

region is more complex; so despite the variety of isotopic spectral shifts collected here, some of the low-frequency Raman features remain unassigned.

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Registry No. $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, 15523-07-6; ^{65}Cu , 14119-06-3; ^{18}O , 14797-71-8; D_2 , 7782-39-0; $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{py})_2$, 15227-71-1; $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{pyz})$, 51798-89-1.

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Structural Studies of Metalloporphyrins. 7.¹ ¹H NMR and Electrochemical Investigation of the (*meso*-5,10,15,20-Tetraarylporphine)cobalt(III) Complexes $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})^2$

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¹H NMR spectra of five-coordinate cobalt(III) *meso*-5,10,15,20-tetraarylporphines $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ ($\text{X} = \text{I, Br, Cl, PF}_6, \text{ClO}_4$; $\text{R} = \text{H, Cl, CH}_3, \text{OCH}_3$) display abnormally broad line widths. The magnitude of this line broadening varies with X and R and generally increases with temperature. Analysis of the data obtained at various temperatures suggests that this phenomenon is due in part to the presence of a small amount of the π -cationic species $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})^+$, which is formed by the following disproportionation reaction: $2\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R}) \rightleftharpoons \text{Co}^{\text{II}}(\text{TPP-}p\text{-R}) + \text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})^+ + \text{X}^-$. Electrochemical data obtained in CH_2Cl_2 solution fully support this assumption. A second, but less important, source of the line broadening appears to be the self-exchange reaction between cobalt(II) and cobalt(III) porphyrins, which results in an exchange of ligand X and of protonated sites.

The magnetic properties of cobalt(III) complexes such as vitamin B₁₂ and various model compounds (cobaloximes, porphyrins) have been the subject of many studies leading to contradictory results and interpretations.³ Although most cobalt(III) complexes are diamagnetic because of their d⁶ low-spin configuration ($S = 0$), some of them having a high-spin configuration are paramagnetic: apart from $\text{Co}^{\text{III}}\text{F}_6^{3-}$ ($S = 2$)⁴ and complexes of the structure $\text{Co}^{\text{III}}(\text{P}(\text{C}_2\text{H}_5)_3)_3\text{X}_3$ ($\text{X} = \text{Cl, Br}$) ($S = 1$)⁵ some macrocyclic cobalt(III) complexes exhibit a paramagnetism⁶ the extent of which varies with the macrocyclic ligand and increases with temperature due to an equilibrium between low-spin and high-spin configurations.⁷⁻⁹ According to some authors,⁷ cobalt(III) porphyrins should be diamagnetic due to the strong ligand field created by the macrocycle. The weak magnetic susceptibility observed for $\text{ClCo}^{\text{III}}(\text{HP})(\text{H}_2\text{O})$ in the solid state could arise from cobalt(II) impurities or from the temperature-independent paramagnetism (TIP).¹⁰

¹H NMR spectroscopy is very sensitive to the magnetic characteristics of compounds. Various features of the species—chemical shifts,⁸ line widths,¹¹ H-H and H-Co coupling constants^{11,12}—have been repeatedly used to study the properties of cobalt(III) complexes and also to obtain structural evidence for the existence of π -cationic species derived from metalloporphyrins.¹³

Two groups of investigators^{14,15} recently observed that, in solution in a noncoordinating solvent, the cobalt(III) porphyrins $\text{ClCo}^{\text{III}}(\text{TPP})$,¹⁴ $[\text{Co}^{\text{III}}(\text{TPP})(\text{H}_2\text{O})_2]\text{ClO}_4$, $[\text{Co}^{\text{III}}(\text{OEP})(\text{H}_2\text{O})_2]\text{ClO}_4$, and $[\text{Co}^{\text{III}}(\text{OEP})(\text{THF})_2]\text{ClO}_4$ ¹⁵ exhibit abnormally broad lines in their ¹H NMR spectra, suggesting a paramagnetic character for these compounds. On the basis of variable-temperature measurements using Evans' method,¹⁶ it was concluded that $\text{ClCo}^{\text{III}}(\text{TPP})$ showed a paramagnetism that increased with temperature.¹⁴

In the present work, we report the results of a ¹H NMR study of various complexes $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ shown in Figure 1, which indicates that the line broadening has multiple origins and that the paramagnetism of these compounds probably does not arise from an equilibrium between low-spin and high-spin forms. Electrochemical data are also presented which, together with the NMR study, lead to other possible explanations for this paramagnetism.

Results and Discussion

I. ¹H NMR Spectra of Complexes $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$. In 0.02–0.03 M solution in CDCl_3 , most of the complexes shown in Figure 1, except those with $\text{X} = \text{I}$, show abnormally broad NMR signals. The extent of broadening varies with the nature of X and R and with temperature.

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- (2) Abbreviations used in this work for porphyrin complexes: HP, hemo-tetraporphyrin; TPP, *meso*-5,10,15,20-tetraphenylporphine; TPP-*p*-R, *meso*-5,10,15,20-tetraarylporphine; OEP, octaethylporphine; H_β refers to the proton of the pyrrole ring.
- (3) For a detailed review on the magnetic properties of vitamin B₁₂ see S. C. Agarwal, *Bull. Soc. Chim. Fr.*, 1-100 (1979).
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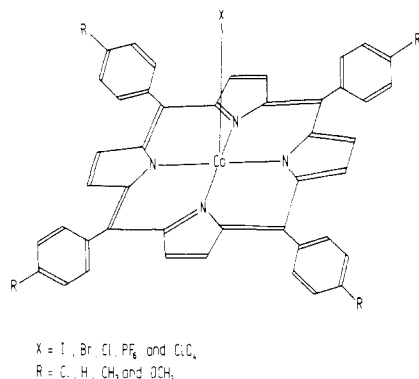


Figure 1. *meso*-5,10,15,20-Tetraarylporphyrins studied in this work.

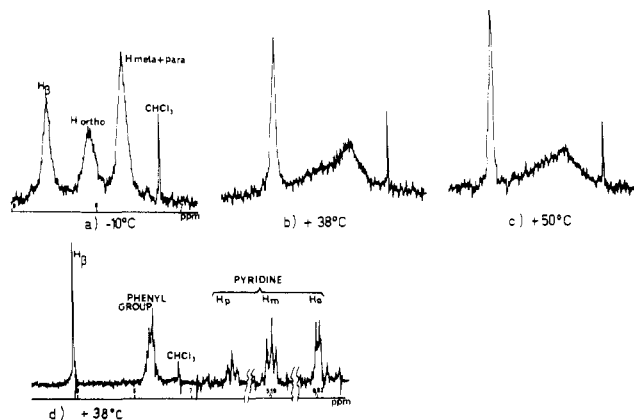
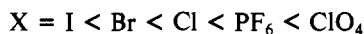


Figure 2. ¹H NMR study of the BrCo^{III}(TPP) complex as a function of temperature and the spectrum (d) of the [Co^{III}(TPP)(py)₂]⁺Br⁻ complex (solvent CDCl₃).

(a) **Influence of Axial Ligand X.** The half-width, $\Delta\nu_{1/2}$, for a given type of proton, varies considerably with X and increases in the order



which is the order of decreasing coordinating ability. For examples, the following values of $\Delta\nu_{1/2}(\text{CH}_3)$ (Hz) were observed:

	X				
	I	Br	Cl	PF ₆	ClO ₄
XCo ^{III} (TPP- <i>p</i> -OCH ₃) at <i>T</i> = 0 °C	2 ± 0.5	11 ± 1	22 ± 1	50 ± 3	≥ 100

From the study of another set of samples we obtained the same values (within experimental error). Maximum broadening is observed for X = PF₆ and ClO₄, and in these cases only a qualitative explanation of the phenomenon can be put forward. For X = Br, the extent of broadening is not so large and the resolution of the spectra allowed a more exhaustive search of the origins of the broadening to be made (Figure 2). For X = I, the lines are not perceptibly broadened.

(b) **Influence of the Phenyl Para Substituent R.** For the same X, $\Delta\nu_{1/2}$ increases as the electron-donating character of R increases but no linear correlation could be found between $\Delta\nu_{1/2}$ and the Hammett σ parameters.¹⁷ For example, with BrCo^{III}(TPP-*p*-R) at *T* = 0 °C the following reproducible values were observed:

	R			
	Cl	H	CH ₃	OCH ₃
$\Delta\nu_{1/2}(\text{H}_\beta)$, Hz	3	8	14	18

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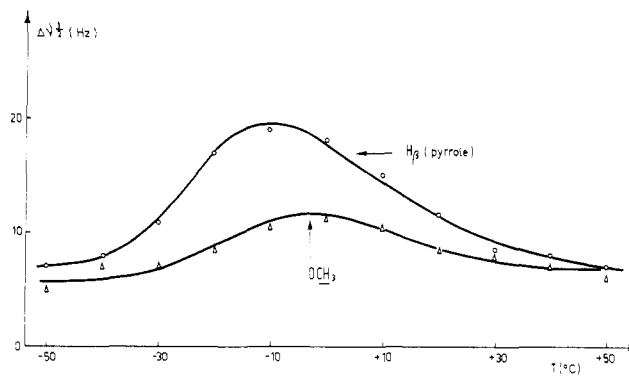


Figure 3. Line widths for the BrCo^{III}(TPP-*p*-OCH₃) complex as a function of temperature in CDCl₃.

(c) **Influence of Temperature *T* (°C).** Measurements of the spectra from -50 to +50 °C revealed that, for a given complex, increasing the temperature generally enhances the broadening of the signals, the change of line width being reversible. However, there are exceptions to the above rule: for example, in the case of BrCo^{III}(TPP-*p*-OCH₃), $\Delta\nu_{1/2}$ values for H_β and OCH₃ go through a maximum and then decrease (Figure 3). The existence of the maximum is not clearly understood, but two possible explanations can be put forward: (a) increase in temperature gives more π radical cation; (b) increased electron spin relaxation rate gives narrower lines (suggestion of a reviewer). The range of temperatures which could be covered was too narrow to see whether this was also the case for the other compounds.

II. Possible Origins of the Line Broadenings. (a) Metal-Centered Paramagnetism. Secondary effects such as quadrupolar relaxation of the cobalt atom (nuclear spin 7/2) and viscosity of the solutions being neglected, line broadening in solution-state NMR spectra appears to have two main origins:¹⁸ (a) the presence of paramagnetic entities; (b) chemical exchange between magnetically nonequivalent sites. Our results with cobalt(III) porphyrins do not seem to agree with the first assumption for the following reasons: First, if paramagnetism were the main cause of line broadening, a relationship should be observed between the $\Delta\nu_{1/2}$ values for the various protons and the distances between these protons and the metal center.¹⁹ Such is not the case: in the spectrum of BrCo^{III}(TPP), for example, $\Delta\nu_{1/2}$ increases in the order H_β < H_{ortho} < H_{meta} < H_{para} (Figure 2) whereas in paramagnetic metallotetraphenylporphyrine, the H_β signals, which are nearer to the metal than any other protons of the molecule, also undergo the largest broadening, whatever the mechanism responsible for line broadening, whether it be the Fermi-contact mechanism (e.g., ClMn^{III}(TPP-*p*-CH₃))²⁰ or the dipolar interaction mechanism (e.g., Co^{II}(TPP-*p*-CH₃)).²¹ Second, the line broadening should be accompanied by the shifts of the signals either to high field or to low field depending on the relative importance of the two mechanisms mentioned above.²⁰⁻²³ In complexes XCo^{III}(TPP-*p*-R) no such shifts have been observed. Theory predicts that metal ions possessing d⁶ high-spin configurations must have electron relaxation times *T*₁ short enough to allow a good resolution of the ¹H NMR spectra of their complexes whatever their geometry.²⁴ This prediction was fully supported by the observation of well-

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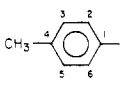
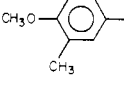
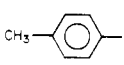
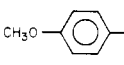
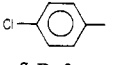
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Table I. Line Widths in Partially Oxidized $Mg^{II}(TPP-p-R)^{13}$ and in $BrCo^{III}(TPP-p-R)$ ($CDCl_3$)

aryl group	temp, °C	rel broadening: $\Delta\nu_{1/2}(H_i)/\Delta\nu_{1/2}(H_{ortho})$				H_β
		H_{ortho}^- (H_2, H_6)	H_{meta}^- (H_3, H_5)	para CH_3 (4- CH_3)	para OCH_3 (4- OCH_3)	
$Mg(TPP-p-R)^{+,a}$						
	c	1	~0.7	~0.9		<0.1
	c	1	~0.7		<0.1	<0.1
$BrCo^{III}(TPP-p-R)^b$						
	20	1	~0.9	~0.8		~0.15
	0	1	~0.8	~0.8		~0.4
	-20	1	~0.9	~0.6		~0.5
	30	1	~0.6		<0.1	<0.1
	20	1	~0.75		<0.1	~0.15
	14	1	~0.9		~0.2	~0.35
	-20	1	~0.9		~0.6	~0.5
	40	1	~0.7		<0.1	<0.1
	20	1	~0.9		<0.1	~0.1

^a Reference 13. ^b This work; uncertainty ± 0.1 . ^c Temperature not indicated.

solved signals in the spectra of the paramagnetic complexes $RCo^{III}(C_{10}H_{14}N_8)L$: however in that case contact shifts were observed.⁸ These results also indicate that the equilibrium between high-spin and low-spin cobalt(III) complexes is fast on the NMR time scale. It should be recalled that the paramagnetic complex $Co^{II}(\text{phen})(ATP)(O_2)$ did not show any noticeable contact or pseudocontact shifts of its protons, and this was explained by delocalization of the unpaired electron on the terminal oxygen of the O_2 molecule.²⁵ Third, the assumption of paramagnetism in cobalt(III) porphyrins cannot rationalize the maximum observed in the curve $\Delta\nu_{1/2} = f(T^\circ C)$ for $BrCo^{III}(TPP-p-OCH_3)$.

We believe that cobalt-centered paramagnetism cannot thus be considered as the main cause of the observed line broadenings.

(b) Existence of a Partial π -Radical-Cationic Character of the Porphyrin Ligand. The relative $\Delta\nu_{1/2}$ values for $BrCo^{III}(TPP-p-CH_3)$ and $BrCo^{III}(TPP-p-OCH_3)$ and the corresponding values for a mixture of $Mg^{II}(TPP-p-R)$ and its π radical cation $Mg^{II}(TPP-p-R)^+$ ($R = CH_3, OCH_3$)¹³ are shown in Table I: comparison of these data reveals a close similarity between the two sets of values. This suggests that the line broadening of the cobalt porphyrin signals could arise from the presence in small quantity of a species having a π radical cation structure and being in fast equilibrium with the cobalt(III) porphyrin itself.

π Radical cations such as $Zn^{II}(TPP)^+$ or $Mg^{II}(TPP)^+$ have ground-state structures $^2A_{2u}$ ²⁶⁻³⁰ in which the density of unpaired electrons is localized mainly on the four nitrogen atoms and on the meso carbon atoms.²⁷⁻³⁰ Besides, it was observed that the ESR spectrum of $Zn(TPP)^+$ shows hyperfine

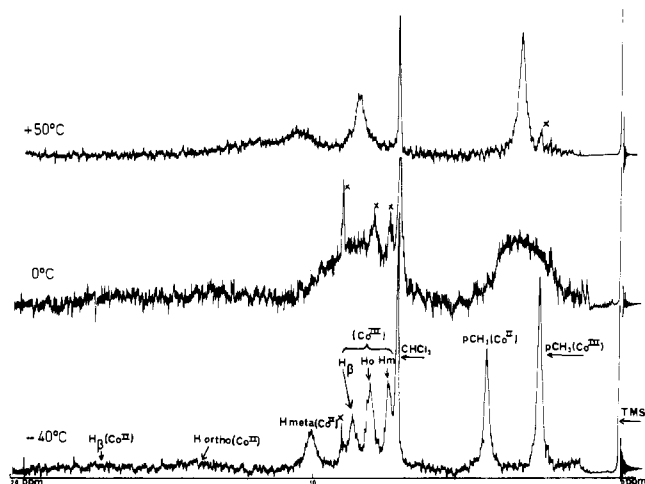
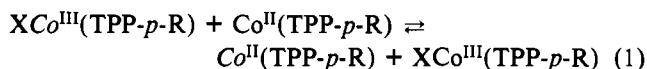


Figure 4. Chemical exchange between $Co^{II}(TPP-p-CH_3)$ and $ClCo^{III}(TPP-p-CH_3)$ complexes as function of temperature in $CDCl_3$. (X = peaks of small amounts of $H_2TPP-p-CH_3$. At 0 °C, the gain is more important than at the two other temperatures, so that the impurity peaks appear more clearly.)

structure from the phenyl and not from the H_β protons.²⁷ Consequently, the phenyl protons, especially H_{ortho} , are more susceptible to the contact interaction than H_β and give rise to larger line broadening. It has also been shown that chemical exchange between analogous sites on $Mg^{II}(TPP)$ and $Mg^{II}(TPP)^+$ is a fast process on the NMR time scale so that $\Delta\nu_{1/2}$ is directly related to the unpaired electron density.¹³ If our results are best explained by assuming the presence of π -radical-cation species in rapid equilibrium with the neutral porphyrin $XCo^{III}(TPP-p-R)$, they do not give any information on its exact structure and on its origin. Before we describe some electrochemistry experiments, which will give a reasonable answer to these two questions, we shall mention another possible cause for the observed line broadening in the NMR spectra.

III. Broadening due to the Chemical Exchange $Co(II) \rightleftharpoons Co(III)$. As shown in Figure 3, the $\Delta\nu_{1/2} = f(T^\circ C)$ curves go through a maximum in the case of $BrCo^{III}(TPP-p-R)$ ($R = CH_3, OCH_3$). These curves are quite similar to those obtained by Swift and Connick^{18,31} by simulation of the proton exchange between a diamagnetic species and small amounts of the corresponding paramagnetic entity. Such an exchange involving $XCo^{III}(TPP-p-R)$ and small amounts of $Co^{II}(TPP-p-R)$ had to be considered seriously inasmuch as cobalt(III) porphyrins always contain traces of cobalt(II), even after several careful purification steps.¹⁰

For a check of this assumption, a variable-temperature NMR study was undertaken of equimolar (0.024 M) mixtures of $XCo^{III}(TPP-p-R)$ and $Co^{II}(TPP-p-R)$ between -50 and +50 °C, in $CDCl_3$. The results are fully consistent with the exchange reaction (1).



When $X = Cl$ and $R = CH_3$ (Figure 4), the signals arising from the two types of porphyrins are distinctly observed at -40 °C with a reasonable resolution. Increase of the temperature results in a progressive broadening of the lines. Coalescence is observed for temperatures T_c , which are different for the various sites. Raising the temperature above T_c results in a narrowing of the lines.

Similar changes have been observed for $X = Br$ and $R = CH_3$. When $X = I$ and $R = CH_3$, in this temperature range,

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only one set of signals was observed, which became narrower as temperature was increased: all T_c must then lie below -50°C for this compound. For $X = \text{PF}_6$, the lines are so broad at all temperatures that it is not possible to measure accurately T_c . As for $X = \text{ClO}_4$, the only detectable signals are those of $\text{Co}^{\text{II}}(\text{TPP}-p\text{-R})$, which undergo shifts to high field and band narrowing as T is increased.²¹ Because of the low solubility of most cobalt porphyrins in CDCl_3 , accurate determinations of T_c are possible only for methyl groups, e.g., $R = \text{CH}_3$ and OCH_3 , as shown by the following values:

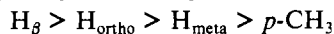
$T_c, ^\circ\text{C}$	X ($\text{XCo}^{\text{III}}(\text{TPP}-p\text{-CH}_3)$)				
	I	Br	Cl	PF_6	ClO_4
$T_c, ^\circ\text{C}$	< -50	-30	0	≥ 10	...

T_c decreases from Cl to I, reflecting an increase in the rate of exchange between cobalt(II) and cobalt(III) porphyrins. Such self-exchange reactions, involving simple electron transfer and ligand exchange, between metal ions in different oxidation states are well-known both for homonuclear and heteronuclear systems.^{32,33} They have been observed for several $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ couples³²⁻³⁶ but seemingly not in the case of cobalt porphyrins. The rate order found here ($I > \text{Br} > \text{Cl}$) is compatible with inner-sphere or outer-sphere mechanisms in which the electron transfer is mediated by the axial ligand X.^{32,33} This is confirmed by the fact that for ligands which have low polarizability and coordinating ability, $X = \text{PF}_6$ and ClO_4 , the coalescence temperature T_c cannot be detected below $+50^\circ\text{C}$. Addition of 1 equiv of $\text{Br}^-\text{N}^+(\text{C}_2\text{H}_5)_4$ to a CDCl_3 solution of $(\text{ClO}_4)\text{Co}^{\text{III}}(\text{TPP}-p\text{-OCH}_3)$ produces a change of the NMR spectrum, which becomes identical with that of $\text{BrCo}^{\text{III}}(\text{TPP}-p\text{-OCH}_3)$, in agreement with the known low affinity of the ClO_4^- anion for cobalt(III).³⁷

The influence of the equatorial ligand on T_c does not seem to be as important: thus $T_c = +3^\circ\text{C}$ for $p\text{-OCH}_3$ in the $\text{ClCo}^{\text{III}}(\text{TPP}-p\text{-OCH}_3)/\text{Co}^{\text{II}}(\text{TPP}-p\text{-OCH}_3)$ exchange and $T_c = 0^\circ\text{C}$ for $p\text{-CH}_3$ in the corresponding $\text{TPP}-p\text{-CH}_3$ system.

Our results clearly indicate the existence of an exchange between analogous sites in cobalt(II) and cobalt(III) porphyrins. This phenomenon is a second cause of line broadening of the signals of the cobalt(III) porphyrins as trace amounts of $\text{Co}^{\text{II}}(\text{TPP}-p\text{-R})$ are always contaminants of cobalt(III) porphyrins.¹⁰ A possible mechanism explaining the simultaneous formation of the cobalt(II) porphyrins and of the π radical cation mentioned above will be discussed below.

IV. Relative Importance of the Factors Influencing $\Delta\nu_{1/2}$. The exchange phenomenon seems however to have a smaller influence on $\Delta\nu_{1/2}$ than the presence of the π radical cation. If the reverse were true, one should observe $\Delta\nu_{1/2}$ for $\text{BrCo}^{\text{III}}(\text{TPP}-p\text{-CH}_3)$ decreasing in the order



because the difference $\Delta\delta_i = \delta_i(\text{Co}^{\text{II}}) - \delta_i(\text{Co}^{\text{III}})$, which determines $\Delta\nu_{1/2}$ at coalescence temperature, decreases in the same order. $\delta_i(\text{Co}^{\text{II}})$ refers to the paramagnetic Co^{II} species,²¹ and $\delta_i(\text{Co}^{\text{III}})$ is taken from $\text{ICo}^{\text{III}}(\text{TPP}-p\text{-CH}_3)$ (whose spectrum is well enough resolved) or from the corresponding six-coordinate derivative (cf. Experimental Part). Experimentally, maximum $\Delta\nu_{1/2}$ is observed for H_{ortho} and minimum for H_β . Moreover, the largest line broadenings are found for $(\text{ClO}_4)\text{Co}^{\text{III}}(\text{TPP}-p\text{-R})$, for which practically no exchange phenomenon was observed.

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V. Possible Disproportionation Reactions of Cobalt(III) Porphyrins. Two possible mechanisms can be put forward which both imply the simultaneous formation of a porphyrin π radical cation and cobalt(II) complex and which can then rationalize our experimental results. These propositions rely on the well-known general redox properties of the metalloporphyrins, which can undergo redox reactions either at the metal^{27,38,39} or on the porphyrin ligand.^{27,39-41} Electron-transfer between metal and ligand is sometimes equally possible.^{28,42}

In the dissociation mechanism eq 2, we further assume that $\text{XCo}^{\text{III}}(\text{TPP}-p\text{-R}) \rightleftharpoons$

$$\overset{\text{A}}{[\text{X}^-\text{Co}^{\text{III}}(\text{TPP}-p\text{-R})^+]} \leftrightarrow \overset{\text{B}}{\text{X}^-\text{Co}^{\text{II}}(\text{TPP}-p\text{-R})^+}] \quad (2)$$

$\text{B} (\text{B}_1) \qquad \qquad \qquad \text{B} (\text{B}_2)$

the positive charge in the dissociated form B is delocalized between cobalt and the macrocyclic ligand. Form B would be best represented as a resonance hybrid between a diamagnetic cobalt(III) structure (B_1) and a paramagnetic cobalt(II) π -radical-cationic form (B_2).

Equation 3 represents a disproportionation reaction leading $2\text{XCo}^{\text{III}}(\text{TPP}-p\text{-R}) \rightleftharpoons$

$$\overset{\text{A}}{\text{Co}^{\text{II}}(\text{TPP}-p\text{-R})} + \overset{\text{D}}{\text{XCo}^{\text{III}}(\text{TPP}-p\text{-R})^+} + \text{X}^- \quad (3)$$

to two distinct paramagnetic species in equal proportions: the cobalt(II) porphyrin (C) and the cobalt(III) π radical cation (D). We shall see that this mechanism is borne out by an electrochemical study of cobalt(III) porphyrins in noncoordinating solvents (see below). Both mechanisms imply the formation of a π radical cation, and this is supported by the results concerning the influence of the para substituent R on the line width $\Delta\nu_{1/2}$: increasing the electron-donating power of the para substituent R should stabilize the π radical cation D, and this should in turn produce an increase of $\Delta\nu_{1/2}$, which is in fact the case. Moreover, for both mechanisms one expects that an increasing of the X^- concentration should displace the equilibrium (eq 2 or eq 3) in favor of $\text{XCo}^{\text{III}}(\text{TPP}-p\text{-R})$ and thus produce a decrease of $\Delta\nu_{1/2}$. Addition of a 10-fold excess of $\text{Br}^-\text{N}^+(\text{C}_2\text{H}_5)_4$ to a solution of $\text{BrCo}^{\text{III}}(\text{TPP}-p\text{-OCH}_3)$ produces a slight decrease of $\Delta\nu_{1/2}$, which can be observed on the H_β and OCH_3 signals. In a second experiment, the same cobalt(III) porphyrin in solution in CDCl_3 was oxidized to the corresponding π radical cation $\text{XCo}^{\text{III}}(\text{TPP}-p\text{-OCH}_3)^+$ by addition of an excess of I_2 according to a known procedure.^{40,41} The NMR spectrum of the oxidized species displayed very broad signals but slow addition of an equimolar amount of $\text{Co}^{\text{II}}(\text{TPP}-p\text{-OCH}_3)$ to this compound produced a decrease of line widths $\Delta\nu_{1/2}$ which, when all cobalt(II) porphyrin had been added, became nearly identical with those observed before oxidation by I_2 . Reaction 3, which incorporates the X^- and $\text{Co}^{\text{II}}(\text{TPP}-p\text{-R})$ species in a mass action law, affords a better explanation of the experimental results than eq 2. Besides, it is known that the metalloporphyrins that have a biradical structure like form B do not in general show ESR spectra,^{43a} because of the strong coupling between the two unpaired electrons. Cobalt(III) porphyrins $\text{XCo}^{\text{III}}(\text{TPP}-p\text{-R})$ in CH_2Cl_2 glass show ESR spectra at 110 K with g values that are typical

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Table II. Electrochemical Studies of *meso*-5,10,15,20-Tetraphenylporphyrins $XCo^{III}(TPP)$ in CH_2Cl_2

porphyrin complexes	$E_{1/2}, V$		$E_{1/2}, V$	slope of graph $E = f[-\log((i_1 - i)/i)]$
	Co(III)/Co(II)	Co(II)/Co(I)		
$ClCo^{III}(TPP)$	-0.055	-0.950	-0.060	-0.116 ± 0.003
$BrCo^{III}(TPP)$	-0.110	-0.950	-0.130	-0.098 ± 0.009
$ICo^{III}(TPP)$	-0.280	-0.950	-0.270	-0.150 ± 0.023
$(ClO_4)Co^{III}(TPP)$	not detd	-0.950		
$(PF_6)Co^{III}(TPP)$	not detd	-0.950		
$Co^{II}(TPP)$	+0.610			
	(Co(II)/Co(III))			

of organic radicals ($g \approx 2$)^{27,28,30,39-41,44} and with line widths that vary significantly from complex to complex ($\Delta\nu_{1/2}$ about 10 G (peak to peak)) but that are reproducible and close to those reported in the literature for the corresponding π radical cation.²⁶ For the spectra studied here, when $X = Br$ and $R = H$, a very broad signal ($\Delta\nu_{1/2} \approx 50$ G), indicative of an interaction between the Br^- anion and the π radical cation, was observed.²⁶ By using a carefully degassed sample of $ClCo^{III}(TPP)$, we observed a signal for $Co^{II}(TPP)$ at 110 K. Without careful degassing, the characteristic pattern of the $Co-O_2$ adduct was observed together with that of the π radical cation: $ClCo^{III}(TPP)^+$. At room temperature, whatever care taken to degas the solution, the signal of the π radical cation could only be observed. Reaction 3 is in better agreement with all the results than reaction 2 and is borne out by electrochemical results.

By using the $(PF_6)Co^{III}(TPP-p-CH_3)$ complex in $CHCl_3$ solvent and α, α -diphenyl- β -picrylhydrazyl (dpph) as the standard sample, we estimated the fraction of π radical cation as equal to 0.7 (± 0.2)% at room temperature. This result is also consistent with electrochemical data.

VI. Electrochemical Studies of $XCo^{III}(TPP)$ in CH_2Cl_2 Solution ($X = I, Br, Cl, PF_6, ClO_4$). The half-wave potentials for the cobalt(III) porphyrins are collected in Table II. These values are the results of linear or cyclic voltammetry measurements.

Linear voltammograms reveal two reduction and one oxidation waves. The first reduction wave occurs at a constant potential, $E(Co^{II}/Co^I) = -0.950$ V, for all the porphyrins studied here. The second reduction wave, which is difficult to observe when $X = PF_6$ or ClO_4 , corresponds to the reduction $Co^{III} \rightarrow Co^{II}$, and the half-wave potential $E(Co^{III}/Co^{II})$ depends markedly on the nature of X as reported previously.⁴⁵ This potential increases in the order $I < Br < Cl$, which is the order of decreasing complexing ability.

Cyclic voltammograms obtained with a Kemula electrode at a sweep rate of 0.300 V/s show two peaks for $X = Cl, Br$, or I at potential values close to the half-wave potentials measured by linear voltammetry (Figure 5). By contrast, $(ClO_4)Co^{III}(TPP)$ and $(PF_6)Co^{III}(TPP)$ cyclic voltammograms show only one peak, at -0.150 and -0.160 V, respectively. However, when the sweep rate is increased to 30 V s^{-1} , an anodic peak is also observed, which is linked to the cathodic one. Thus, whatever the nature of X , the reduction $Co^{III} \rightarrow Co^{II}$ can be made reversible on a mercury electrode, but the rates are much greater when X is a halide ion than when it is PF_6 or ClO_4 . The oxidation wave for all cobalt(III) porphyrins is found at $+0.600$ V on a mercury electrode and is assigned to the oxidation of the macrocyclic ligand (eq 4)

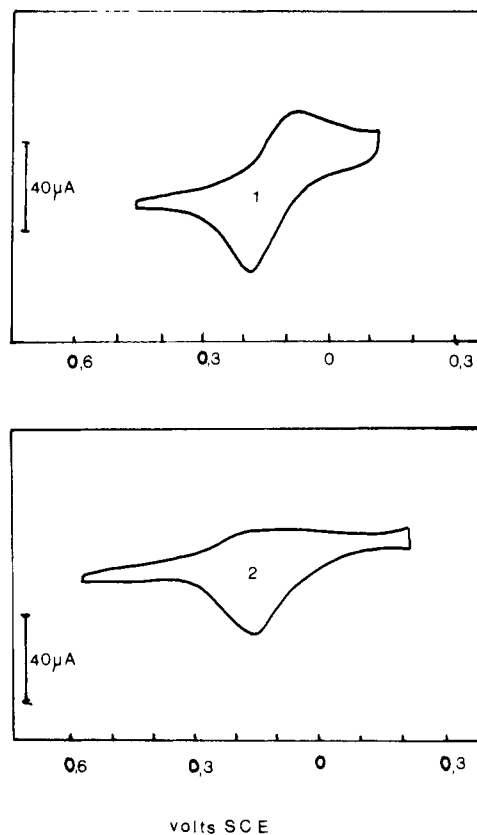
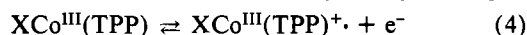


Figure 5. Cyclic voltammograms of solutions of 3.0×10^{-4} M $XCo^{III}(TPP)$ complexes in 0.1 M $n-Bu_4NClO_4/CH_2Cl_2$; voltammogram 1, $X = Br$ (similar curves obtained for $X = I$ and Cl); voltammogram 2, $X = ClO_4$ (similar curve with $X = PF_6$).

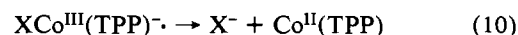
leading to the corresponding π radical cation. The fact that the potential for this wave is the same for all X ligands excludes an oxidation reaction such as (5). It should be recalled that

$$2XCo^{III}(TPP) + Hg \rightarrow HgX_2 + 2Co^{III}(TPP)^+ + 2e^- \quad (5)$$

this value is very similar to the half-wave potentials measured for the oxidation of $Mg^{II}(OEP)$ ^{43a} or $Zn^{II}(TPP)$ ^{43b} to the corresponding π radical cations but different from the reported value for the ligand oxidation of $Co^{II}(TPP)$ at the platinum electrode ($+0.860$ V).^{39b} The oxidation potential of $Co^{II}(TPP)$ was reported to be $+0.520$ ^{39a} or $+0.650$ V.^{39b} It is therefore tempting to postulate that the loss of an electron from the porphyrin ring (eq 6), rather than from cobalt (eq 7) as postulated previously, constitutes the first step in the oxidation of $Co^{II}(TPP)$ and is followed by a metal-to-ligand electron transfer (eq 8), the rate of which should be dependent on X .



The reduction of $XCo^{III}(TPP)$ into $Co^{II}(TPP)$ should also be a two-step process (eq 9, 10), each step being different from



any of those postulated for the oxidation reaction. In this case, the electron transfer (eq 9) would involve the axial ligand X , in agreement with the experimentally observed dependence of $E(Co^{III}/Co^{II})$ on the nature of X .

Two important consequences follow from these considerations:

(1) The electrochemical interconversion between $Co^{II}(TPP)$ and $XCo^{III}(TPP)$ is not reversible as far as the principle of

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(45) L. A. Truxillo, Thesis, University of New Orleans, Dec 1974.

microscopic reversibility is concerned: the oxidation–reaction involves first the removal of an electron from the porphyrin ligand, the first step of the reduction reaction being an electron transfer to the XCo moiety.

(2) Although the half-wave potentials may differ significantly from the true redox potentials, the values observed or reported³⁹ for the one-electron oxidation of Co^{II}(TPP) into XCo^{III}(TPP) and XCo^{III}(TPP) into XCo^{III}(TPP)⁺ on a mercury or platinum electrode render the assumption of a disproportionation reaction of XCo^{III}(TPP) (eq 3) not unrealistic. It is possible from these data to roughly calculate the formation constant *K* for this disproportionation reaction by using the relationship

$$(0.0591/n) \log K = E_1 - E_2$$

In this equation *E*₁ and *E*₂ are the true redox potentials for XCo^{III}(TPP)/Co^{II}(TPP) and XCo^{III}(TPP)⁺/XCo^{III}(TPP). The estimated value for *E*₁ lies between the experimental reduction potential of XCo^{III}(TPP) and the experimental oxidation potential of Co^{II}(TPP): ca. +0.37 V. The value used for *E*₂ is +0.860 V,^{39b} which is the most unfavorable one for the disproportionation reaction. Calculation of the formation constant from the above equation leads to a value *K* = 10^{-8.3}. On the assumption that the concentration of XCo^{III}(TPP) is 10⁻¹ M, the concentration of the paramagnetic species Co^{II}(TPP) or XCo^{III}(TPP)⁺ should be 3.8 × 10⁻⁴ M. The total amount of paramagnetic species would thus correspond to 0.8% of the total concentration of cobalt complexes.

VII. Dependence of the Disproportionation Reactions of Cobalt(III) Porphyrins on Their Structure. (a) Extent of the Disproportionation Reaction. The equilibrium constant for the above disproportionation reaction is certainly very small because, except for NMR and ESR spectroscopy, we have not been able, using other physical methods, to get evidence for the presence of the π radical cations. We measured the magnetic susceptibility of some of these complexes, using Evans' method,¹⁶ and found meaningless small values due to the low solubility of these compounds, in contrast to the results for ClCo^{III}(TPP).¹⁴ The electronic spectra of the cobalt(III) porphyrins did not show the absorption bands between 500 and 700 nm, characteristic of the π radical cations and related structures.^{26–29,39,40,44,46}

It should be stressed that the π radical cations XCo^{III}(TPP-*p*-R)⁺, detected by NMR and ESR spectroscopy, are formed by disproportionation of the parent five-coordinate porphyrins only when the latter are dissolved in weakly complexing solvent such as CH₂Cl₂ or CDCl₃. In a coordinating solvent *S* (e.g., Me₂SO), or in the presence of a good ligand (e.g., pyridine), six-coordinate diamagnetic complexes having the structure [Co^{III}(TPP-*p*-R)₂S]⁺X⁻ are formed.¹⁴ For example, in the presence of 2 equiv of pyridine, [Co^{III}(TPP-*p*-R)(py)₂]⁺X⁻ is obtained, its ¹H NMR spectrum being independent of the nature of X and showing well-resolved signals for all protons (Figure 2). In the solid state, the complexes XCo^{III}(TPP-*p*-R) are also diamagnetic as indicated by magnetic susceptibility measurements^{47,48} and absence of ESR signal.

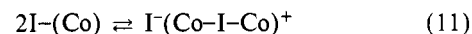
(b) Influence of the Axial Ligand X on the Structure of the π Radical Cation. For a given R substituent, the relative order of broadening for the various protons of the porphyrin ligand

varies with the nature of X. With ClCo^{III}(TPP), the line width is about the same for H_β, H_{ortho} and H_{meta,para}¹⁴ whereas with BrCo^{III}(TPP-*p*-R), the H_β singlets are much narrower. According to our proposals, this would mean that the delocalization of the unpaired electron of the π radical cation varies with the ligand X. This is in line with results reported in the literature on the influence of the axial ligand X on the electron density distribution of the π radical cations derived from other metalloporphyrins.^{27,28,30,44} For example in the species M(TPP)⁺X⁻ (M = Mg, Zn, Cd; X = ClO₄, F, Br, I) displacement of X = ClO₄ by X = halide induces a 10% increase of the spin density on the macrocyclic nitrogen atoms.⁴⁹

VIII. Other Causes of Line Broadening. At low temperature, we observed that the signals of H_{ortho} in ICo^{III}(TPP-*p*-CH₃) showed increased multiplicity (Figure 6). This splitting, which is reversible, arises from the existence of diastereotopic sites for these protons, due to simultaneous slow rotation of the phenyl group and slow "inversion" of the Co–X bond on the NMR time scale.^{50,51} This phenomenon, which can be observed only when the line broadenings due to paramagnetism or chemical exchange are negligible, is by no means related to the latter and has been already studied in great detail under more favorable conditions by other authors.^{52–54}

We must also mention the peculiar behavior of ICo^{III}(TPP-*p*-Cl), which, according to our assumptions, should show a well-resolved spectrum with negligible line broadening; in fact, broad lines are observed, which get narrower when the temperature is increased (Figure 7).

Iodocobalt complexes are known to easily form binuclear associations,⁵⁵ which are in equilibrium with the mononuclear entity,⁵⁶ according to eq 11. Such an equilibrium, if it is



moderately fast on the NMR time scale, could explain the features observed in Figure 7, although we have no definite proof of that.

Conclusion

The line-broadenings observed in the ¹H NMR spectra of five-coordinate cobalt(III) porphyrins XCo^{III}(TPP-*p*-R) in CDCl₃ solution are probably due to a paramagnetism arising from the presence of small amounts of the corresponding π radical cations XCo^{III}(TPP-*p*-R)⁺ and of cobalt(II) porphyrins.⁶³ The amount of π radical cation that has an ²A_{2u} structure²⁶ increases in the order



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 (47) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakatmoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976).
 (48) Magnetic susceptibility measurements that were carried out on a solid sample of (ClO₄)Co^{III}(TPP-*p*-OCH₃) have shown that this complex is essentially diamagnetic and does not contain more than 1% of paramagnetic impurities, most likely traces of Co^{II}(TPP-*p*-OCH₃).^{10,2f} We thank Dr. Girerd from Professor Kahn's laboratory (Université d'Orsay) for these measurements.

- (49) See ref 44, p 86 (and references cited therein).
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 (51) S. S. Eaton, D. M. Fishwild, and G. R. Eaton, *Inorg. Chem.*, **17**, 1542 (1978).
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 (54) R. V. Snyder and G. N. La Mar, *J. Am. Chem. Soc.*, **98**, 4419 (1976).
 (55) D. Baumann, H. Endres, H. J. Keller, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 853 (1973).
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 (60) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
 (61) P. Rothmund and A. R. Menotti, *J. Am. Chem. Soc.*, **70**, 1808 (1948).
 (62) M. Lange, Thesis, Paris, 1981, p 160.
 (63) Shortly after our paper had been submitted for publication, two related papers [K. Yamamoto, M. Kohno, and H. Ohya-Nishiguchi, *Chem. Lett.*, 255 (1981); *Bull. Chem. Soc. Jpn.*, **54**, 1923 (1981)] were published. The authors also investigated the nature of the paramagnetic species with results consistent with ours. However they paid attention mostly to the characterization of the π radical cation by ESR study, while we were also interested in its origin.

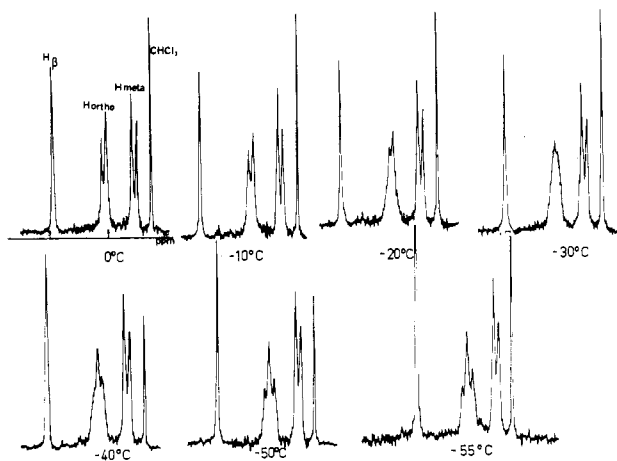


Figure 6. ^1H NMR study of the $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$ complex as a function of temperature. (Only signals of aromatic protons are reproduced.)

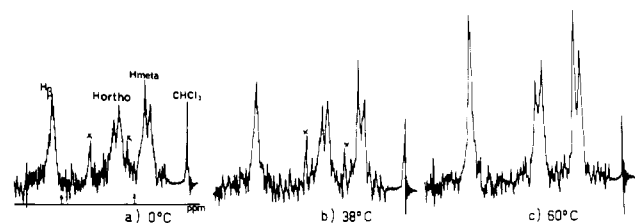


Figure 7. ^1H NMR study of the $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-Cl})$ complex as a function of temperature (X: impurities).

The presence of cobalt(II) porphyrin also makes possible a chemical exchange between this complex and $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$, and this constitutes a second but minor cause of broadening. These explanations are supported by an electrochemical study of the same porphyrins in CH_2Cl_2 solution, which shows that the redox potentials of these species are compatible with a disproportionation reaction of the cobalt(III) porphyrins into the π radical cation and cobalt(II) porphyrin. This reaction, which is an intrinsic property of these complexes in solution in a noncoordinating solvent, would also explain that $\text{XCo}^{\text{III}}(\text{TPP})$ with $\text{X} = \text{Br}$ and Cl catalyze, although less efficiently than $\text{Co}^{\text{II}}(\text{TPP})$, the oxygenation of indole derivatives.⁵⁷ The catalytic activity would be due, in fact, to the presence of small amounts of $\text{Co}^{\text{II}}(\text{TPP})$, which would be the true catalyst of the reaction.⁵⁸

Finally, the hypothesis that the studied phenomenon should be due to fortuitous impurity is ruled out because of (1) the reproducibility of the measurements by both NMR and electrochemical techniques, (2) experimental data, which differ depending on the nature of X or R but can be logically rationalized, and (3) similar results obtained by other authors⁶³ whose interpretation is consistent with ours.

Experimental Part

Porphyrins $\text{TPPH}_2\text{-}p\text{-R}$, prepared according to Adler et al.,⁵⁹ are converted into their cobalt(II) complexes $\text{Co}^{\text{II}}(\text{TPP-}p\text{-R})$ ⁶⁰ and then oxidized to the cobalt(III) porphyrins $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ in the presence of the suitable mineral acid $\text{HX} = \text{HI}, \text{HBr}, \text{HCl}, \text{HPF}_6$, or HClO_4 . The following procedure was employed. $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ compounds were prepared by the reaction of a CHCl_3 solution of $\text{Co}^{\text{II}}(\text{TPP-}p\text{-R})$ (300 mg/150 mL) with a slight excess of an aqueous 5% HX solution. The reaction was followed by UV-visible spectroscopy (the Soret bands of the cobalt(II) and cobalt(III) porphyrins are at 410–415 and 437–440 nm, respectively) by taking aliquots of the reaction mixture and diluting them with pyridine. At the end of the reaction the CHCl_3 layer was washed with water, and the CHCl_3 solution was concentrated. Solids (~300 mg) were obtained by allowing pentane to diffuse into the solution. This material was recrystallized by dissolving it in CHCl_3 and diffusing pentane into

the solution. Thus only noncoordinating solvents were used throughout the preparation and purification (average yield 80%). Microanalyses do not give an accurate determination of the elemental composition. For instance: Anal. Calcd for $\text{BrCo}^{\text{III}}(\text{TPP})$ ($\text{C}_{44}\text{H}_{28}\text{N}_4\text{BrCo}$): C, 70.32; H, 3.73; N, 7.46; Br, 10.64. Found: C, 69.40; H, 3.82; N, 7.22; Br, 10.10. Calcd for $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-Cl})$ ($\text{C}_{44}\text{H}_{24}\text{N}_4\text{Cl}_2\text{ICo}$): C, 56.43; H, 2.56; N, 5.99; Cl, 15.16; I, 13.56. Found: C, 55.19; H, 2.58; N, 5.71; Cl, 15.53; I, 12.24. With the other complexes, deviations between calculated and observed percentages are of the same importance and arise from the presence, in variable amounts, of solvents of crystallization, CHCl_3 and pentane, as was found previously for other porphyrin complexes. For removal of the small amounts of solvents, the following procedure⁶² was used. The crystalline solid was crushed in a mortar and then dried under vacuum (10^{-2} mmHg) at 100 °C for several hours and the operation renewed four times. This treatment applied to the complex $\text{BrCo}^{\text{III}}(\text{TPP})$ (dried at 60 °C) led to a compound giving a correct elemental analysis (deviations $\leq 0.3\%$) but was not applied to the other compounds used in this study. There were no detectable differences in the NMR spectra of the complex $\text{BrCo}^{\text{III}}(\text{TPP})$ before and after careful drying, except for the signals due to pentane. In a few cases (Figure 4), traces of the porphyrin free base could be detected in the spectra.

$\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ compounds are best characterized by their six-coordinate derivatives $[\text{Co}^{\text{III}}(\text{TPP-}p\text{-R})(\text{py})_2]^+\text{X}^-$, which are obtained by addition of 2 equiv of pyridine to a solution of the five-coordinate complex $\text{XCo}^{\text{III}}(\text{TPP-}p\text{-R})$ and which, for a given R, show identical ^1H NMR spectra.

Proton NMR spectra (CDCl_3 solution; internal reference $\text{Me}_4\text{Si} = 0$ ppm) were recorded on a Perkin-Elmer R-32 spectrometer, equipped with a variable-temperature accessory. Chemical shifts of the six-coordinate derivatives are as follows (ppm). $\text{R} = \text{Cl}$: H_β , 9.07 (s); phenyl group (H_{ortho} and H_{meta}), AA'BB' system centered at 7.72; py H_{para} , 6.33 (t); py H_{meta} , 5.20 (t); py H_{ortho} , 0.76 (d). $\text{R} = \text{H}$: H_β , 9.07 (s); phenyl group, 7.5–8 (m); py H_{para} , 6.35 (t); py H_{meta} , 5.19 (t); py H_{ortho} , 0.83 (d). $\text{R} = \text{CH}_3$: H_β , 9.09 (s); phenyl group (H_{ortho} and H_{meta}), AA'BB' system centered at 7.59; Ph para CH_3 , 2.63 (s); py H_{para} , 6.31 (t); py H_{meta} , 5.16 (t); py H_{ortho} , 0.83 (d). $\text{R} = \text{OCH}_3$: H_β , 9.08 (s); phenyl group, system AA'MM'; Ph H_{ortho} , 7.74; Ph H_{meta} , 7.22; Ph para OCH_3 , 4.03 (s); py H_{para} , 6.31 (t); py H_{meta} , 5.14 (t); py H_{ortho} , 0.83 (d).

For electrochemical measurements the solvent was Spectrograde CH_2Cl_2 , which was twice distilled. The supporting electrolyte, $n\text{-Bu}_4\text{NClO}_4$, was dissolved in acetone and precipitated by adding ether. This procedure was carried out three times. It was dried under vacuum at 50 °C. The concentration of $n\text{-Bu}_4\text{NClO}_4$ was 10^{-1} M. The solutions were prepared by dissolving metalloporphyrin complexes in CH_2Cl_2 under N_2 atmosphere. Potentials were measured against a saturated aqueous calomel electrode separated from the solution by a bridge of CH_2Cl_2 saturated with $n\text{-Bu}_4\text{NClO}_4$.

Polarographic data were obtained with use of a capillary dropping-mercury electrode at a controlled drop time of 1.5 s by using a Tacussel potentiostat, Type PRG 5, connected to a Tacussel recorder, EPL 1. Cyclic voltammetric data were obtained by using a Tacussel potentiostat, Type PRT 20.2X, fitted with a Tacussel pilot unit, Type TP PRT. Data were acquired on a Tektronix oscilloscope, Type R 5103 N, after amplification by a Tacussel differential amplifier, Type ADTP. A standard hanging-mercury-drop electrode was employed.

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Registry No. $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)$, 82150-29-6; $\text{BrCo}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)$, 36995-21-8; $\text{ClCo}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)$, 82150-28-5; $(\text{PF}_6)\text{-Co}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)$, 82150-27-4; $(\text{ClO}_4)\text{Co}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)$, 82150-23-0; $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$, 80642-17-7; $\text{BrCo}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$, 34829-90-8; $\text{ClCo}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$, 80642-16-6; $(\text{PF}_6)\text{Co}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$, 82150-17-2; $(\text{ClO}_4)\text{Co}^{\text{III}}(\text{TPP-}p\text{-CH}_3)$, 82150-22-9; $\text{ICo}^{\text{III}}(\text{TPP})$, 82150-21-8; $\text{BrCo}^{\text{III}}(\text{TPP})$, 60166-11-2; $\text{ClCo}^{\text{III}}(\text{TPP})$, 60166-10-1; $(\text{PF}_6)\text{Co}^{\text{III}}(\text{TPP})$, 82150-20-7; $(\text{ClO}_4)\text{Co}^{\text{III}}(\text{TPP})$, 76402-67-0; $\text{ICo}^{\text{III}}(\text{TPP-}p\text{-Cl})$, 82150-19-4; $\text{BrCo}^{\text{III}}(\text{TPP-}p\text{-Cl})$, 82150-18-3; $[\text{Co}^{\text{III}}(\text{TPP-}p\text{-OCH}_3)(\text{py})_2]^+$, 65832-47-5; $[\text{Co}^{\text{III}}(\text{TPP-}p\text{-CH}_3)(\text{py})_2]^+$, 65832-48-6; $[\text{Co}^{\text{III}}(\text{TPP})(\text{py})_2]^+$, 66527-41-1; $[\text{Co}^{\text{III}}(\text{TPP-}p\text{-Cl})(\text{py})_2]^+$, 65832-49-7; $\text{Co}^{\text{II}}(\text{TPP-}p\text{-CH}_3)$, 19414-65-4; $\text{Co}^{\text{II}}(\text{TPP})$, 14172-90-8.