq. 12. The values are in good agreement with those evaluated for the **4**–pyridine base systems within an experimental error. All the formation constants obtained in this work are listed in Table 1.

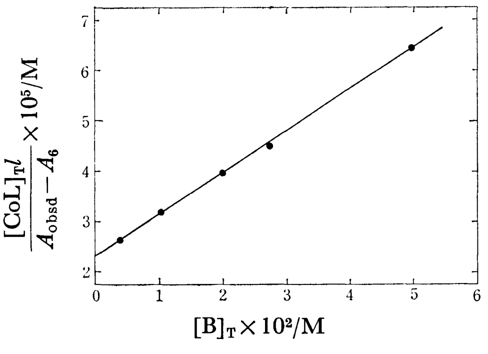
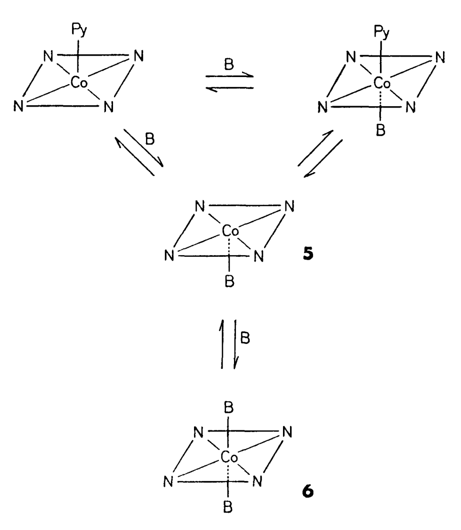


Fig. 4. Determination of K_2 and $\Delta\varepsilon_{II}$ values for the cobalt corrole (**3**)-pyridine (B) system on the basis of Eq. 12: [**3**] = 7.19 × 10^{-6} M in acetone at 25.0± 0.1 °C.



Scheme 1.

Interaction between Cobalt(II) Corrole Anion and Pyridine. The ESR spectra for the anionic cobalt(II)–corrole complex were not observed at room temperature probably due to short spin-lattice relaxation time. The (2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)cobaltate(II) ion shows an ESR spectrum at 77 K with three g-values (g_1, g_2, and g_3) as shown in Fig. 5. Eight hyperfine splitting lines through interaction with ^{59}Co

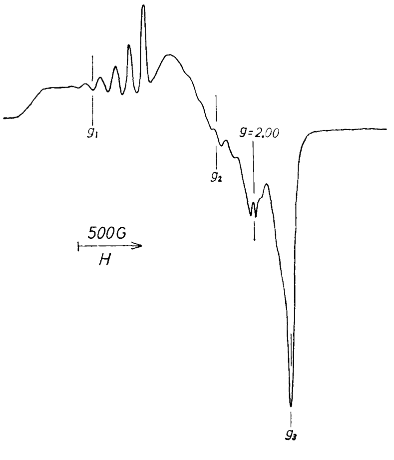


Fig. 5. ESR spectrum of the (2,3,17,18-teramethyl-7,8,12,13-tetraethylcorrolato)cobaltate(II) ion in N,N-dimethylformamide at 77 K. Thecobalt(III) corrole (**4**) was reduced with $NaBH_4$ in N,N-dimethylformamide.

TABLE 1. FORMATION CONSTANTS FOR THE PYRIDINE COMPLEXES OF COBALT(III) CORROLES[a)]

Pyridine base[b)]	pK_a(BH$^+$)[c)]	3		4
		K_1/M^{-1}	K_2/M^{-1}	K_2/M^{-1}
4-CNPy	1.90	$(1.95\pm0.05)\times10^3$	6.56	1.03×10
Py	5.19	$(1.69\pm0.12)\times10^4$	3.79×10	4.40×10
4-CH_3Py	6.02	$(6.58\pm0.19)\times10^4$	9.82×10	1.21×10^2
4-NH_2Py	9.11	$(7.78\pm0.29)\times10^5$	4.51×10^2	5.52×10^2
3-AcPy	3.18	$(1.07\pm0.09)\times10^5$	1.15×10^2	1.89×10^2
3-HOPy	4.86	$(1.83\pm0.13)\times10^4$	1.35×10	3.50×10
3-CH_3Py	5.68	$(3.50\pm0.16)\times10^4$	5.65×10	7.62×10
2-CH_3Py	5.97	$(1.09\pm0.16)\times10^2$	1.10×10^{-1}	1.67×10^{-1}

a) Measured in acetone at 25.0±0.1 °C. b) Py, pyridine; 4-CNPy, 4-cyanopyridine; 4-CH_3Py, 4-methylpyridine; 4-NH_2Py, 4-aminopyridine; 3-AcPy, 3-acetylpyridine; 3-HOPy, 3-hydroxypyridine; 3-CH_3Py, 3-methylpyridine; 2-CH_3Py, 2-methylpyridine. c) Cited from "Handbook of Biochemistry and Molecular Biology. Physical and Chemical Data," Vol. 1, 3rd ed, ed by G. D. Fasman, CRC Press, Inc., Cleveland, Ohio (1976).

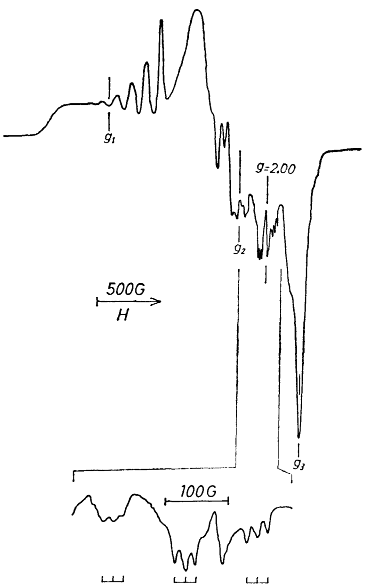
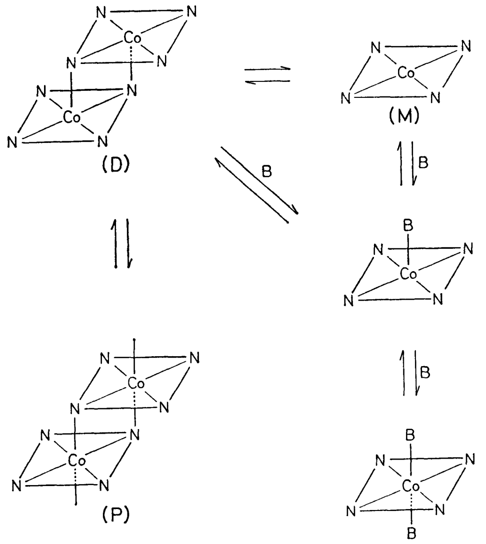


Fig. 6. ESR spectrum of the (2,3,17,18-tetramethyl-7,8,-12,13-tetraethylcorrolato)cobaltate(II) ion in *N,N*-dimethylformamide-pyridine (3 : 1 by volume) at 77 K. The g_2 component is expanded as shown in the lower part; triplet superhyperfine structure is observed.



Scheme 2.

nucleus (I=7/2) are also observed in the g_1 and g_2 ranges, indicating that the central cobalt is in a low spin state (S=1/2). Upon addition of pyridine, a triplet superhyperfine structure can be seen on the hyperfine lines of the g_2 component as shown in Fig. 6. This may be caused by the interaction between nitrogen nucleus of the axially coordinated pyridine molecule and electron occupying the d_{z^2} obrital of the nuclear cobalt. Further spectral change was not observed by increasing the pyridine content. Consequently, only one pyridine molecule can be coordinated to the anionic cobalt(II)-corrole complex.

Discussion

The solution equilibria for the cobalt(III) corrole in the presence of amine bases can be illustrated by Scheme 2. The cobalt(III) corrole forms polymeric species in an organic solvent most plausibly through metal–nitrogen bonding in a manner as suggested for the copper(II) complex of phthalocyanine.[10)] The presence of such polymeric species is significant in a concentration range above 5×10^{-3} M as detected by the accumulative NMR measurements. The first equilibrium constants (K_1) for the formation of pyridine adducts of **3** are larger by one order of magnitude than those for the cobalt(II) complex of 1,19-disubstituted tetradehydrocorrin.[2)] This is attributed to the greater electrophilicity of nuclear cobalt in trivalent state. The second equilibrium constants (K_2) are much smaller than the K_1-values by an order of 10^2—10^3 due to the so-called *trans effect* in a manner as observed for the axial ligation of pyridine to tetrakis(4-*N*-methylpyridyl)porphincobalt(III).[11)] The equilibrium constant (K_i, $i=1$ or 2) can be correlated with the basicity of pyridine bases (pK_a) by Eq. 13 for the axial coordination of pyridine bases to the cobalt corroles except for 2-methyl- and 3-acetylpyridine, as shown in Fig. 7.

$$\log K_i = a\cdot pK_a + b \qquad (13)$$

The *a*- and *b*-parameters thus evaluated are listed in

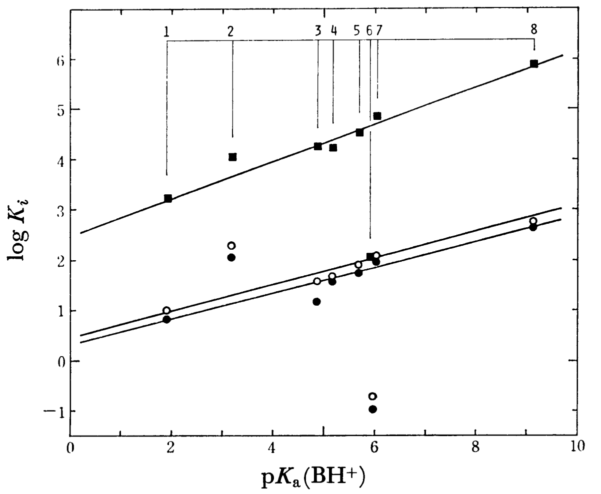


Fig. 7. Correlations between formation constant (K_i) and amine basicity: ■, K_1 for the **3**-amine system; ●, K_2 for the **3**-amine system; ○, K_2 for the **4**-amine system. Amines: 1, 4-CNPy; 2, 3-AcPy; 3, 3-HOPy; 4, Py; 5, 3-CH_3Py; 6, 2-CH_3Py; 7, 4-CH_3Py; 8, 4-NH_2Py (see Table 1 for abbreviations).

Table 2. Lower coordination ability of 2-methylpyridine with respect to the correlation line given by Eq. 13 is attributed to the steric hindrance effect due to the interaction between the corrole skeleton and the 2-methyl group of the pyridine base. The free energy loss by the steric effect is estimated to be 3.5 kcal/mol (25 °C) for the penta-coordination step, while 3.8 kcal/mol (25 °C) for the hexa-coordination process. That the free energy loss for the latter coordination process is comparable to that for the former is quite reasonable because no extra steric effect would be expected for the latter. On the other hand, 3-acetylpyridine shows a greater formation constant for its pK_a-value. The dπ-pπ interaction betweeen the nuclear cobalt and the pyridine nitrogen, which is facilitated by the 3-acetyl group, would be responsible for such apparent increase in formation constant.

The equilibrium data for the present set of pyridine bases can be referred to the Hammett equation for which the coordination equilibrium with pyridine (K_i^0) is taken as a reference and suffix i stands for either 1 or 2.

$$\log K_i/K_i^0 = \rho\sigma. \qquad (14)$$

The evaluated ρ values are listed in Table 2 along with other reference data of relevant cobalt(II) complexes.

It must be noted that both a and $-\rho$ values for the present cobalt(III)–corrole systems are considerably larger than the corresponding values for cobalt(II) complexes of protoporphyrin[12] and tetrakis(p-methoxyphenyl)porphyrin.[13] The values for the first coordination step of **3** is even larger than those for Co(II)–TDHC in spite of the fact that TDHC and corrole are anionic ligands with charges of −1 and −3, respectively. The a and ρ values suggest that the nuclear cobalt in cobalt(III) corrole is more electronegative than those in cobalt(II) complexes listed in Table 2, even though the total electric charges at the coordination site of corrole and porphyrin complexes are neutral and that of TDHC complex is positive (+1). It should be pointed out, however, that the a and $-\rho$ values for cobalt(III) corroles in the second coordination process are more or less comparable to those for Co(II)–TDHC. This seems to indicate that the extent of σ- and π-bonding characters of the coordinate bond formed in the final coordination step of cobalt(III) corroles is nearly the same as that of Co(II)–TDHC, since the former complexes secure the trans effect of the initially coordinated pyridine bases.

When the cobalt corrole is reduced at the nuclear cobalt from trivalent to bivalent state, only one pyridine molecule can be coordinated at its axial sites and hexa-coordination is no longer possible as confirmed by ESR measurements. Cobalt(III) corrinoid forms the hexa-coordinated complexes with amine bases at its axial positions but cobalt(II) corrinoid yields the bis(pyridine) complex only at a very high pyridine concentration, whereas bis(dimethylglyoximato)cobalt(II) takes on two pyridine ligands readily.[14] In this respect, the present tetrapyrrolic ligand gives out an equatorial ligand effect on the nuclear cobalt in a manner analogous to that observed for corrinoid. In other words, the axial ligation behavior of cobalt corrinoid is more or less analogous to that of cobalt corrole and differs a great deal from that of cobaloxime.

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TABLE 2. BRØNSTED[a)] AND HAMMETT[b)] PARAMETERS FOR THE COORDINATION OF PYRIDINE BASES

Coordination equilibrium	Co-Chelate system[c)]	a	b	$-\rho$	Ref.
$CoL + B \rightleftharpoons CoLB$	Co(III) corrole (**3**)	0.37	2.5	2.0	This work
	Co(II)-TDHC	0.24	2.1	1.6	2
	Co(II)-PP(IX)DME	0.06	—	0.6	12
	Co(II)-p-MeOTPP	0.19	1.7	1.0	13
$CoLB + B \rightleftharpoons CoLB_2$	Co(III) corrole (**3**)	0.26	0.32	1.3	This work
	Co(III) corrole (**4**)	0.27	0.42	1.4	This work

a) Refer to Eq. 13. b) Refer to Eq. 14. c) Ligand abbreviations: TDHC, 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin; PP(IX)DME, protoporphyrin IX dimethyl ester; p-MeOTPP, 5,10,15,20-tetrakis(p-methoxyphenyl)porphyrin.

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