Structure and Photochemistry of Dicyanocobalt(III) Tetraphenylporphyrin. Photochromic Reaction Caused by Photodissociation of Axial Ligand

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Chlorocobalt(III) tetraphenylporphyrin, (Cl)Co^{III}TPP, reacts with potassium cyanide in dichloromethane or benzene containing 18-crown-6 to give a green solution of [crown-K^+][$(CN)_2Co^{III}TPP^-$]. The molecular structure of [crown-K^+][$(CN)_2Co^{III}TPP^-$] is identified by X-ray crystallography. In methanol, (Cl)Co^{III}TPP plus KCN also gives a green solution of [$(CN)_2Co^{III}TPP^-$]. The green methanol solution containing 1.4×10^{-4} M KCN turns orange by continuous photolysis with a 250-W mercury lamp for 5 min. The orange solution returns to green when it is kept in the dark for 5 min. The kinetic study suggests that [$(CN)_2Co^{III}TPP^-$] dissociates CN^- by continuous photolysis, giving rise to the formation of the orange species, $(CH_3OH)(CN)Co^{III}$TPP. The photoproduct, $(CH_3OH)(CN)Co^{III}$TPP, regenerates the green species, [$(CN)_2Co^{III}TPP^-$], by reaction with CN^-. The laser photolysis study of [$(CN)_2Co^{III}TPP^-$] in methanol demonstrates that photodissociation of CN^- takes place within 20 ns after the 355-nm laser pulse, resulting in the formation of two transients, **I** (short-lived) and **II** (long-lived). The absorption spectra of both transients are similar to that of $(CH_3OH)(CN)Co^{III}$TPP. These transients eventually return to [$(CN)_2Co^{III}TPP^-$]. The decay of species **I** follows first-order kinetics with a rate constant $k = 2 \times 10^6$ s^{-1}, independent of the concentration of KCN. Species **II** is identified as $(CH_3OH)(CN)Co^{III}$TPP, which is observed with the continuous photolysis of the solution. The laser photolysis of [crown-K^+][$(CN)_2Co^{III}TPP^-$] in dichloromethane gives the transient species, which goes back to the original complex according to first-order kinetics with a rate constant $k = 5 \times 10^6$ s^{-1}. [crown-K^+][$(CN)_2Co^{III}TPP^-$] is concluded to photodissociate the axial CN^- to form [crown-K^+CN^-][$(CN)Co^{III}$TPP] in which an oxygen atom of the crown moiety in [crown-K^+CN^-] is coordinated to the cobalt(III) atom of [$(CN)Co^{III}$TPP] at the axial position. The intracomplex reverse reaction of [crown-K^+CN^-][$(CN)Co^{III}$TPP] leads to the regeneration of [crown-K^+][$(CN)_2Co^{III}TPP^-$]. The structure and the reaction of the transient species **I** observed for [$(CN)_2Co^{III}TPP^-$] in methanol are discussed on the basis of the laser photolysis studies of [crown-K^+][$(CN)_2Co^{III}TPP^-$] in dichloromethane.

Introduction

Synthetic metalloporphyrins with the central metals Fe^{III}, Co^{III}, and Mn^{III} react with CN^- to give dicyanide complexes.[1−14] In particular, the cyanide complexes of Fe^{III} porphyrins have been extensively studied by X-ray crystallography, NMR, electron spin resonance, and Raman spectroscopy for an understanding of the effects of the axial CN^- on the electronic structures.[1−9]

The molecular structures of the cyano-metalloporphyrins studied hitherto are limited to Fe^{III} and Mn^{III} porphyrins,[1,12,14] which have two CN^- anions at the axial positions. The crystal structures of the cyanide complexes of cobalt porphyrins have not been reported. This is partly because of the difficulty in preparation of the crystals of the cyanide complex.

Studies on the interaction between cyanide anions and Co^{III} complexes are important not only in coordination chemistry but also in toxicology. Because of the high affinity of CN^- anions for cobalt complexes, hydroxocobalamin[15−17] and water-soluble Co^{III} porphyrins[18] have been investigated as an effective antidote

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to the lethal effects of cyanide anions. The mechanism of the detoxification clearly involves the formation of cyanide complexes.

In previous papers, we have studied photochemical reactions of Co^{III} porphyrins with neutral axial ligands, pyridine and isonitriles.[19,20] These complexes readily undergo photodissociation of the axial ligands to give Co^{III} porphyrins. However, the Co^{III} porphyrins with anionic axial ligands such as Cl^- and NO_2^- were found to yield Co^{II} porphyrins by photolysis.[19,21] In the present study, we examined the photochemical reactions of the cyanide complexes of Co^{III} tetraphenylporphyrins, which have two CN^- at the axial positions.

This paper reports (1) the crystal structure of the dicyanide complex of cobalt(III) tetraphenylporphyrin, in which the counterion is K^+ trapped in 18-crown-6, (2) the mechanistic studies for the formation of the dicyanide complex of cobalt(III) tetraphenylporphyrin, $[(CN)_2Co^{III}TPP^-]$, in methanol, and (3) the photochemical reactions of $[(CN)_2Co^{III}TPP^-]$ studied by continuous photolysis and nanosecond laser flash photolysis.

Experimental Section

Reagent-grade potassium cyanide, 18-crown-6, toluene, benzene, dichloromethane, and methanol were used without further purification. Chlorocobalt(III) tetraphenylporphyrin, $(Cl)Co^{III}TPP$, was synthesized and purified according to the procedure previously reported.[22]

The crown complex, $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$, was synthesized according to the method described below. To a 200-cm^3 benzene solution of $(Cl)Co^{III}TPP$ (1.0 g) and 18-crown-6 (2.0 g), KCN (0.5 g) was added with vigorous stirring for 2.0 h at room temperature. After filtration of the solid residuals from the reaction mixture, hexane was slowly added to the solution. The dark green crystals of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$ thus obtained were recrystallized twice from toluene solutions. ^{1}NMR (500 MHz, $CDCl_3$, the solvent peak at δ 7.24 was used as an internal standard): δ 8.75 (8H, s), δ 8.09 (8H, d), δ 7.62 (12H, m), δ 2.65 (24H, s). Anal. Calcd for $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]\cdot{}^1/_2CH_3C_6H_5\cdot H_2O$: C, 67.70; H, 5.32; N, 7.71. Found: C, 67.53; H, 5.32; N, 7.63. For the structure determination by X-ray crystallography, $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$ was recrystallized again from the toluene solution.

Diffraction data of a single crystal of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]\cdot{}^1/_2CH_3C_6H_5\cdot H_2O$ (0.47 × 0.09 × 0.06 mm) were collected on a Rigaku Raxis-CS2 imaging plate diffractometer equipped with graphite-monochromated Mo Kα radiation and a cooling device operating at 115 K. Indexing was performed from three oscillation images, which were exposed for 4.0 min. The camera radius was 143.5 mm. Readout was performed in the 0.1-mm pixel mode. Cell constants and an orientation matrix for data collections corresponded to a monoclinic cell with the following dimensions: $a = 20.024(3)$ Å, $b = 25.386(6)$ Å, $c = 22.64(1)$ Å, $\beta = 103.562(3)°$, and $V = 11\,186(5)$ Å^3. The calculated density is 1.30 g/cm^3 for $Z = 4$, and the formula weight is 2182.4. The space group is uniquely determined to be $P2_1/n$ (No. 14) by the systematic absences of $h0l$, $h + 1 = 2n + 1$, and $0k0$, $k = 2n + 1$.

The intensity data were collected to a maximum 2θ value of 60.1°. A total of 40 frames with 3.0° oscillation images were collected, each being exposed for 30 min. A total of 16 728 reflections were collected. The data were corrected for Lorentz and polarization effects but not for absorption effects.

The structure was solved by direct methods[23] and expanded using Fourier methods. The non-hydrogen atoms were refined isotropically. Hydrogen atoms in the structure were included but not refined. The final cycle of full-matrix least-squares refinement was based on 7387 observed reflections ($I > 3.0\sigma(I)$) and converged (largest parameter shift was 0.03 times its standard deviation) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.137$, $R_w = \{\sum w(|F_o| - |F_c|)^2/wF_o{}^2\}^{1/2} = 0.210$. The standard deviation for an observation of unit weight was 1.68. The weighting scheme was based on counting statistics and included a factor ($p = 0.20$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.85 and -1.14 e$^-$/Å^3, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were included in F_c;[25] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[26] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[27] All calculations were performed using the TeXsan[28] crystallographic software package.

Absorption spectra were recorded on a Hitachi 330 spectrophotometer. Laser photolysis was carried out with a Nd:YAG laser (model HY 500 from JK Lasers Ltd.) equipped with second (532 nm), third (355 nm), and fourth (266 nm) harmonic generators. The transient spectra were measured by the ICCD detector (DH520-18F-01 from Andor Technology Ltd.). To monitor the decay of the transient absorption, the output from the photomultiplier (R 758 from Hamamatsu) was conducted to the digital storage oscilloscope (model Gould 630 from Gould Instrument System Ltd.). A 250-W mercury lamp (USH 250 D from Ushio Inc.) with cutoff filters was used as a light source for continuous photolysis.

Results

Structure of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$. Figure 1 shows the molecular structure of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$ determined by X-ray crystallography. From the projection of the *ac* plane, the dicyanocobalt(III) porphyrin in crystals was found to have the structure $\{[crown\text{-}K^+\cdot H_2O]_2[(CN)_2Co^{III}TPP^-]\}[(CN)_2Co^{III}TPP^-]\cdot C_7H_8$, in which one of the two $[(CN)_2Co^{III}TPP^-]$ takes two $[crown\text{-}K^+]$. Two water molecules, O13 and O15, were refined with a disorder model. The atomic coordinates except for hydrogen atoms are listed in Table 1S. Bond distances and angles are listed in Tables 2S and 3S, respectively.

Figure 2 shows the perspective view of the $\{[crown\text{-}K^+\cdot H_2O]_2[(CN)_2Co^{III}TPP^-]\}^+$ moiety with the disordered H_2O molecules. Selected interatomic distances are listed in Table 1. The Co−C(CN) separations are 1.98(2) and 1.94(2) Å. These values are close to that of vitamin B_{12} (1.92 Å).[29] The C−N bond lengths of the cyanide ions, 1.09(2) and 1.13(2) Å, are similar to those of $[(CN)_2Mn^{III}TPP^-]$ (1.15(2) and 1.16(2) Å)[12]

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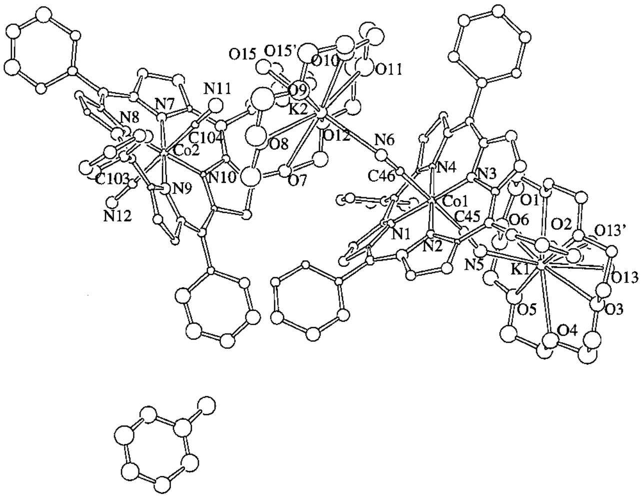

Figure 1. Stereoscopic view of $\{[\text{crown-K}^+\cdot\text{H}_2\text{O}]_2[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]\}[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]\cdot\text{C}_7\text{H}_8$.

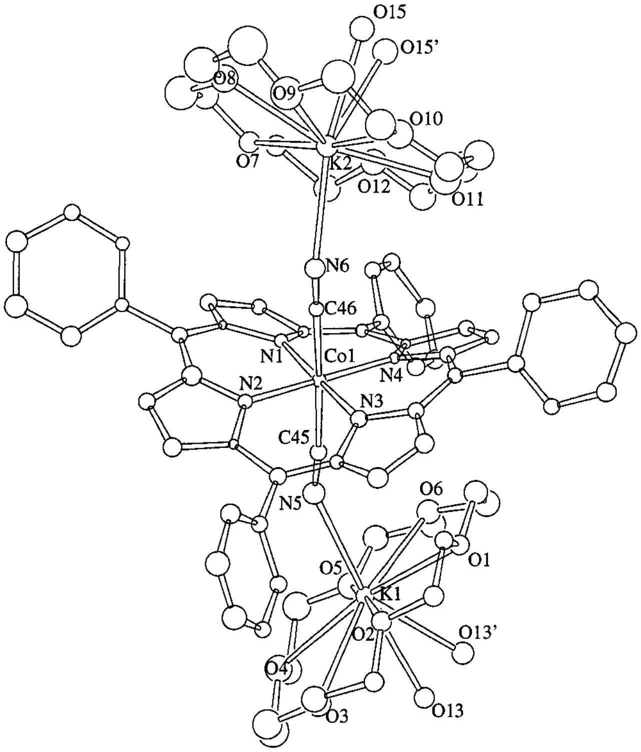

Figure 2. Molecular structure of the $[\text{crown-K}^+\cdot\text{H}_2\text{O}]_2[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ moiety with disordered H_2O molecules.

and $[(\text{CN})_2\text{Fe}^{\text{III}}\text{TPP}^-]$ (1.147(3) Å).[1] Because the distance N11−O15 (and O13) is 2.77−2.85 Å, a hydrogen bond is probably formed between CN (N11) and H_2O (O13 or O15).

The C_{CN}−Co−C_{CN} bond angle is obtained as 176.3(8)°. Thus, the C_{CN}−Co−C_{CN} bond is almost linear as in the cases of $[(\text{CN})_2\text{Mn}^{\text{III}}\text{TPP}^-]$ and $[(\text{CN})_2\text{Fe}^{\text{III}}\text{TPP}^-]$. The N−C−Co angles are 174(2)/178(2) and 175(2)/176(2)°, indicating that the CN groups are linearly coordinated to the central cobalt atom.

The ^{1}H NMR spectrum measured in $CDCl_3$ is interpreted in terms of the formation of $[\text{crown-K}^+][(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ by dissolving the crystals of $\{[\text{crown-K}^+]_2[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]\}[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$.

The absorption spectrum of $[\text{crown-K}^+][(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ in a dichloromethane (CH_2Cl_2) solution differs markedly from that of $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$. The absorption peaks of $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$ in CH_2Cl_2 are located at 406 nm ($\epsilon = 1.27 \times 10^5$ M^{-1} cm^{-1}) and 540 nm ($\epsilon = 1.36 \times 10^4$ M^{-1} cm^{-1}). However, $[\text{crown-K}^+][(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ in CH_2Cl_2 gives absorption peaks at 625 and 580 nm in the Q-band region and at 447 nm ($\epsilon = 1.02 \times 10^5$ M^{-1} cm^{-1}) in the Soret band region. In comparison with $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$, the two bands show a remarkable shift to red when the dicyanide complex is formed.

Table 1. Selected Bond Distances[a]

atoms	distance	atoms	distance
Co(1)−N(1)	1.94(1)	K(1)−O(6)	2.80(2)
Co(1)−N(2)	1.92(1)	K(1)−O(13)	2.74(2)
Co(1)−N(3)	1.94(2)	K(1)−O(13′)	2.77(3)
Co(1)−N(4)	1.94(1)	K(1)−N(5)	2.81(2)
Co(1)−C(45)	1.94(2)	K(2)−O(7)	2.83(1)
Co(1)−C(46)	1.98(2)	K(2)−O(8)	2.82(2)
Co(2)−N(7)	1.96(2)	K(2)−O(9)	3.00(2)
Co(2)−N(8)	1.92(2)	K(2)−O(10)	2.71(2)
Co(2)−N(9)	1.94(2)	K(2)−O(11)	2.82(2)
Co(2)−N(10)	1.91(1)	K(2)−O(12)	2.88(2)
Co(2)−C(103)	1.93(2)	K(2)−O(15)	2.80(3)
Co(2)−C(104)	1.88(2)	K(2)−O(15′)	2.78(3)
K(1)−O(1)	2.78(1)	K(2)−N(6)	2.84(2)
K(1)−O(2)	2.80(1)	N(5)−C(45)	1.13(2)
K(1)−O(3)	2.92(2)	N(6)−C(46)	1.09(2)
K(1)−O(4)	2.94(2)	N(11)−C(104)	1.22(2)
K(1)−O(5)	2.77(2)	N(12)−C(103)	1.16(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

As will be described later, the absorption spectrum of $[\text{crown-K}^+][(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ in CH_2Cl_2 is similar to that of $[(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ in methanol. The absorption peaks of the Soret and Q bands of the latter are slightly red-shifted in comparison with those of the former because of solvent effects. The photochemical product cannot be detected upon continuous irradiation of $[\text{crown-K}^+][(\text{CN})_2\text{Co}^{\text{III}}\text{TPP}^-]$ in dichloromethane by the mercury lamp with a cutoff filter ($\lambda < 360$ nm) for 20 min.

Reaction of (Cl)Co$^{\text{III}}$TPP and KCN in Methanol. According to the previous conductometric studies, $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$ in alcohols undergoes ionic dissociation:[30]

$$(\text{Cl})\text{Co}^{\text{III}}\text{TPP} + 2\text{CH}_3\text{OH} \rightarrow [(\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+][\text{Cl}^-] \tag{1}$$

$$[(\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+][\text{Cl}^-] \rightleftarrows (\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+ + \text{Cl}^- \tag{2}$$

The major species (99.6%) of $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$ (ca. $<10^{-4}$ M) in methanol is the six-coordinate species $(\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+$. The molar absorption coefficient, ϵ, of $(\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+$ in methanol has been obtained as 2.73×10^5 M^{-1} cm^{-1} at 425 nm.

Figure 3 shows the absorption spectra observed for the methanol solution of 1.5×10^{-5} M $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$ at various concentrations of KCN. At low concentrations of KCN ([KCN] $< 3.86 \times 10^{-5}$ M), the absorption peak of $(\text{Cl})\text{Co}^{\text{III}}\text{TPP}$ located at 426 nm shifts slightly to red by ca. 3 nm with an increase in the concentration of KCN. The small change in the absorption spectrum is likely to result from the formation of $(\text{CH}_3\text{OH})(\text{CN})\text{Co}^{\text{III}}\text{TPP}$:

$$(\text{CH}_3\text{OH})_2\text{Co}^{\text{III}}\text{TPP}^+ + \text{CN}^- \rightleftarrows (\text{CH}_3\text{OH})(\text{CN})\text{Co}^{\text{III}}\text{TPP} + \text{CH}_3\text{OH} \tag{3}$$

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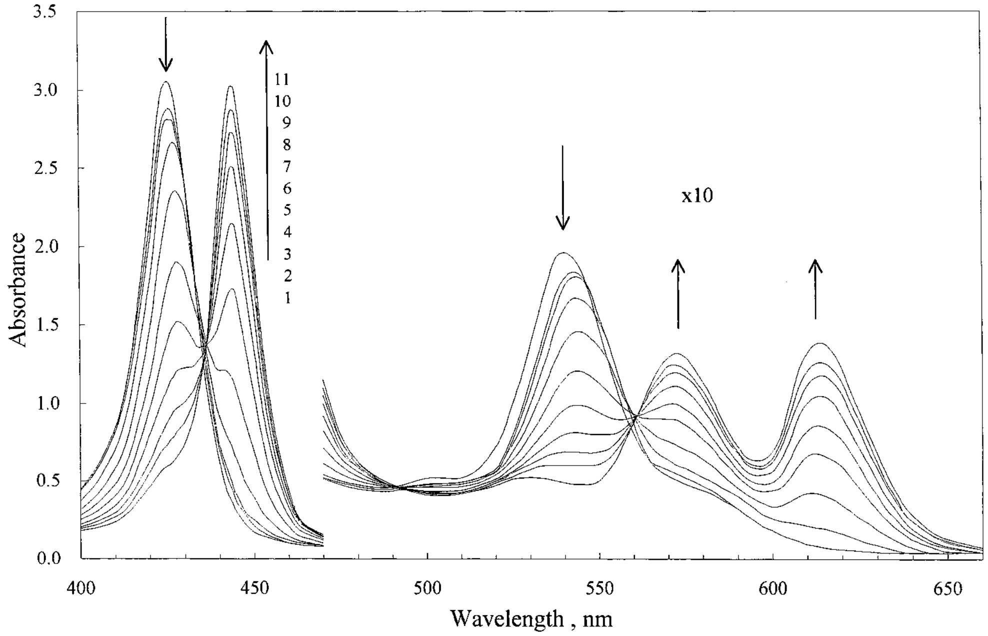

Figure 3. Absorption spectral changes observed for the methanol solution of (Cl)Co^{III}TPP at various concentrations of KCN: (1) 0.0 M, (2) 9.65 × 10^{-6} M, (3) 1.93 × 10^{-5} M, (4) 4.86 × 10^{-5} M, (5) 5.79 × 10^{-5} M, (6) 7.72 × 10^{-5} M, (7) 9.65 × 10^{-5} M, (8) 1.16 × 10^{-4} M, (9) 1.35 × 10^{-4} M, (10) 1.54 × 10^{-4} M, and (11) 7.7 × 10^{-4} M.

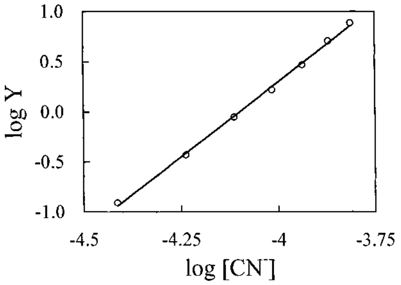

Figure 4. Plot of log *Y* vs log [CN$^-$] (see text).

The equilibrium reaction 3 mostly shifts to the right side at [KCN] = 3.86 × 10^{-5} M.

A remarkable change in the absorption spectrum is observed when [KCN] > 3.86 × 10^{-5} M: new absorption bands appear at 443, 572, and 612 nm. The spectral change at higher concentrations of KCN is interpreted in terms of the further association of CN$^-$ to (CH$_3$OH)(CN)Co^{III}TPP:

$$(\mathrm{CH_3OH})(\mathrm{CN})\mathrm{Co^{III}TPP} + n\mathrm{CN^-} \overset{K_n}{\rightleftharpoons} [(\mathrm{CN})_{n+1}\mathrm{Co^{III}TPP}]^{n-} + \mathrm{CH_3OH} \quad (4)$$

From eq 4, the absorbance at wavelength λ, D^λ, is formulated as[5]

$$Y = (D^\lambda - D_0^{\ \lambda})/(D^\lambda - D_\infty^{\ \lambda}) = K_n[\mathrm{CN^-}]^n \qquad (5)$$

where D_0^λ and D_∞^λ are the absorbances at [KCN] = 3.86 × 10^{-5} M and at an "infinite" concentration of CN$^-$, respectively. Equation 5 is rewritten as

$$\log(Y) = \log(K_n) + n\log[\mathrm{CN^-}] \qquad (6)$$

Figure 4 shows the plot of log *Y* obtained at λ = 440 nm vs log[CN$^-$]. The plot gives a straight line with a slope n = 3.0 and the intercept log(K_n) = 12.3 (±0.2) by least-squares fittings. The former value, n = 3, implies that three CN$^-$ ions are necessary for the formation of the green species. However, cobalt porphyrin has only two axial positions, and thus coordination of three CN$^-$ to the central cobalt atom of (CH$_3$OH)(CN)Co^{III}TPP is very unlikely. The assumption that KCN is fully dissociated in methanol leads to [CN$^-$] = [K$^+$]. Thus, one CN$^-$ and two K$^+$ are presumably responsible for n = 3:

$$(\mathrm{CH_3OH})(\mathrm{CN})\mathrm{Co^{III}TPP} + \mathrm{CN^-} + 2\mathrm{K^+} \overset{K_3}{\rightleftharpoons} \{[\mathrm{K^+}]_2[(\mathrm{CN})_2\mathrm{Co^{III}TPP^-}]\}^+ + \mathrm{CH_3OH} \quad (7)$$

The spectroscopic studies mentioned above suggest that the green species produced by the reaction of (Cl)Co^{III}TPP and KCN in methanol is a cationic species, {[K$^+$]$_2$[(CN)$_2$Co^{III}TPP$^-$]}$^+$, in which two CN$^-$ ions are coordinated to the central cobalt atom. It is likely that two K$^+$ are necessary to stabilize the green anionic species, [(CN)$_2$Co^{III}TPP$^-$], in methanol.

The ^{1}H NMR spectra (500 MHz, CD$_3$OD, tetramethylsilane is used as an internal standard) were measured for (Cl)Co^{III}TPP and the green species, [(CN)$_2$Co^{III}TPP$^-$]. The former gives δ 9.34 (8H, s), δ 8.26 (8H, d), and δ 7.87 (12H, m), and the latter gives δ 8.74 (8H, s), δ 8.14 (8H, d), and δ 7.72 (12H, m). These NMR spectra indicate that both (CH$_3$OH)$_2$Co^{III}TPP$^+$ and [(CN)$_2$Co^{III}TPP$^-$] have C_{4h} symmetry; the ortho protons of the phenyl group in these porphyrins are equivalent. The δ value of the pyrrole proton in the cobalt(III) porphyrin markedly shifts to the higher field by the effects of the CN$^-$ coordination.

Isolation and crystallization of both (CH$_3$OH)(CN)Co^{III}TPP and [(CN)$_2$Co^{III}TPP$^-$] from the methanol, ethanol, and acetone solutions was not successful. When the solution is concentrated, the cyanide complexes readily polymerize to give fine powders that are insoluble in both organic and inorganic solvents.

Photochromic Reaction of [(CN)$_2$Co^{III}TPP$^-$] in Methanol. When a methanol solution of 1.1 × 10^{-5} M (Cl)Co^{III}TPP containing 1.4 × 10^{-4} M KCN was irradiated by a 250-W mercury lamp with a cutoff filter (λ < 360 nm) for 5.0 min, the color of the solution turned from green to orange. The absorption spectrum observed at 5 s after 5.0 min of irradiation was found to be almost identical with that of (CH$_3$OH)(CN)Co^{III}TPP. The original absorption spectrum was restored when

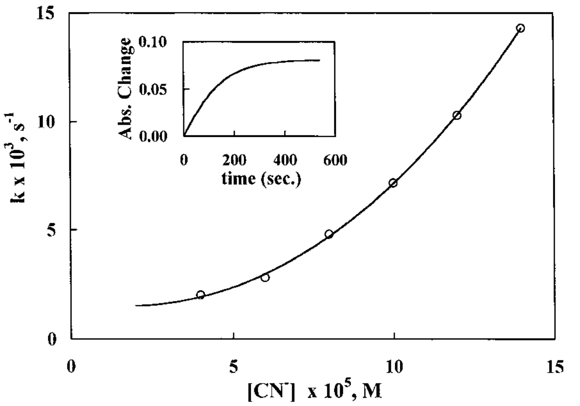

Figure 5. Rate constants, *k*, for regeneration of $[(CN)_2Co^{III}TPP^-]$ in methanol, represented as a function of [CN]. The inset is the rise curve of the absorbance change at 445 nm observed after the continuous photolysis of $[(CN)_2Co^{III}TPP^-]$ in methanol containing 1.88×10^{-4} M KCN.

the irradiated solution was preserved in the dark for 10 min. On the basis of these findings, the photochemical reaction of $[(CN)_2Co^{III}TPP^-]$ is expressed by eq 8.

$$\{[K^+]_2[(CN)_2Co^{III}TPP^-]\}^+ + CH_3OH \overset{h\nu}{\rightleftharpoons} (CH_3OH)(CN)Co^{III}TPP + CN^- + 2K^+ \quad (8)$$

The orange product, $(CH_3OH)(CN)Co^{III}TPP$, regenerates $\{[K^+]_2[(CN)_2Co^{III}TPP^-]\}^+$ according to eq 8. Hereafter, we denote $\{[K^+]_2[(CN)_2Co^{III}TPP^-]\}^+$ in methanol as $[(CN)_2Co^{III}TPP^-]$.

As shown in the inset of Figure 5, the rate for the regeneration of $[(CN)_2Co^{III}TPP^-]$ was measured by monitoring the absorbance, *D*, of the irradiated solution at 445 nm. The increase in *D* strictly follows first-order kinetics with the rate constant *k*.

$$(D_\infty - D) = (D_\infty - D_0)\,[1 - \exp(-kt)] \quad (9)$$

Here D_0 and D_∞ are the absorbances at 455 nm measured at $t = 0$ and at an "infinite" time after 5.0 min irradiation by the mercury lamp, respectively.

Figure 5 shows the plot of *k* represented as a function of the concentration of CN^-. The plot exhibits a concave upward curve with an increase in the concentration of CN^-. From eq 7, the rate constant *k* for the regeneration of $[(CN)_2Co^{III}TPP^-]$ is formulated as

$$k = k_b + k_f[CN^-][K^+]^2 = k_b + k_f[CN^-]^3 \quad (10)$$

where k_f is the forward rate constant of eq 7 and k_b is the backward rate constant: $K_3 = k_f/k_b$. The k_b value is estimated as 1.5×10^{-3} s^{-1} from Figure 5. The plot of $\log(k - k_b)$ versus $\log[CN^-]$ gives a straight line with a slope of 3 and the intercept $\log k_f = 9.7 \pm 0.1$ by least-squares fittings. From k_f and k_b obtained here, $\log K_3$ is calculated as 12.5 ± 0.2. This value is in good agreement with that (12.3 ± 0.2) obtained from the spectroscopic studies described above.

Laser Photolysis of $[(CN)_2Co^{III}TPP^-]$ in Methanol. The 355-nm laser photolysis studies were carried out for the green methanol solution containing 1.1×10^{-5} M $[(CN)_2Co^{III}TPP^-]$ and 1.23×10^{-2} M KCN. Figure 6 shows the transient spectra detected at 20 ns and 1 μs after a laser pulse. The transient spectrum (a) was detected at 20-ns decays according to first-order kinetics with a rate constant of 8.4×10^6 s^{-1}, leaving the transient spectrum (b) detected at 1.0 μs, which decays over a few milliseconds. The 20-ns spectrum has a positive peak at 435 nm and a negative one at 448 nm. The 1.0-μs spectrum has positive and negative peaks at 430 and 445 nm, respectively. No permanent products were observed after photolysis, indicating that the two transient species, **I** (short-lived) and **II** (long-lived), are produced by the laser flash photolysis. Both transients, **I** and **II**, eventually return to $[(CN)_2Co^{III}TPP^-]$. The rate constant for the decay of the transient **I** is found to be independent of the concentration of CN^- in the concentration range between 1.0×10^{-4} and 1.23×10^{-2} M.

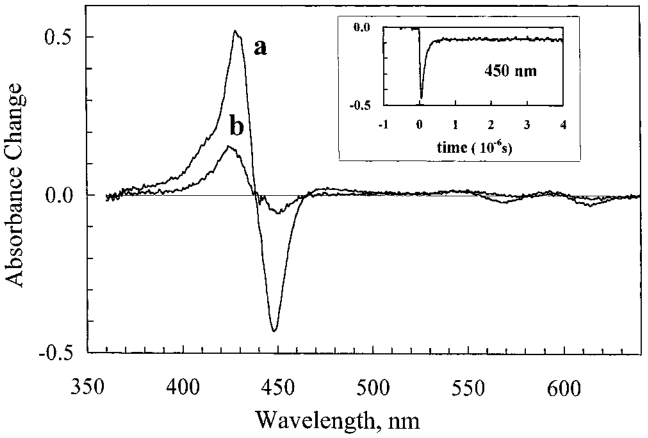

Figure 6. Transient absorption spectra observed for the methanol solution of 1.1×10^{-5} M $[(CN)_2Co^{III}TPP^-]$ and 1.23×10^{-2} M KCN at (a) 20 ns and (b) 1.0 μs after the 355-nm laser pulse. The inset is the decay of the absorbance monitored at 450 nm.

The absorption spectra of the transients were obtained with the method previously reported.[31,32] When the parent molecule gives the transient species after the laser pulse, the absorbance change at λ, $\Delta D(\lambda)$, is given by

$$\Delta D(\lambda) = \alpha(D_{tr}(\lambda) - D_0(\lambda)) \quad (11)$$

Here α is a variable number, $0 < \alpha < 1.0$, dominated by the energy of the laser pulse; $D_{tr}(\lambda)$ and $D_0(\lambda)$ are the absorbances of the transient species and the parent molecule, respectively. Equation 11 is rewritten as

$$D_{tr}(\lambda) = D_0(\lambda) + \Delta D(\lambda)/\alpha \quad (12)$$

With the use of various α, $D_{tr}(\lambda)$ is obtained as a function of λ. When the α value is appropriate, the plot of $D_{tr}(\lambda)$ versus λ gives the absorption spectrum of the transient species. The appropriate value of α is determined on the basis of the assumption that the transient species has a smooth and undistorted absorption band in the Soret band region. From the transient absorption spectra detected at 20 ns and 1 μs, the absorption spectrum of the transient **I** was found to have a Soret band peak at 439 ± 2 nm with $\epsilon = (2.5 \pm 0.3) \times 10^5$ M^{-1} cm^{-1}. Similarly, the transient **II** exhibits the Soret band peak at 430 ± 2 nm with $\epsilon = (2.3 \pm 0.3) \times 10^5$ M^{-1}cm^{-1}. The absorption spectrum of the transient **II** is found to be almost identical with that of $(CH_3OH)(CN)Co^{III}TPP$ in methanol.

The quantum yields, ϕ, for the formation of the two transients were determined with the use of the laser photolysis method. The absorbance change, $\Delta D(\lambda)$, observed for $[(CN)_2Co^{III}TPP^-]$ in methanol at 20 ns after the 355-nm pulse is represented by[33]

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$$\Delta D(\lambda) = \phi\, \Delta\epsilon(\lambda)\, I_{\mathrm{abs}}\, N_{\mathrm{A}}^{-1} \qquad (13)$$

Here I_{abs}, $\Delta\epsilon(\lambda)$, and N_{A} are the number of photons absorbed, the difference in the molar absorption coefficient at λ between $[(CN)_2Co^{III}TPP^-]$ and the transient, and Avogadro's number, respectively. For determination of I_{abs}, a benzene solution of benzophenone with the same absorbance at 355 nm as that for the methanol solution of $[(CN)_2Co^{III}TPP^-]$ was used as a standard solution for monitoring the T−T absorption of the triplet benzophenone after the pulse. The absorbance, ΔD_{T}, of the triplet benzophenone at 20 ns after the pulse is described as

$$\Delta D_{\mathrm{T}} = \phi_{\mathrm{T}}\epsilon_{\mathrm{T}} I_{\mathrm{abs}} N_{\mathrm{A}}^{-1} \qquad (14)$$

where ϕ_{T} is the triplet yield of benzophenone ($\phi_{\mathrm{T}} = 1.0$) and ϵ_{T} is the molar absorption coefficient of the triplet benzophenone ($\epsilon_{\mathrm{T}} = 7.8 \times 10^3$ M^{-1} cm^{-1} at 530 nm) in benzene.[34] From eqs 13 and 14, ϕ is expressed as

$$\phi = \phi_{\mathrm{T}}(\epsilon_{\mathrm{T}}/\Delta\epsilon)^{-1}(\Delta D/\Delta D_{\mathrm{T}}) \qquad (15)$$

With the use of the molar absorption coefficients of the transients **I** and **II**, the quantum yields for the formation of the transients **I** and **II** are determined as 0.1 (±0.02) and 0.02 (±0.005), respectively.

Laser Photolysis of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$. The laser photolysis studies of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ in a dichloromethane solution were carried out. Figure 7 shows the transient absorption spectrum observed for 1.0×10^{-5} M $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ after 355-nm laser pulsing. The spectrum measured at 20 ns after the pulse has a positive band at 440 nm and a negative one at 460 nm. From the transient spectrum, the Co−CN bond in $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ is concluded to be dissociated upon laser flash photolysis. The decay of the transient strictly follows first-order kinetics with the rate constant of 6.2×10^5 s^{-1}. Thus, the structure of the transient is suggested to be $[\text{crown-K}^+CN^-][(CN)Co^{III}TPP]$. Presumably, the oxygen atom in the $[\text{crown-K}^+CN^-]$ moiety is coordinated to the central cobalt atom. The photochemical reaction of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ is illustrated in Scheme 1.

In methanol and ethanol solutions, $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ (ca. 1.0×10^{-5} M) thermally decomposes within 30 min to give an orange solution. The product exhibits an absorption spectrum identical with that of $(CH_3OH)(CN)Co^{III}TPP$ in methanol. Irradiation of the solution by the mercury lamp accelerated the rate for the decomposition. The laser photolysis of the methanol solution revealed that the transient spectrum detected at 20 ns after the pulse is similar to the difference spectrum obtained by subtracting the spectrum of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ from that of $(CH_3OH)(CN)Co^{III}TPP$. The decay of the transient follows first-order kinetics with a rate constant of 1.0×10^7 s^{-1}, leaving the photoproduct, $(CH_3OH)(CN)Co^{III}TPP$. In Table 2 are listed the decay rate constants of the transient measured after laser photolysis of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ in several solvents. The rate constants obtained with methanol and ethanol solutions are much larger than those with nonalcoholic solutions. It is noted that the thermal and photoaccelerated decomposition of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ is limited to the alcoholic solutions studied.

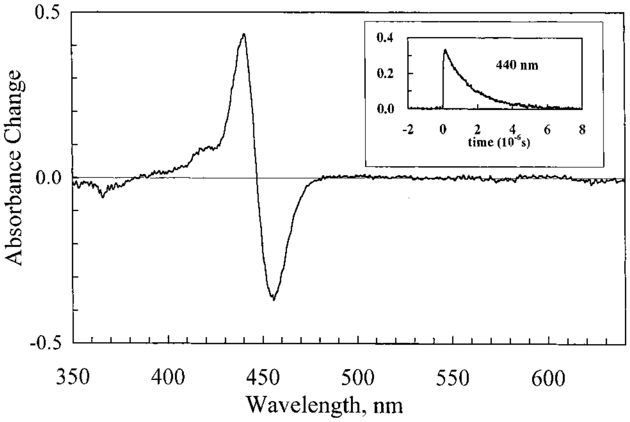

Figure 7. Transient absorption spectrum observed for the dichloromethane solution of 1.0×10^{-5} M $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ at 20 ns after the 355-nm laser pulse. The inset is the decay of the absorbance monitored at 440 nm.

Scheme 1

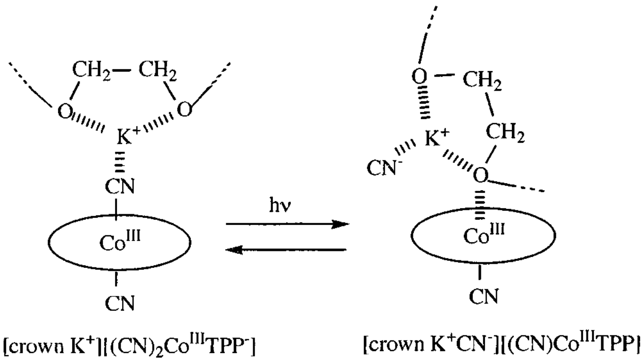

Table 2. First-Order Decay Rate Constants of the Transient Species Produced by Laser Photolysis of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ in Several Solvents

solvent	rate constant × 10^{-6}, s^{-1}	solvent	rate constant × 10^{-6}, s^{-1}
toluene	0.73	acetone	0.66
dichloromethane	0.62	ethanol	3.3
acetonitrile	0.59	methanol	10.3

Discussion

A methanol solution of $(Cl)Co^{III}TPP$ changes its color from red to green with the addition of KCN. Although isolation of the green species from the methanol solution could not be done, the origin of the green solution is ascribed to the formation of the dicyanide complex, $[(CN)_2Co^{III}TPP^-]$. A similar color change is also observed when KCN and 18-crown-6 are added to a benzene solution of $(Cl)Co^{III}TPP$. The X-ray structure determination of $[\text{crown-K}^+][(CN)_2Co^{III}TPP^-]$ indicates that the two axial cyanide anions are necessary for the observed color change of $Co^{III}TPP^+$.

A number of studies on the ligand exchange reaction of iron(III) porphyrins by cyanide ions have been carried out.[6,31,35−37] The formation of the dicyanide complexes of iron(III) porphyrins has been interpreted in terms of the stepwise ligand exchange mechanism.[1] The monocyanide complex initially produced further reacts with CN$^-$, resulting in the formation of the dicyanide complex of iron(III) porphyrins.

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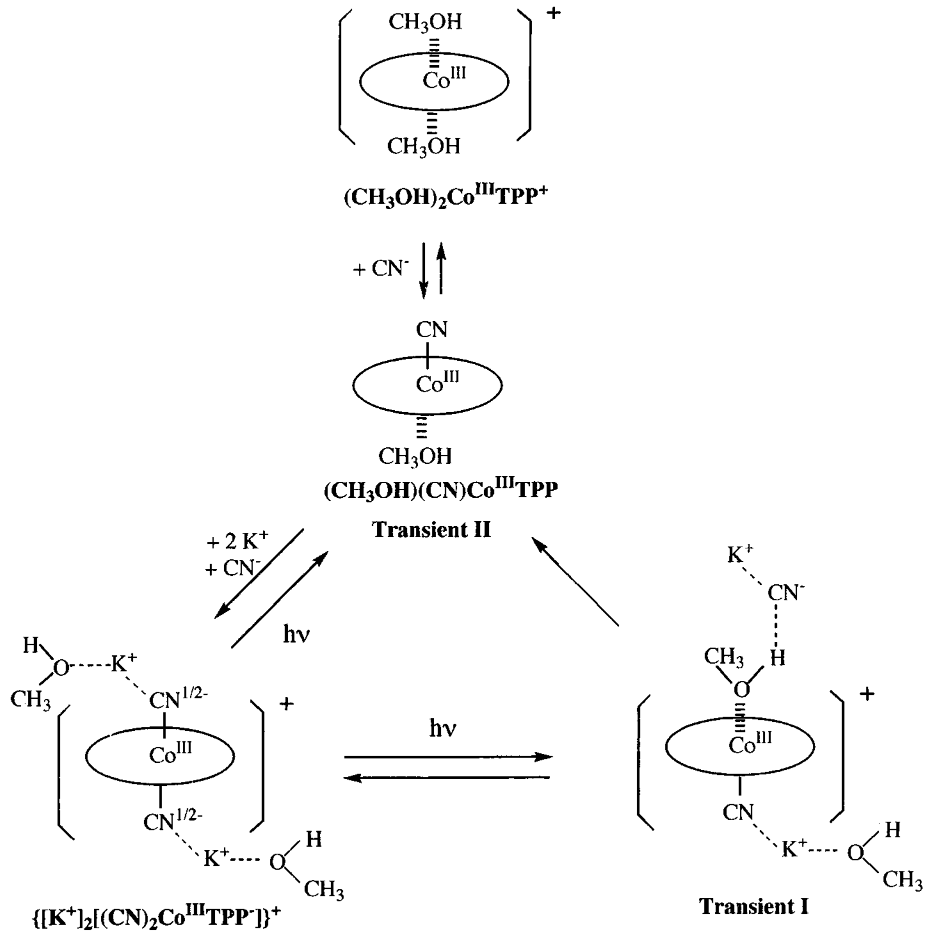
Scheme 2



A methanol solution of 1.1 × 10^{-5} M $(Cl)Co^{III}TPP$ also exhibits stepwise equilibria by the addition of KCN; the first step equilibrium at [KCN] < 3.86 × 10^{-5} M is ascribed to the formation of $(CH_3OH)(CN)Co^{III}TPP$, and the second step is ascribed to the formation of the green species. The ^1H NMR measurement of the green species in CD_3OD reveals that the chemical shifts of the pyrrole and phenyl protons are close to those of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$. Thus, the green species in methanol is ascribed to $[(CN)_2Co^{III}TPP^-]$.

The spectroscopic titration of $(CH_3OH)_2Co^{III}TPP^+$ by KCN in methanol indicates that two K^+ and two CN^- ions are necessary for the formation of the stable green species, $[(CN)_2Co^{III}TPP^-]$. The counterions, K^+, are suggested to stabilize $[(CN)_2Co^{III}TPP^-]$ in methanol solutions.

A methanol solution of ca. 1.0 × 10^{-5} M $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$ gradually decomposes to yield $(CH_3OH)(CN)Co^{III}TPP$.

$$[crown\text{-}K^+][(CN)_2Co^{III}TPP^-] + CH_3OH \rightleftarrows [crown\text{-}K^+] + CN^- + (CH_3OH)(CN)Co^{III}TPP \quad (16)$$

Probably, $[(CN)_2Co^{III}TPP^-]$ in methanol is not stable unless the counterion $[crown\text{-}K^+]$ is located nearby the axial CN^-.

The methanol solution of $[(CN)_2Co^{III}TPP^-]$ displays photochromism. The continuous photolysis of $[(CN)_2Co^{III}TPP^-]$ in methanol containing KCN gives $(CH_3OH)(CN)Co^{III}TPP$ as a photoproduct, which thermally returns to $[(CN)_2Co^{III}TPP^-]$. The kinetic studies on the regeneration of $[(CN)_2Co^{III}TPP^-]$ clearly indicate that, in agreement with the spectroscopic titration study mentioned above, two K^+ ions and one CN^- ion are essential for the formation of $[(CN)_2Co^{III}TPP^-]$ from $(CH_3OH)(CN)Co^{III}TPP$. The laser photolysis of $[(CN)_2Co^{III}TPP^-]$ in methanol gives transients **I** and **II**. The long-lived transient **II** is assigned to $(CH_3OH)(CN)Co^{III}TPP$, which is produced by full dissociation of the axial CN^-. The short-lived transient **I** decays according to first-order kinetics. Thus, the transient **I** cannot be produced from the full dissociation of CN^-. It is likely that the dissociated CN^- is located nearby the central cobalt atom. Scheme 2 shows the thermal and photochemical reactions of $[(CN)_2Co^{III}TPP^-]$ in methanol. Because CN^- makes a strong hydrogen bond with alcohols, the dissociated CN^- is probably trapped by the axial methanol of $(CH_3OH)(CN)Co^{III}TPP$. The structure of the transient **I** is assumed to be $(CN^-\cdots HOCH_3)(CN)Co^{III}TPP$, in which the oxygen atom of the $(CN^-\cdots HOCH_3)$ moiety is coordinated to the central Co^{III} atom. The intracomplex ligand exchange reaction of $(CN^-\cdots HOCH_3)(CN)Co^{III}TPP$ leads to the regeneration of $[(CN)_2Co^{III}TPP^-]$ in methanol. Although there is no experimental evidence, the interconversion from transient **I** to transient **II** is one of the possible pathways to the photochemically induced full dissociation of the axial CN^- from $[(CN)_2Co^{III}TPP^-]$ in methanol.

Conclusion

In benzene or chloroform, $(Cl)Co^{III}TPP$ reacts with KCN in the presence of 18-crown-6, resulting in the formation of $[crown\text{-}K^+][(CN)_2Co^{III}TPP^-]$. The X-ray structure determination demonstrates that both the $C_{CN}-Co-C_{CN}$ and $N-C-Co$ bonds are almost linear. When KCN is added to the methanol solution of $(Cl)Co^{III}TPP$, the dicyanocomplex, $[(CN)_2Co^{III}TPP^-]$, is also produced, and the structure is confirmed by NMR measurements. The methanol solution of $[(CN)_2Co^{III}TPP^-]$ is found to exhibit photochromism; the continuous photolysis of $[(CN)_2Co^{III}TPP^-]$ yields $(CH_3OH)(CN)Co^{III}TPP$, which thermally returns to $[(CN)_2Co^{III}TPP^-]$. From the kinetic studies, it is suggested that potassium ions are necessary to stabilize $[(CN)_2Co^{III}TPP^-]$ in methanol. The laser photolysis of $[(CN)_2Co^{III}TPP^-]$ in methanol gives two transients: $(CH_3OH)(CN)Co^{III}TPP$ and $(CN^- \cdots HOCH_3)Co^{III}TPP$. The decay of $(CN^- \cdots HOCH_3)Co^{III}TPP$ follows first-order kinetics with a rate constant of 8.4×10^6 s^{-1}. Because the rate constant is independent of the concentration of CN^-, $(CN^- \cdots HOCH_3)Co^{III}TPP$ probably returns to $[(CN)_2Co^{III}TPP^-]$ via an intracomplex ligand exchange reaction.

Supporting Information Available: Tables listing bond lengths and angles (except for hydrogen atoms), positional parameters, and *B*(eq). This material is available free of charge via the Internet at http://pubs.acs.org.

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