Transition-metal Complexes of Pyrrole Pigments. XIII. Reduction and Coordination Behaviors of the Cobalt(II) Complexes of 1,19-Disubstituted Tetradehydrocorrins as Demonstrated by the Presence of Various Bases*

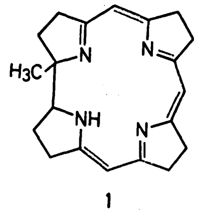
Yukito Murakami and Yasuhiro Aoyama

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

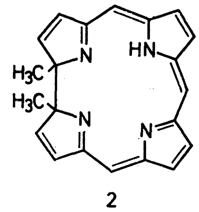
(Received August 27, 1975)

The interaction of various bases with the cobalt(II) complexes of 1,19-disubstituted tetradehydrocorrins (Co(II)–TDHC) was investigated. The parent cobalt(II) complexes were shown to undergo ready reduction at the nuclear cobalt(II) with the unsolvated hydroxide ion as well as with bulky triethylamine. A relatively large positive reduction potential of Co(II)–TDHC is responsible for these novel electron transfer reactions. Less hindered amines (B), on the other hand, failed to show such electron transfer reactions with the cobalt(II) complexes and Co(II)–TDHC became the pentacoordinated complex by taking up an amine base in the axial position: $\text{Co(II)–TDHC}+\text{B} \rightleftharpoons \text{B–Co(II)–TDHC}$. For the interaction of 4-substituted pyridines with the cobalt(II) complex, the general behavior of the equilibrium constants was interpreted in terms of the amine basicity and the Hammett equation by referring to the corresponding behavior of the porphyrin complexes. The weaker coordination tendency of some aliphatic amines and hindered pyridines toward Co(II)–TDHC was attributed to their electronic and steric effects in the coordination process. The intrinsic correlation between electronic and stereochemical characteristics pertaining to the tetradehydrocorrin skeleton and the nature of nuclear cobalt(II) was discussed on the basis of these observations.

In order to provide the chemical basis for the enzymatic functions of naturally occurring macrocyclic complexes such as metal corrinoids and porphyrins, extensive investigations have been carried out on the redox properties of a series of synthetic macrocyclic complexes of various electronic characters.[1–4] Among the biological redox systems, vitamin B_{12}, which involves a corrin framework (**1**), has attracted particular attention from the viewpoint of its unique ability to form a Co(III)–C σ bond.[5,6] The cobalt(I) species has been widely recognized as the key intermediate in the alkylation of vitamin B_{12} and a number of synthetic cobalt complexes have been shown to undergo alkylation *via* nucleophilic reactions of the cobalt(I) intermediates generated by reduction of the parent cobalt(II) or cobalt(III) complexes.[6–12] The redox property of a cobalt complex would be controlled by several factors, such as the cavity size provided by a macrocyclic skeleton which incorporates a cobalt ion, the electronic structure of a macrocyclic ligand, and so on. Attempts have been made to clarify the structural characteristics of these macrocycles which lead to the formation of stable Co(III)–C bonds,[1,11,12] but no satisfactory explanation has been given so far for the significance of the corrinoid structure. In connection with the chemistry of corrinoids, the tetradehydrocorrins (**2**), which have a macrocyclic framework closely related to the corrins (**1**), have been prepared and their metal complexes have been investigated from several structural viewpoints.[13–15] On the basis of these structural studies, the interaction of the hydroxide ion and various organic bases with the cobalt(II) complexes of 1,19-disubstituted tetradehydrocorrins was investigated in the present study. This work, therefore, may elucidate the effects of electronic and stereochemical structures pertaining to the tetradehydrocorrin skeleton on the reactivity of nuclear cobalt(II).



1



2

Experimental

Electronic spectra were taken on a Hitachi EPS-2 recording spectrophotometer. NMR spectra were recorded on a Varian A-60 spectrometer. Solvents for spectroscopic measurements were prepared by the standard procedures.[16] Sodium hydroxide and potassium hydroxide of analytical grade were obtained from commercial sources. Diethylammonium chloride was recrystallized twice from ethanol–ether and dehydrochlorinated with sodium hydroxide. Free diethylamine was recovered by fractional distillation after being dried over potassium hydroxide. Similarly, triethylamine was obtained from triethylammonium chloride recrystallized twice from ethanol. Other liquid amines (pyridine, 2-methyl- and 4-methylpyridine, 2,4,6-trimethylpyridine, butylamine, and piperidine) were refluxed with potassium hydroxide and then fractionally distilled. Commercially available 4-cyanopyridine and imidazole were recrystallized from aqueous ethanol and benzene, respectively. 4-Aminopyridine was prepared by ammonolysis of (4-pyridyl)pyridinium dichloride[17] and recrystallized twice from benzene. The purity of these organic amines was checked by gas chromatographic analysis. Dibenzo-18-crown-6 and its potassium hydroxide complex were prepared after Pedersen.[18]

Tetradehydrocorrinatocobalt(II) Perchlorates (7a and 7b). 8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatocobalt(II) perchlorate (**7a**) was prepared after Johnson *et al.*[19,20] with slight modifications. First, 2,4-dimethyl-3-

---

* Contribution No. 378 from this Department. Part XII: Y. Murakami, K. Sakata, Y. Tanaka, and T. Matsuo, This Bulletin, **48**, 3622 (1975).

acetyl-5-ethoxycarbonylpyrrole was converted to 2,4-dimethyl-3-ethyl-5-ethoxycarbonylpyrrole (**3**, yield 90%) by essentially the same procedure as applied for the synthesis of 2,3,4-triethyl-5-ethoxycarbonylpyrrole.[21] Then, **3** was brominated at the 2-methyl group and further converted to 3,3′-diethyl-4,4′-dimethyl-5,5′-diethoxycarbonyldipyrromethane (**4**, yield 87%) *via* solvolytic coupling of the resulting 2-bromomethyl derivative.[22] The dipyrromethane (**4**) was recrystallized from aqueous ethanol (mp 123.5—125 °C; lit,[23] 126 °C) and hydrolyzed quantitatively with sodium hydroxide to give 3,3′-diethyl-4,4′-dimethyl-5,5′-dicarboxydipyrromethane (**5**). 2-Formyl-3,4,5-trimethylpyrrole underwent condensation with **5** in the presence of hydrogen bromide to afford 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbiladiene-ac dihydrobromide (**6**) according to the general procedure of Johnson *et al.*[19] (yield 30—65%). Aeration of a mixture of biladiene-ac dihydrobromide **6** and cobalt acetate tetrahydrate in ethanol followed by addition of sodium perchlorate afforded the tetradehydrocorrinatocobalt(II) perchlorate (yield 35—40%); recrystallized from acetone-benzene. The preparation of 2,8,12,18-tetrakis(2-ethoxycarbonylethyl)-1,3,7,13,17,-19-hexamethyltetradehydrocorrinatocobalt(II) perchlorate (**7b**) has been described previously.[15]

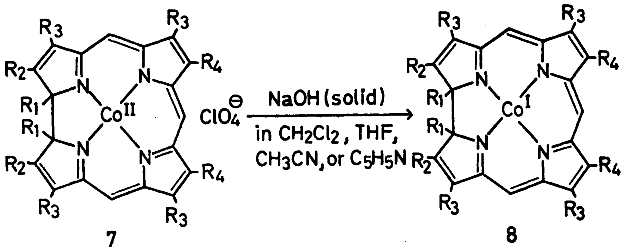
NMR Spectrum of Tetradehydrocorrinatocobalt(I) (8b). To a dichloromethane solution (5 ml) of **7b** (50 mg) was added solid sodium hydroxide (1.0 g) under nitrogen atmosphere, and the mixture was stirred for 2 hr at room temperature. Sodium hydroxide was then removed by filtration. The electronic spectrum of the filtrate indicated the complete conversion of **7b** to **8b**. Most of the solvent was carefully removed under dry nitrogen. The NMR spectrum of the residue (**8b**): δ 1.49 (6H, s, 1,19-$C\underline{H}_3$), 1.85 and 2.45 (both 6H, s, 3,7,13,17-$C\underline{H}_3$), 9.78 (2H, s, 5-$\underline{H}$ and 15-$\underline{H}$), 10.82 (1H, s, 10-$\underline{H}$), 1.27 (12H, t, $CO_2CH_2C\underline{H}_3$), 3.6—4.5 (16H, multi, $CH_2C\underline{H}_2CO_2C\underline{H}_2CH_3$) and 2.9—3.4 (8H, multi, $C\underline{H}_2CH_2CO_2CH_2CH_3$).

Reduction of 7a with the Potassium Hydroxide Complex of Dibenzo-18-crown-6. Into a benzene solution of **7a** (1×10^{-5} M) was added the potassium hydroxide complex of dibenzo-18-crown-6 in an excess amount. The mixture was stirred for 5 min under nitrogen. The electronic spectrum of the mixture showed that **7a** was completely converted to the tetradehydrocorrinatocobalt(I) (**8a**). Controlled experiments were carried out by addition of a calculated amount of a benzene solution of the potassium hydroxide complex (1.5×10^{-2} M).

Determination of Equilibrium Constants for the Complex Formation Between 7a and Amine Bases. The interaction of **7a** with an amine base was investigated by measuring the visible spectra of a series of solutions in which the concentration of an amine was varied in about 10^2-fold range on one side and that of **7a** maintained constant (3×10^{-5} M) on the other. According to the Benesi-Hildebrand relationship, the equilibrium constant for the complex formation between **7a** and an amine base was determined on the basis of spectral changes observed upon addition of an amine.

Results and Discussion

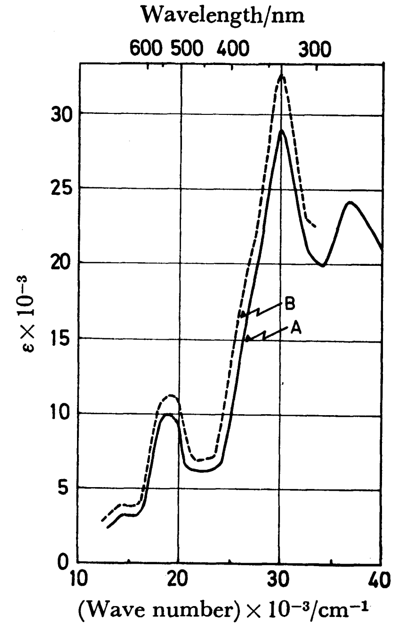
Reduction of Tetradehydrocorrinatocobalt(II) Perchlorates with Hydroxide Ion. The reaction of tetradehydrocorrinatocobalt(II) perchlorates (**7a** and **7b**, Co(II)–TDHC hereafter) with sodium hydroxide was investigated at room temperature. When the reaction was carried out in an aprotic solvent (dichloromethane, THF, acetonitrile, or pyridine) with solid sodium hydroxide, the product was identified as the tetradehydrocorrinatocobalt(I) complex (**8a** or **8b**, Co(I)–TDHC hereafter, refer to Eq. (1)) due to the following facts: (1) the electronic spectrum of the product (**8a**) was almost identical with that of 1,19-diethoxycarbonyl-8,12-diethyl-2,3,7,13,17,18-hexamethyltetradehydrocorrinatocobalt(I) (**8c**) obtained by reduction of the corresponding cobalt(II) complex with sodium film[13] (Fig. 1); (2) the product (**8b**) was diamagnetic and showed a sharp NMR spectrum, suggesting the d^8 configuration of cobalt(I); and (3) the product was oxidized by oxygen only slowly back to the parent cobalt(II) complex, but instantaneously upon treating with iron(III) chloride, as observed for **8c**.[13]



7 8

(1)

a: $R_1 = R_2 = R_3 = CH_3$, $R_4 = C_2H_5$
b: $R_1 = R_3 = CH_3$, $R_2 = R_4 = CH_2CH_2CO_2C_2H_5$
c: $R_1 = CO_2C_2H_5$, $R_2 = R_3 = CH_3$, $R_4 = C_2H_5$



Fug. 1. Electronic spectra of 8,12-diethyl-1,2,3,7,13,17,-18,19-octamethyltetradehydrocorrinatocobalt(I) (**8a**) at room temperature: A, in dichloromethane; B, in pyridine.

As shown in Fig. 2, the electronic spectrum of the parent cobalt(II) complex (**7a**) shows an appreciable solvent dependence. This spectral behavior seems to indicate a further coordination of one pyridine molecule at the axial position of the complex, which is consistent with the corresponding ESR data.[13,15] In contrast, the electronic spectrum of the cobalt(I) species (**8a**) does not show any significant change upon changing the solvent from dichloromethane to pyridine. This fact

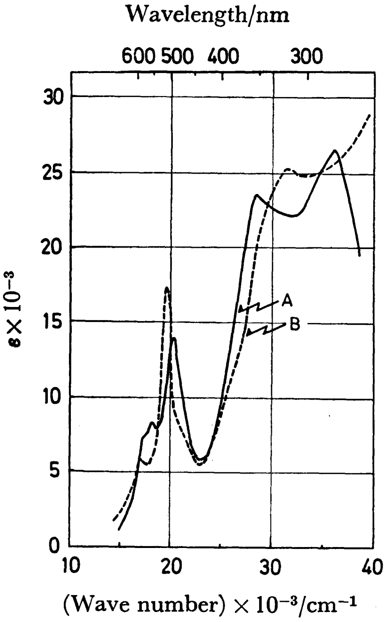
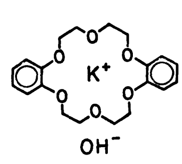


Fig. 2. Electronic spectra of 8,12-diethyl-1,2,3,7,13,17,-18,19-octamethyltetradehydrocorrinatocobalt(II) perchlorate (**7a**) at room temperature: A, in dichloromethane; B, in pyridine.

indicates that the reduced complex has no further ability to coordinate with an organic base. The reduction of Co(II)-TDHC failed in both dichloromethane and methanol solutions, even though the saturation level of sodium hydroxide concentration was maintained. These results indicate that the novel electron transfer from sodium hydroxide to Co(II)-TDHC takes place on the solid surface of the base. In marked contrast, the ready reduction of Co(II)-TDHC was again observed in an aprotic solvent (acetonitrile, THF, or benzene) with potassium hydroxide solubilized *via* complex formation with a cyclic polyether, dibenzo-18-crown-6 (**9**). Controlled experiments showed that Co(II)-TDHC was completely reduced to Co(I)-TDHC with less than 3 equivalents of the crown complex, indicating that the active reducing reagent was certainly the hydroxide ion and not any impurity which may exist in alkaline hydroxide. The observed successful reduction of Co(II)-TDHC may be attributed to the absence of any solvation effects for the hydroxide ion. The hydroxide ion at the solid surface or in an aprotic solvent may exist in a naked state without any significant solvation, and is consequently active enough to transfer an electron to an appropriate acceptor, *i.e.* Co(II)-TDHC. The activation of inorganic anions through the complex formation with crown polyethers has been reported for some nucleophilic and oxidation reactions.[24-26]



9

The electron-transfer mechanism for the hydroxide-Co(II)-TDHC system is not fully understood. Gillard has suggested that an unstable intermediate cobalt(II) species is present in the ligand substitution of a cobalt(III) complex, as promoted with a hydroxide ion (Eq. (2)).[27]

$$\mathrm{L_5Co(III)\text{-}Br + OH^- \longrightarrow (L_5Co(II)\cdot OH) + Br^-}$$
$$\mathrm{\longrightarrow L_5Co(III)\text{-}OH + Br^-} \qquad (2)$$

Cobalt(II) corrinoids[28,29] as well as bis(dimethylglyoximato)cobalt(II)[28,30] have been known to undergo disproportionation in alkaline solutions to the corresponding cobalt(I) and cobalt(III) complexes. A mechanistic distinction, however, should be made between those reactions and the present novel reduction of Co(II)-TDHC. The hydroxide ion transfers an electron to the cobalt(II) complex in the present reaction without its final coordination to or causing disproportionation of Co(II)-TDHC. Such a strong oxidizing power of Co(II)-TDHC is consistent with its higher positive reduction potential relative to other analogous cobalt complexes (Table 1).

There are a number of papers which have reported the successful preparation of coordination compounds containing Co(III)-C σ bonds.[6-12] The nucleophilic attack of a cobalt(I) species on an appropriate alkyl donor seems to provide the most suitable method for such preparative purposes. The present Co(I)-TDHC appears to be an exception for this kind of reaction. Addition of methyl iodide to a solution of Co(I)-TDHC did not result in the formation of a Co(III)-C bond, and no other reaction was detected as proceeding in the system. This result can be understood in the light of the electrochemical data listed in Table 1. The nucleophilicity of various cobalt(I) complexes seems to follow the order of the Co(II)-Co(I) reduction potential.[6,31] The Co(I)-Bae complex, among the complexes listed in Table 1, reacts even with bromobenzene, while Co(I)[(DO)(DOH)pn]P$(C_6H_5)_3$ does not show any reactivity toward propyl bromide even after a prolonged time.[9] Thus, the lack of any nucleophilicity of Co(I)-TDHC appears to be reasonable on the basis of its reduction-oxidation trend, as listed in Table 1. In conclusion, the effects of the corrin and tetradehydrocorrin rings on the reduction-oxidation

Table 1. Co(II)-Co(I) reduction potentials for the Co^{II}L complexes

L[a]	Bae	Salen	Saloph	$(DH)_2$	B_{12r}	(DO)(DOH)pn	**7a**	**7c**
$E_{1/2}$ (V *vs.* S.C.E.)	−1.50	−1.38	−1.35	−1.24	−1.02	−0.85	−0.25	−0.16
Ref.	9	42	42	42	9	9	43	13

a) Bae, *N,N'*-ethylenebis(acetylacetoniminato); Salen, *N,N'*-bis(salicylidene)ethylenediamino; Saloph, *N,N'*-bis(salicylidene)-*o*-phenylenediamino; $(DH)_2$, bis(dimethylglyoximato); (DO)(DOH)pn, 1-(diacetylmonoximato-imino)-3-(diacetylmonoximeimino)propane; B_{12r}, vitamin B_{12r}.

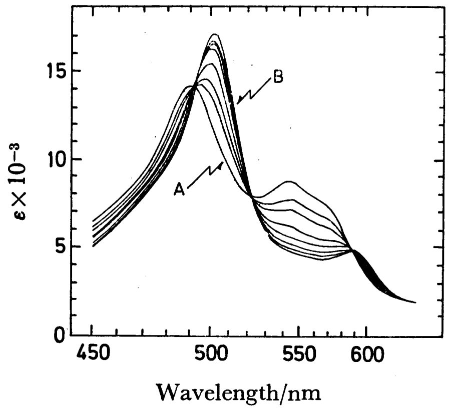


Fig. 3. Electronic spectra of the tetradehydrocorrinatocobalt(II) perchlorate (**7a**) (3.47×10^{-5}M) in dichloromethane at various concentrations of 4-methylpyridine: 0, 7.93×10^{-5}, 1.59×10^{-4}, 3.97×10^{-4}, 7.93×10^{-4}, 1.59×10^{-3}, and 3.02×10^{-3} M (read from A to B).

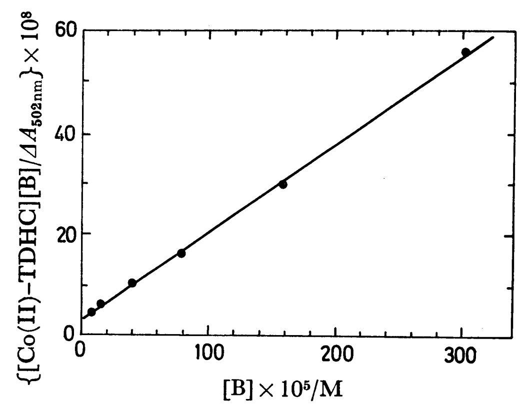


Fig. 4. Benesi-Hildebrand plot for the complex-forming equilibrium between 4-methylpyridine (B) and Co(II)–TDHC (**7a**).

behavior of the nuclear cobalt are not so alike as would be judged from the similarity in their skeletal structures.

Interaction of Tetradehydrocorrinatocobalt(II) Perchlorates with Amine Bases. The electronic spectrum of Co(II)–TDHC dissolved in dichloromethane underwent variation upon addition of any of the following amine bases: substituted pyridines (4-NH_2, 4-CH_3, 4-CN, 2-CH_3, and 2,4,6-$(CH_3)_3$), imidazole, and aliphatic amines (butyl, diethyl, and piperidine). Since the spectral feature is almost identical with that for the pyridine adduct shown in Fig. 2, the cobalt(II) ion becomes pentacoordinated by having an amine base in the axial position as the fifth ligand. The spectral variations upon addition of 4-methylpyridine are shown in Fig. 3 as an example. The effect of amine concentration on the spectral change was consistent with the following solution equilibrium:

$$\mathrm{Co(II)\text{-}TDHC} + \mathrm{B} \overset{K}{\rightleftarrows} \mathrm{B\text{-}Co(II)\text{-}TDHC} \tag{3}$$

where B stands for an amine base. The observations of isosbestic points at 491, 523, and 590 nm and the unit slope for the plots of log([B–Co(II)–TDHC]/[Co(II)–TDHC]) *vs.* log[B] are further evidence for the 1: 1 complex formation for each of the amine ligands treated, in contrast to the case of the cobalt(II) porphyrin system for which the ESR data suggested the formation of 1: 2 (metal complex to base) complexes.[32] The equilibrium constants (K) were obtained from the intensity change at 502 nm by adopting the Benesi-Hildebrand-type relation[33] (Eq. (4)).

$$\frac{[\mathrm{Co(II)\text{-}TDHC}][\mathrm{B}]}{\Delta A} = \frac{1}{\Delta\varepsilon\cdot K} + \frac{[\mathrm{B}]}{\Delta\varepsilon} \tag{4}$$

In this equation, [Co(II)–TDHC] and [B] stand for the total concentrations of **7a** and amine, respectively, $\Delta\varepsilon$ is the difference in molar extinction coefficient between Co(II)–TDHC and B–Co(II)–TDHC, and ΔA represents the extent of the absorbance change upon addition of amine bases. A good linear correlation based on Eq. (4) is observed, as shown in Fig. 4 for the Co(II)–TDHC–4-methylpyridine system: $K=5.90\times10^{3}\mathrm{M}^{-1}$ and $\Delta\varepsilon=0.578\times10^{4}$. This $\Delta\varepsilon$ value is in good agreement with that obtained upon addition of a large excess of 4-methylpyridine (0.584×10^{4}). Equilibrium constants for other amines were obtained in a similar manner, and are summarized in Table 2.

TABLE 2. FORMATION CONSTANTS FOR THE AMINE COMPLEXES OF Co(II)–TDHC (**7a**)[a]

Amine[b]	$\mathrm{p}K_a(\mathrm{BH}^+)$	K, M^{-1}
Py	5.19	1.95×10^{3}
4-NH_2Py	9.11	1.60×10^{4}
4-MePy	6.02	5.90×10^{3}
4-CNPy	1.90	3.00×10^{2}
2-MePy	5.97	5.16
2,4,6-Me_3Py	7.48	4.11
Im	7.25[c]	9.85×10^{3}
n-BuNH_2	10.59	1.85×10^{3}
Et_2NH	10.98	*ca.* 1.5×10^{0}[d]
Pip	11.22	1.15×10^{3}

a) Measured in dichloromethane at 15 °C. b) Py, pyridine; 4-MePy, 4-methylpyridine; 4-NH_2Py, 4-aminopyridine; 4-CNPy, 4-cyanopyridine; 2-MePy, 2-methylpyridine; 2,4,6-Me_3Py, 2,4,6-trimethylpyridine; Im, imidazole; *n*-BuNH_2, butylamine; Et_2NH, diethylamine; Pip, piperidine. c) Statistically corrected for two hydrogens in ImH^+. d) Determined at low concentrations of diethylamine: see Ref. 41.

The equilibrium constants for the formation of pyridine and imidazole adducts of **7a** are comparable in magnitude to those for the porphyrin complexes, but significantly larger than those for the Schiff base complexes, as shown in Table 3. This is consistent with the prediction based on the electrochemical data, *i.e.*, the more negative the cobalt(II)-cobalt(I) reduction potential the smaller the equilibrium constant. Apparently, there exists no systematic correlation between log K and amine basicity, as shown in Fig. 5, without considering the structural characteristics of the amine bases. However, if the 4-substituted pyridines are taken up, the following correlation is established by a least squares analysis, where $a=0.24$ and $b=2.1$:

$$\log K = a\mathrm{p}K_a + b \tag{5}$$

TABLE 3. FORMATION CONSTANTS FOR THE $Co^{II}LB$ COMPLEXES[a)]

L[b)]	B[b)] Py	Im	MeIm	Ref.
TDHC (**7a**)[c)]	1.95×10^3	9.85×10^3		This work
PP(IX)DME[d)]	6.0×10^3	4.4×10^3	5.0×10^3	38
		4.5×10^3	5.1×10^3	36
p-MeOTPP[e)]	4.85×10^2	1.40×10^3	2.37×10^3	37
Saloph[f)]	2.0×10^2	1.2×10^3		44
Salen			2.3×10	44
			2.6×10	45

a) Formation constants are given in M^{-1}. b) Py, pyridine; Im, imidazole; MeIm, 1-methylimidazole; TDHC, tetradehydrocorrin; PP(IX)DME, protoporphyrin IX dimethyl ester; *p*-MeOTPP, $\alpha,\beta,\gamma,\delta$-tetrakis(*p*-methoxyphenyl) porphyrin; Saloph, *N,N'*-bis-(salicylidene)-*o*-phenylenediamino; Salen, *N,N'*-bis-(salicylidene)ethylenediamino. c) In dichloromethane at 15 °C. d) In toluene at 23 °C. e) In toluene at 25 °C. f) In dichloromethane at 25 °C.

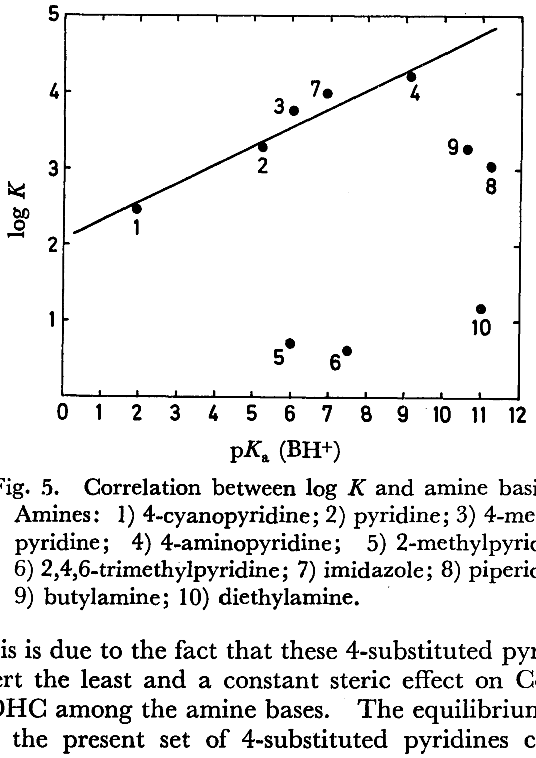


Fig. 5. Correlation between log K and amine basicity. Amines: 1) 4-cyanopyridine; 2) pyridine; 3) 4-methylpyridine; 4) 4-aminopyridine; 5) 2-methylpyridine; 6) 2,4,6-trimethylpyridine; 7) imidazole; 8) piperidine; 9) butylamine; 10) diethylamine.

This is due to the fact that these 4-substituted pyridines exert the least and a constant steric effect on Co(II)–TDHC among the amine bases. The equilibrium data for the present set of 4-substituted pyridines can be referred to the Hammett equation with $\rho=1.6$ (Eq. (6)):

$$-\log K/K_0 = \rho\sigma \qquad (6)$$

where K is for a substituted pyridine and K_0 for pyridine, and σ is the Hammett substituent constant. Such a linear free energy relationship has been reported for the complex-forming equilibria between 4-substituted pyridines and metalloporphyrins.[34–38] It is interesting to note that both a and ρ values for the present Co(II)–TDHC (**7a**) system are considerably larger than the corresponding values for the cobalt(II) complexes of protoporphyrin (a=0.09, ρ=0.6)[38] and tetrakis(*p*-methoxyphenyl)porphyrin (a=0.19, ρ=1.0).[37] The current interpretation of a[39] and ρ values may lead to an important conclusion that the nuclear cobalt in Co(II)–TDHC is more electronegative than in cobalt(II) porphyrins, and the pyridine nitrogen in $X-C_5H_4N-$Co(II)–TDHC is much more electron deficient than in the corresponding cobalt(II) porphyrin complexes. This is again what might be expected from the extremely positive cobalt(II)–cobalt(I) reduction potential of Co(II)–TDHC (Table 1).

A large decrease in K value was observed for some hindered pyridines, such as 2-methylpyridine and 2,4,6-trimethylpyridine (Fig. 5). This may be attributed to the front strain exerted between these amines and Co(II)–TDHC in the coordination process. The coordination of pyridines to metalloporphyrins is also subject to a similar steric effect.[34,35,37] The formation constant of the 2,4,6-trimethylpyridine complex of cobalt(II) tetrakis(*p*-methoxyphenyl)porphyrin is 1.5 log unit less than that expected from the basicity of the amine.[37] This effect is even larger in the present system and the formation constants for 2-methyl- and 2,4,6-trimethylpyridine are reduced by 3 log units more than expected (Fig. 5). In addition to the repulsion between the in-plane π-electron system of the macrocyclic ligand and the 2- and/or 6-methyl groups of the substituted pyridines, another steric interaction seems to interfere greatly with the coordination of 2-methyl- and 2,6-dimethylpyridines to Co(II)–TDHC. This other significant steric effect may arise from the interaction of the angular methyl groups placed at the 1- and 19-positions of the macrocyclic ligand and the substituted pyridines.

Aliphatic amines form complexes with Co(II)–TDHC which are less stable than those derived from substituted pyridines, on the basis of the basicity scale shown in Fig. 5. The extra stabilization observed for the pyridine complexes may be attributed to the π-back bonding from the nuclear cobalt to the pyridine moiety. It is interesting to note that imidazole has an affinity toward Co(II)–TDHC which falls relatively well on the $\log K-pK_a$ correlation line for the 4-substituted pyridines. It has been generally realized, on the other hand, that imidazole behaves as a better π-electron acceptor relative to pyridine.[37] The present result indicates, therefore, that π-back donation from the nuclear cobalt to the π^*-orbital of the fifth ligand such as imidazole and pyridine derivatives would not be so marked as predicted for the porphyrin complexes,[40] due to the significant electronegative character of cobalt in Co(II)–TDHC.

Because of the bulkiness of triethylamine, it demonstrates the least coordination tendency toward Co(II)–TDHC among the amine bases used in this work. The spectrum of Co(II)–TDHC (**7a**) (2×10^{-5}M in dichloromethane) remained unchanged upon addition of triethylamine (up to 10^{-2} M.) However, when the concentration of the amine was adjusted to the 10^{-1} to 1 M range, the reduction of **7a** took place to afford Co(I)–TDHC (**8a**). The reduction product gave a spectrum identical with that observed for the cobalt(I) complex obtained upon treating with sodium hydroxide. The observed electron transfer from triethylamine to Co(II)–TDHC is of considerable interest since the less hindered amines resulted not in electron transfer but in coordination to Co(II)–TDHC.[41] These results may be interpreted in a consistent manner as follows: (1) the electron transfer takes place appreciably in a long range scheme (outer sphere mechanism), since triethylamine has the least tendency of coordination toward Co(II)–TDHC due to its sterically hindered structure; (2) less hindered amines donate two electrons in a stepwise manner to Co(II)–TDHC microscopically and the first electron is transferred to the Co(II)–TDHC through the outer sphere mechanism. The resulting Co(I)–TDHC intermediate and the electron defficient amine may couple together to give the corresponding coordination compound. The entire mechanistic scheme is given by Eq. (7).

$$\begin{tikzcd}
 & \mathrm{Co(II)\text{-}TDHC} + \mathrm{NR^1R^2R^3} \arrow[d, shift left, leftarrow] \arrow[d, shift right] & \\
 & {[\mathrm{Co(I)\text{-}TDHC} + \cdot\overset{+}{\mathrm{N}}\mathrm{R^1R^2R^3}]} \arrow[dl] \arrow[dr] & \\
\begin{array}{c}\mathrm{Co(I)\text{-}TDHC} + \cdot\overset{+}{\mathrm{N}}\mathrm{R^1R^2R^3}\\ (\mathrm{R^1, R^2, R^3\text{: alkyl}})\end{array} & & \begin{array}{c}\mathrm{R^1R^2R^3N\text{-}Co(II)\text{-}TDHC}\\ (\mathrm{R^1\text{: H and}}\\ \mathrm{R^2, R^3\text{: H or alkyl}})\end{array}
\end{tikzcd} \tag{7}$$

References

1) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, "Bioinorganic Chemistry," ed. by R. F. Gould, Advan. Chem. Ser. No. 100, Amer. Chem. Soc., (1971), p. 44.

2) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Amer. Chem. Soc.*, **96**, 3109 (1974), and references therein.

3) J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *ibid.*, **94**, 5502 (1972).

4) N. Takvoryan, K. Farmery, V. Katovic, F. L. Lovecchio, E. S. Gore, L. B. Anderson, and D. H. Busch, *ibid.*, **96**, 731 (1974).

5) Reviews: (a) H. A. O. Hill, "Inorganic Biochemistry," Vol. 2, ed. by G. L. Eichhorn, Elsevier Scientific Publishing Co., Amsterdam (1973), Chapter 30. (b) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}," Academic Press, London (1972). (c) S. Fukui and T. Toraya, *Kagaku*, **28**, 570, 676, and 786 (1973).

6) Reviews: (a) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968). (b) G. Costa, *Coord. Chem. Rev.*, **8**, 63 (1972). (c) A. Biggotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, **4**, 41 (1970). (d) Y. Murakami, *Kagaku*, **28**, 12 (1973). (e) D. Dodd and M. D. Johnson, *Organometal. Chem. Rev.*, **52**, 1 (1973).

7) G. Costa, G. Mestroni, and L. Stefani, *J. Organometal. Chem.*, **7**, 493 (1967).

8) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *ibid.*, **6**, 181 (1966).

9) G. Costa, G. Mestroni, and E. de Savorgnani, *Inorg. Chim. Acta*, **3**, 323 (1969).

10) D. A. Clark, R. Grigg, and A. W. Johnson, *Chem. Commun.*, **1966**, 208.

11) E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 3201 (1969).

12) K. Farmery and D. H. Busch, *Inorg. Chem.*, **11**, 2901 (1972).

13) N. S. Hush and I. S. Woolsey, *J. Amer. Chem. Soc.*, **94**, 4107 (1972).

14) N. S. Hush and I. S. Woolsey, *J. Chem. Soc., Dalton*, **1974**, 24.

15) Y. Murakami, K. Sakata, Y. Tanaka, and T. Matsuo, This Bulletin, **48**, 3622 (1975).

16) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley Interscience, New York, N. Y. (1970).

17) A. Albert, *J. Chem. Soc.*, **1951**, 1376.

18) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

19) D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc. C*, **1966**, 30.

20) A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, **1961**, 2418.

21) H. W. Whitlock and R. Hanauer, *J. Org. Chem.*, **33**, 2169 (1968).

22) For example: G. P. Ansenault, E. Bullock, and S. F. MacDonald, *J. Amer. Chem. Soc.*, **82**, 4384 (1960).

23) H. Fischer and P. Halbig, *Justus Liebigs Ann. Chem.*, **447**, 123 (1926).

24) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 4024 (1972).

25) C. L. Liotta, H. P. Harris, M. McDermott, T. Gonzalez, and K. Smith, *Tetrahedron Lett.*, **1974**, 2417.

26) H. D. Durst, *ibid.*, **1974**, 2421.

27) R. D. Gillard, *J. Chem. Soc. A*, **1967**, 917.

28) G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

29) R. Yamada, S. Shimizu, and S. Fukui, *Biochemistry*, **7**, 1713 (1968).

30) M. G. Swanwick and W. A. Waters, *J. Chem. Soc. B*, **1971**, 1059.

31) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.* **91**, 3341 (1969).

32) F. A. Walker, *ibid.*, **92**, 4235 (1970).

33) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

34) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

35) C. H. Kirksey and P. Hambright, *ibid.*, **9**, 958 (1970).

36) D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, **95**, 1142 (1973).

37) F. A. Walker, *ibid.*, **95**, 1150 (1973).

38) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, **95**, 1796 (1973).

39) J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, **1958**, 2001.

40) (a) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Amsterdam (1964), Chapter 3. (b) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **92**, 2991 (1970).

41) In the presence of diethylamine at very high concentrations (>0.1 M), the spectrum of Co(II)–TDHC (**7a**) indicated the existence of both Co(I)–TDHC and (diethylamine)–Co(II)–TDHC, suggesting that some electron transfer from diethylamine to Co(II)–TDHC took place.

42) G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer. *J. Chem. Soc. A*, **1970**, 2870.

43) C. M. Elson, A. Hamilton, and A. W. Johnson, *J, Chem. Soc., Perkin I*, **1973**, 775.

44) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 1374 (1971).

45) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *ibid.*, **92**, 5752 (1970).