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Contribution from the Laboratoire de Chimie Bioorganique et Bioinorganique, Institut de Chimie Moléculaire, URA 1384 du CNRS, Bat. 420, Université de Paris-Sud, 91405 Orsay, France, and Laboratoire d'Electrochimie Analytique et Appliquée, ENSCP, URA 216 du CNRS, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Structural Studies of Metalloporphyrins. 9. "Looping-Over" Cobalt Porphyrins: Coordinating Properties and Application to Dioxygen Fixation and Activation

L. Salmon,[†] C. Bied-Charreton,*[,†] A. Gaudemer,[†] P. Moisy,[‡] F. Bedioui,[‡] and J. Devynck[‡]

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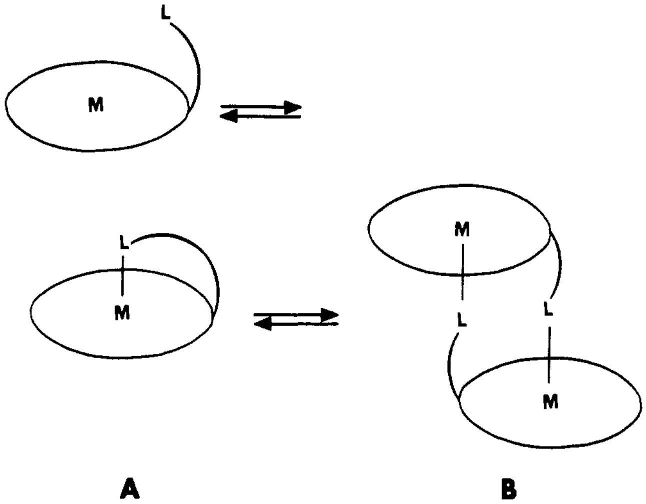
"Looping-over" cobalt tetraarylporphyrins bearing an imidazole or a primary amino group attached by alkyl chains varying from three to five methylene groups to the meta position of one of the phenyls have been shown by ESR spectroscopy to form intermolecular dimers in toluene. No evidence for dimer formation was found for the corresponding ortho substituted compounds. Both porphyrins bind dioxygen, but ESR spectroscopy indicates that meta-substituted cobalt porphyrins bind O_2 only at higher concentrations, which suggests the existence of dimeric species, whereas some of the ortho-substituted ones form dioxygen adducts whatever their concentration, in agreement with the presence of monomeric dioxygen adducts. Cobalt "looping-over" porphyrins however bind O_2 less strongly than the *n*-butylamine or *N*-methylimidazole complexes of CoTTP. The oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen was used to test the catalytic efficiency of the cobalt porphyrins: the rate of oxidation is largely dependent on the position and the length of the tether, the ortho-substituted porphyrins being more efficient than the meta-substituted ones. Addition of triethylamine to the reaction mixture increases the rate of oxidation by factors varying between 4 and 30. This effect can be assigned in part to a partial conversion of the phenol to the more oxidizable phenolate anion.

Introduction

The binding of dioxygen to cobalt(II) complexes has been extensively studied.[1] With Schiff-base and porphyrin complexes of Co(II), various techniques, including ESR and spectroscopic measurement of oxygen binding constants k_{O_2}, have demonstrated that reversible dioxygen fixation is greatly enhanced by the presence of fifth ligand. It was also found[2] that Co(II) complexes with five-coordinate Schiff-base ligands were much more efficient as catalysts for oxidation of hindered phenols than four-coordinate ones, because they have a greater affinity for dioxygen.

Several types of porphyrins having a fifth covalently attached ligand, typically imidazole or pyridine, have been previously studied as models of hemoglobins and myoglobins.[3] On the other hand, very few studies of the catalytic efficiency of such metalloporphyrins have been reported.[4] Imidazole- or pyridine-appended tetraphenylporphyrin (TPP) derivatives have been prepared with an amide linkage to a single aminophenyl group[5] or to a pyrrole-side chain residue[6] or with an ether linkage to a hydroxyphenyl group.[7] Ibers et al.[8] prepared cobalt(II) "looping-over" porphyrins with an appended pyridine ligand and studied oxygen binding by these porphyrins using visible spectroscopy. These compounds did not show a greater affinity for molecular oxygen than CoTPP(3-methylpyridine). We have recently reported[9] the synthesis of "looping-over" zinc porphyrins witn *n*-butylamine attached at the ortho or meta position of one of the phenyl rings. By NMR spectroscopy, we showed that, in the case of the ortho-substituted porphyrins, an equilibrium between a monomeric species A (intramolecular binding) and a dimeric species B (intermolecular binding) was attained, whereas in the case of the meta-substituted complexes, only dimeric species were present (Scheme I).

Scheme I



We have extended this work to cobalt(II) "looping-over" porphyrins having an amino or imidazole ligand covalently attached to one of the phenyl groups. The aims of this study were as follows: evaluation of inter- vs intramolecular binding of ligand to the metal atom in both the presence and the absence of molecular oxygen using electrochemical methods and ESR spectroscopy; comparison of the oxygen affinity of the cobalt(II) "looping-over" porphyrins with the corresponding Co(TTP)L complexes (TTP = tetra-*p*-tolylporphyrin) with L = *n*-butylamine or *N*-methylimidazole; comparison of the catalytic efficiency of the complexes in the oxidation of 2,6-di-*tert*-butylphenol.

Experimental Section

Spectral Measurements. Visible spectra were recorded in dichloromethane solutions, on a Perkin-Elmer Lambda 5 spectrophotometer at 296 K. NMR spectra were measured on a Bruker AM250 instrument in deuterated chloroform solutions at 296 K.

ESR spectra were recorded in toluene solutions on a Bruker ER 200E X-band spectrometer with 100-KHz field modulation, equipped with

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[†] Université de Paris-Sud.

[‡] ENSCP, URA 216 du CNRS.

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low-temperature experiment accessories (ER-4III VT). The field sweep was calibrated with an NMR gaussmeter and field frequency calibration was achieved by using TCNQ⁻Li⁺ ($g = 2.0026$). Deoxygenated solutions were obtained by bubbling argon through the solution for 1 h at least. I is the height of the low-field peak (cf. Figure 7); since ESR spectra are recorded under strictly identical conditions, we make the assumption that I is proportional to the surface of the peak, which in turn is proportional to the concentration of the "Co(III)–$O_2^{\bullet-}$" form.

Electrochemical Instrumentation. All reactants were reagent grade and used as received. Electrolytic solutions were routinely deoxygenated with argon. Electrochemical studies were performed with a three-electrode potentiostatic system (Tacussel). The working electrodes were: a vitreous-carbon disk Tacussel electrode ($A = 0.070$ cm²) or a gold disk Tacussel electrode ($A = 0.0314$ cm²) previously polished. The potentials are expressed by reference to the aqueous SCE placed in a separate compartment containing the supporting electrolyte.

The diffusion control of the voltammetric currents has been checked by applications of the Levich equations for hydrodynamic voltammetry ($I_d = 0.620nFAD^{2/3}\ \nu^{-1/6}\omega^{1/2}C$) at a rotating disk electrode[10] and by application of the Randles–Sevick equations for cyclic voltammetry ($I_p = 0.269n^{3/2}AD^{1/2}v^{1/2}C$) at a stationary disk electrode,[10] where I_d and I_p (A) are the limit diffusion and peak current intensities respectively, n is the electron number, A is the electrode area (cm²), C is the concentration of the diffusion species (mol·cm⁻³), ω is the angular velocity (rad·s⁻¹), v is the sweeping potential rate (V·s⁻¹), ν is the kinematic viscosity, and D is the diffusion coefficient (cm²·s⁻¹).

The D values have been calculated by applications of these equations. The value of ν for DMSO + Bu_4NBF_4 was 1.79×10^{-2} St.

General Procedure for the Oxidation of 2,6-Di-*tert*-butylphenol. To a toluene solution of the starting phenol (4×10^{-2} M) was added the catalyst cobalt(II) porphyrin (4×10^{-3} M). The solution was stirred at room temperature in a flask connected to a gas buret ($p_{O_2} = 1.1$ atm). At the end of the oxygen uptake, the solution was evaporated and the organic compounds purified on a silica gel column (Merck 70-230 mesh) developed with hexane. The proportions of the different products have been calculated from integration of the NMR spectra (precision 5%).

Synthesis of Porphyrins 1a–12a. All solvents, gases, and starting products were reagent grade and used without further purification except for dichloromethane and chloroform, which were dried and redistilled. In the following text, non-metalated compounds will be designated by numbers **1a–12a** and cobalt complexes, by numbers **1b–12b**.

Products **1a**, **3a**, **8a**, **9a**, **10a**, and **12a** were synthesized as described in refs 7a,b and 9. Products **2a** and **4a** were synthesized in a manner similar to that for product **3a**, using excesses of 1,3-dibromopropane and 1,5-dibromopentane, respectively.

5-(2-(3-Bromopropyl)phenoxy)-10,15,20-tritolylporphine (2a). NMR (ppm/TMS): 9.02 (8 H), −2.53 (2 H), ring protons; 7.62 (6 H), 8.25 (6 H), 2.79 (9 H), tolyl protons; 8.18 (1 H), 7.78 (1 H), 7.43 (1 H), 7.32 (1 H), phenoxy protons; 4.05 (2 H), 2.35 (2 H), 1.51 (2 H), side-chain protons.

5-(2-(5-Bromopentyl)phenoxy)-10,15,20-tritolylporphine (4a). NMR (ppm/TMS): 8.92 (8 H), −2.64 (2 H), ring protons; 8.17; (6 H), 7.58 (6 H), 2.77 (9 H), tolyl protons; 8.08 (1 H), 7.78 (1 H), 7.38 (1 H), 7.32 (1 H), phenoxy protons; 3.90 (2 H), 2.32 (2 H), 1.03 (2 H), 0.92 (2 H), 0.48 (2 H), side-chain protons.

5-(3-(4-Bromobutyl)phenoxy)-10,15,20-tritolylporphine (10a). NMR (ppm/TMS): 8.89 (8 H), −2.71 (2 H), ring protons; 8.13 (6 H), 7.58 (6 H), 2.77 (9 H), tolyl protons; 7.85 (1 H), 7.80 (1 H), 7.66 (1 H), 7.32 (1 H), phenoxy protons; 4.23 (2 H), 3.55 (2 H), 2.15 (2 H), 2.08 (2 H), side-chain protons.

Products **5a**, **6a**, **7a**, and **11a** have been synthesized by using the parent bromo compounds **2a**, **3a**, **4a**, and **10a** by the method described in ref 7c.

5-(2-(3-(1-Imidazolyl)propyl)phenoxy)-10,15,20-tritolylporphine (5a). NMR (ppm/TMS): 8.88 (8 H), −2.68 (2 H), ring protons; 8.08 (6 H), 7.55 (6 H), 2.71 (9 H), tolyl protons; 8.22 (1 H), 7.75 (1 H), 7.42 (1 H), 7.21 (1 H), phenoxy protons; 3.75 (2 H), 2.58 (2 H), 1.30 (2 H), side-chain protons; 6.68 (1 H), 6.58 (1 H), 5.85 (1 H), imidazole protons.

5-(2-(4-(1-Imidazolyl)butyl)phenoxy)-10,15,20-tritolylporphine (6a). NMR (ppm/TMS): 8.95 (8 H), −2.62 (2 H), ring protons; 8.14 (6 H), 7.60 (6 H), 2.75 (9 H), tolyl protons; 8.03 (1 H), 7.76 (1 H), 7.42 (1 H), 7.22 (1 H), phenoxy protons; 3.81 (2 H), 2.48 (2 H), 0.87 (2 H), 0.64 (2 H), side-chain protons; 6.60 (1 H), 6.08 (1 H), 5.07 (1 H), imidazole protons.

5-(2-(5-(1-Imidazolyl)pentyl)phenoxy)-10,15,20-tritolylporphine (7a). NMR (ppm/TMS): 9.00 (8 H), −2.54 (2 H), ring protons; 8.20 (6 H), 7.62 (2 H), 2.75 (9 H), tolyl protons; 8.14 (1 H), 7.78 (1 H), 7.42 (1 H), 7.32 (1 H), phenoxy protons; 3.91 (2 H), 1.56 (2 H), 1.06 (2 H), 0.86 (2 H), 0.42 (2 H), side-chain protons; 7.84 (1 H), 7.12 (1 H), 6.04 (1 H), imidazole protons.

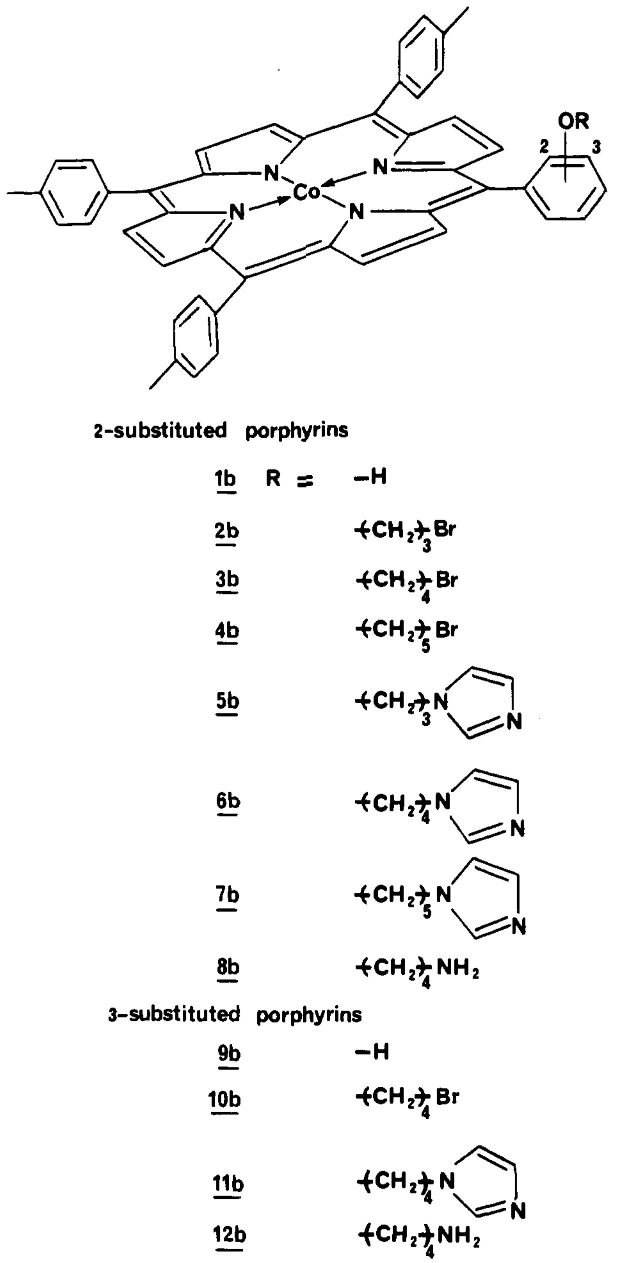

Figure 1. Cobalt porphyrins prepared in this work.

5-(3-(4-(1-Imidazolyl)butyl)phenoxy)-10,15,20-tritolylporphine (11a). NMR (ppm/TMS): 9.00 (8 H), −2.61 (2 H), ring protons; 8.17 (6 H), 7.57 (6 H), 2.75 (9 H), tolyl protons; 7.90 (1 H), 7.64 (1 H), 7.46 (1 H), 7.27 (1 H), phenoxy protons; 4.02 (2 H), 3.86 (2 H), 1.90 (2 H), 1.68 (2 H), side-chain protons; 7.83 (1 H), 7.07 (1 H), 6.84 (1 H), imidazole protons.

Synthesis of Cobalt Porphyrins 1b–12b. The metalations, which were followed by visible spectroscopy, were carried out by the procedure described by Adler and colleagues.[11] Visible spectra of metalated and non-metalated porphyrins are in full agreement with the proposed structures.

Results and Discussion

A. Synthesis of "Looping-Over" Cobalt Porphyrins. Two different sets of "looping-over" porphyrins (Figure 1), possessing either an imidazole or a primary amino group attached by a chain of three to five methylene groups to the phenyl group at either the ortho or meta position have been synthesized by using procedures described previously.[7,9] With the meta-substituted

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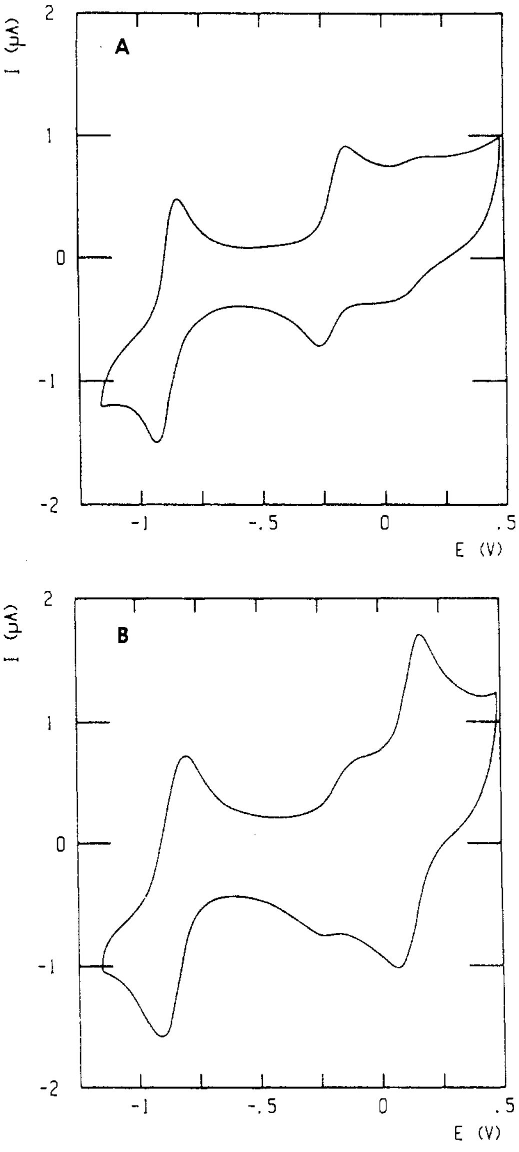

Figure 2. Cyclic voltammograms (A) of compound **8b** (5×10^{-4} M) and (B) of compound **6b** (5×10^{-4} M), in DMSO + Bu_4NBF_4 (0.1 M) at a gold electrode (A = 0.0314 cm^2). v = 0.1 V·s^{-1}.

structure, only intermolecular coordination is sterically possible, as shown with the corresponding zinc porphyrins.[9] The NMR spectra of the various porphyrin ligands agree with the proposed structures (see Experimental Section). For the ortho-substituted cobalt(II) porphyrins and their adducts with dioxygen, ESR spectroscopy and electrochemistry were used to try to establish whether intra- or intermolecular coordination of the tethered ligand occurs.

B. Electrochemical Studies of "Looping-Over" Cobalt(II) Porphyrins. Evidence for binding of the group attached to the porphyrin ring to Co(III) has been obtained by voltammetry performed on a gold or a vitreous-carbon electrode. The investigation has mainly been focused on the study of the Co(III)/Co(II) system as this redox couple is the one involved in the axial complexation. Two "looping-over" porphyrins, **6b** and **8b**, have been chosen for the strongly complexing power of the base fixed on the loop.

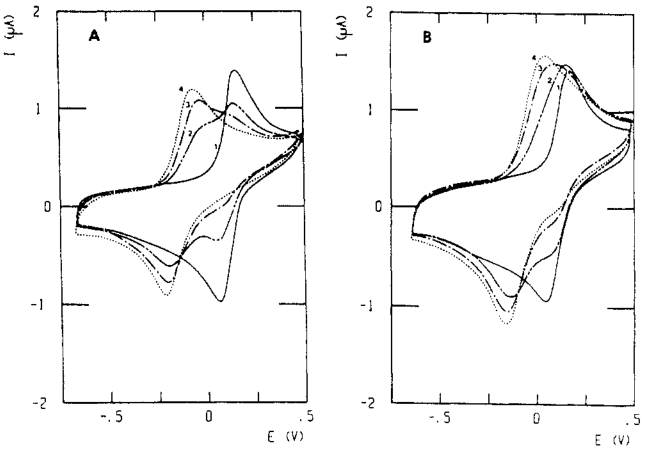

Figure 3. Cyclic voltammograms of CoTPP (5×10^{-4} M) in DMSO + Bu_4NBF_4 (0.1 M) at a gold electrode (A = 0.0314 cm^2), v = 0.1 V·s^{-1}, with added ligand: (A) n-butylamine, with (1) C = 0, (2) $C = 2 \times 10^{-4}$ M, (3) $C = 5 \times 10^{-4}$ M, and (4) $C = 10^{-3}$ M; (B) N-methylimidazole, with (1) C = 0, (2) $C = 2 \times 10^{-4}$ M, (3) $C = 5 \times 10^{-4}$ M, and (4) $C = 10^{-3}$ M.

Table I. Cyclic Voltammetry Parameters of "Looping-Over" Porphyrins **6b** and **8b** and CoTTP + Added Ligand (n-Butylamine ($nBuNH_2$) or N-Methylimidazole (N-MeIm)) in DMSO or CH_2Cl_2 + Bu_4NBF_4 (0.1 M)[a]

	DMSO[b]				CH_2Cl_2[c]			
	Co(II)/ Co(III)		Co(I)/ Co(II)		Co(II)/ Co(III)		Co(I)/ Co(II)	
porphyrin	$E_{1/2}$	ΔE_p	$E_{1/2}$	ΔE_p	$E_{1/2}$	ΔE_p	$E_{1/2}$	ΔE_p
CoTTP	0.11	0.115	−0.84	0.09	0.765	0.09	−0.71	0.09
CoTTP + $nBuNH_2$[d]	0.11 −0.115	0.115 0.19	−0.84	0.09	−0.05	0.64	−0.71	0.09
CoTTP + N-MeIm[d]	0.11 −0.035	0.115 0.25	−0.84	0.09	−0.15	0.80	−0.71	0.09
6b	0.12 −0.16	0.12 0.190	−0.94	0.12				
8	0.13 −0.165	0.11 0.130	−0.90	0.10				

[a] Potential sweeping rate = 0.1 V·s^{-1}; $E_{1/2}$ (V) = $(E_{p_a} + E_{p_c})/2$, vs ECS; ΔE_p (V) = $E_{p_a} - E_{p_c}$. [b] Gold electrode (A = 0.0314 cm^2). [c] Vitreous carbon electrode (A = 0.070 cm^2). [d] x = [added ligand]/[porphyrin] = 1; x = 1.

Cyclic voltammetric curves of complexes **6b** and **8b** in DMSO solution are shown in Figure 2A,B. In methylene chloride, the compounds present poorly defined curves. Figure 3 represents the cyclic voltammograms of CoTTP in the presence of n-butylamine (Figure 3A) and N-methylimidazole (Figure 3B) in DMSO. The comparison of the electrochemical behavior of the "looping-over" porphyrins **6b** and **8b** with that of CoTTP plus 1 equiv of the present free ligand L (L = n-butylamine or N-methylimidazole) should provide evidence for axial intra- or intermolecular complexation in the case of **6b** and **8b**. The characteristic data are reported in Table I.

Voltammograms show that the "looping-over" porphyrins exist, both in DMSO and in CH_2Cl_2, in two forms: complexed, with $E_{1/2}$ = −0.16 V/SCE, and noncomplexed, with $E_{1/2}$ = 0.12 V/SCE.

Analysis of variation of the cyclic voltammetry peak intensity as a function of the potential scan rate over the range 0.02 V·s^{-1} through −4 V·s^{-1}, using the Randles–Sevick equation (see Experimental Section) demonstrates that the diffusion of CoTTP and of the "looping-over" cobalt porphyrins controls the Co(III)/Co(II) and Co(II)/Co(I) electrochemical reactions. The result was confirmed by analysis of the variations of the height of the hydrodynamic voltammetric waves as a function of the electrode rotation rate according to the Levich equation (see Experimental Section). An example of experimentally hydrodynamic voltammetry curves of complex **6b** in DMSO is shown in Figure 4.

The diffusion coefficient D of Co^{II}TTP and "looping-over" Co(II) porphyrins calculated from hydrodynamic voltammetry data (for the reactions Co(III)/Co(II) and Co(II)/Co(I) in DMSO) are reported in Table II. These coefficients can be compared to those obtained for Co^{III}TTP and "looping-over" cobalt(III) porphyrins in the same medium. The Co(III) complexes were obtained by electrolysis of the parent porphyrins at +0.5 V/SCE. The large difference between the D values of Co(II)

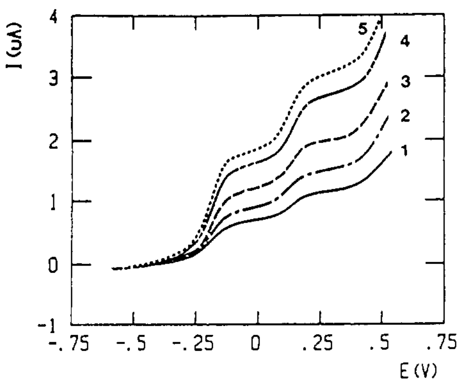

Figure 4. Hydrodynamic voltammograms of compound **6b** (5×10^{-4} M) in DMSO + Bu_4NBF_4 (0.1 M) at a rotating electrode ($A = 0.0314$ cm^2; $v = 0.01$ V·s^{-1}): (1) $\omega = 28$ rad·s^{-1}; (2) $\omega = 56.4$ rad·s^{-1}; (3) $\omega = 111$ rad·s^{-1}; (4) $\omega = 225$ rad·s^{-1}; (5) $\omega = 280$ rad·s^{11}.

Table II. Diffusion Coefficients (cm^2·s^{-1}) of CoTTP and "Looping-Over" Cobalt Porphyrins **6b** and **8b**, in DMSO + Bu_4NBF_4 (0.1 M)

	10^7D	
porphyrin	Co(II)	Co(III)
CoTTP	8.6 ± 0.2	6.1 ± 0.2
8b	4.5 ± 0.2	
6b	5.3 ± 0.2	2.4 ± 0.2

Table III. Stability Constants of $Co^{III}TTP$ + L Complexes (L = $nBuNH_2$ or *N*-MeIm) and Looping-Over Porphyrins **6b** and **8b** in DMSO + Bu_4NBF_4 (0.1 M)

porphyrin	log K^{xxx}	porphyrin	log K^{xxx}
CoTTP + $nBuNH_2$ (1:1)	3.5 ± 0.1	**8b**	3 ± 0.1
CoTTP + *N*-MeIm (1:1)	3.5 ± 0.1	**6b**	3.8 ± 0.1

and Co(III) forms of complex **6b** cannot arise from a change in oxidation state, but could be attributed to dimerization by intermolecular complexation of Co(III). Thus, complex **6b** exists under a dimeric intermolecular complexed form, corresponding to the equilibrium between form A (monomer) and form B (dimer) (Scheme I). Attempts to measure the diffusion coefficients of the other "looping-over" Co(II) porphyrins proved unsuccessful.

Evidence for intermolecular complexation has been reported for homologous "looping-over" Zn(II) porphyrins by ^1H NMR studies.[9] Bettelheim et al.[12] suggest, in the case of porphyrins having a complexing function (amine or hydroxy) attached on the phenyl groups of the ring, that both the presence of electrolyte (NBu_4 ClO_4) and the amine and hydroxy substituents help to promote dimerization of these porphyrins.

The stability constants for complexation reaction in DMSO

$$K = \underset{\text{dimer}}{[LCo^{III}{}_2]}/\underset{\text{monomer}}{[LCo^{III}]^2} = [B]/[A]^2$$

can be assessed from the ratio of the intensities of the two peaks of the Co(III)/Co(II) redox couple. These intensities are in fact directly proportional to the concentration of the complexed and noncomplexed Co(III) forms. The stability constant values are reported in Table III and are compared to the stability constants of $LCo^{III}TTP$ complexes

$$L + Co^{III}TTP \rightleftarrows LCo^{III}TTP$$

with $K = [LCo^{III}TTP]/[L][Co^{III}TTP]$ and L = *n*-butylamine or *N*-methylimidazole.

The apparent complexation constants show that the stability of the "looping-over" cobalt(III) porphyrin loop complexed from and the stability of $LCo^{III}TTP$ are similar and of the same order of magnitude as those reported for $LCo^{III}TPP$ complexes (TPP = tetraphenylporphin) in DMSO.[13] In addition, we can note that the shifts of $E_{1/2}$ when going from complexed to the noncomplexed forms ($\Delta E_{1/2} = -0.280$ and -0.295 V for **6b** and **8b**, respectively) are quite comparable to -0.06 log K values.

Finally, it should be noted that DMSO, which is a strongly coordinating solvent, exerts a "buffer" effect on axial complexation. Then it can be expected that, in less coordinating solvents like methylene chloride or toluene, such complexes should be even more stable. However, we have observed a severe decrease in the electrochemical reversibility of the Co(III)/Co(II) reaction (as measured by the peak potential separation) both for the "looping-over" porphyrins and for the (CoTTP + L) system in methylene chloride. This made the calculation of the stability constants impossible in this medium.

C. ESR Spectroscopy. In frozen toluene solutions at 110 K, $Co^{II}TTP$ exhibits a well-known ESR spectrum from which the various *g* and *A* values can be extracted (Figure 5a).[14] Addition of 1 equiv of an amine: pyridine, *n*-butylamine, or *N*-methylimidazole, results in characteristic alterations of the spectra (Figure 5b) due to significant changes in the hyperfine coupling constants $A_{//}$ and $A_{\perp}$. The ESR spectra of cobalt(II) "looping-over" porphyrins **1b**, **3b**, and **9b**, which lack a nitrogen function on the chain, exhibit spectra with $A_{\parallel}$ and $A_{\perp}$ values very similar to those of $Co^{II}TTP$ (ca. 150–170 and 167–189 G, respectively). For all the "looping-over" porphyrins that have an $-NH_2$ or an imidazole group at the end of the tether, the $A_{\parallel}$ coupling constants (ca. 80–85 G) and the characteristic splitting of the lines into triplets due to the superhyperfine coupling of the electron with the nitrogen atom of the ligand (Figure 5c) are consistent with the coordination of this group to the cobalt atom ($15 < A_{Co-N} < 17$ G). As a consequence, the meta-substituted complexes exist predominantly as dimeric pentacoordinated species. In the case of the ortho-substituted compounds, no conclusion can be drawn from the ESR data.

D. Binding of Dioxygen by Cobalt(II) "Looping-Over" Porphyrins. ESR characteristics have been reported for various dioxygen adducts of porphyrins[14] and Schiff-base complexes.[15] At low temperature (110 K), the O_2–CoTTP complex exhibits a complex spectrum corresponding to a mixture of the two species $Co^{II}TTP$ and $Co^{III}(TTP)O_2{}^{\bullet-}$, which disappears above 180 K. Addition of a stoichiometric amount of a Lewis base results in a more intense signal with values of the hyperfine constants $A_{\parallel}$ and $A_{\perp}$ which depend on the structure of L (ca. 16–18 and 10–12 G, respectively). Although there is no simple correlation between the pK_a of the base and the values of $A_{\parallel}$ and $A_{\perp}$, the latter decreases as the electron-donating ability of the ligand increases, suggesting a concomitant increase of unpaired electron density on bound dioxygen.

In order to determine if the "looping-over" cobalt(II) porphyrins formed stable six-coordinated oxygen adducts, we have studied their ESR spectra in aerated solvents at various temperatures ranging from 110 K to 260 K, a temperature range in which dioxygen concentrations is nearly constant.[16] The spectra obtained for frozen solutions of complexes **6b** and **8b** ($T = 110$ K) clearly show that both compounds form dioxygen adducts at this temperature (Figure 6). By contrast, complexes **1b**, **3b**, and **9b**, which do not bear a ligand on the chain exhibit spectra very similar to CoTTP. As the temperature is raised, complexes **6b** and **8b** show the characteristic isotropic spectra of $LCo^{III}(TTP)O_2{}^{\bullet-}$ species (Figure 7).

In order to compare the dioxygen-binding abilities of complexes **6b** and **8b** to those of the corresponding CoTTP–amine complexes,

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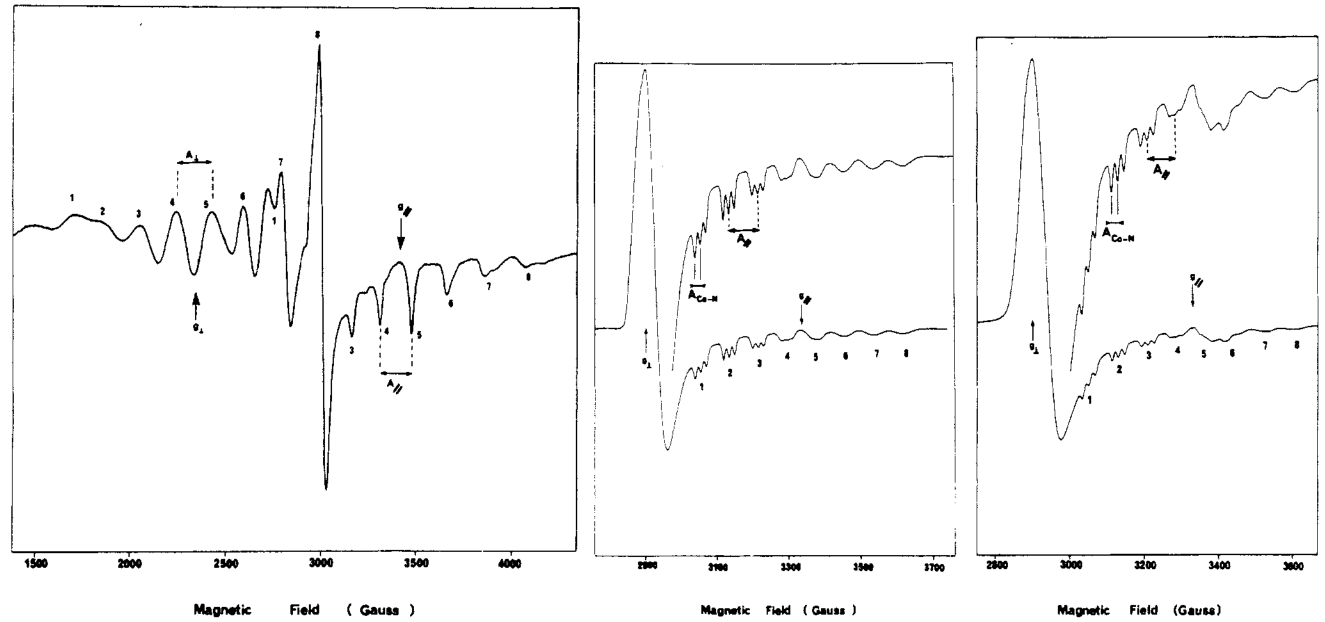

Figure 5. (a) Left: ESR spectrum porphyrin **9b** in frozen toluene ($T = 125$ K). (b) Middle: ESR spectrum of porphyrin CoTTP + $nBuNH_2$ in frozen deoxygenated toluene ([porphyrin] = [added ligand] = 5×10^{-3} M; $T = 105$ K). (c) Right: ESR spectrum of porphyrin **7b**, in frozen deoxygenated toluene ([**7b**] = 5×10^{-3} M; $T = 105$ K).

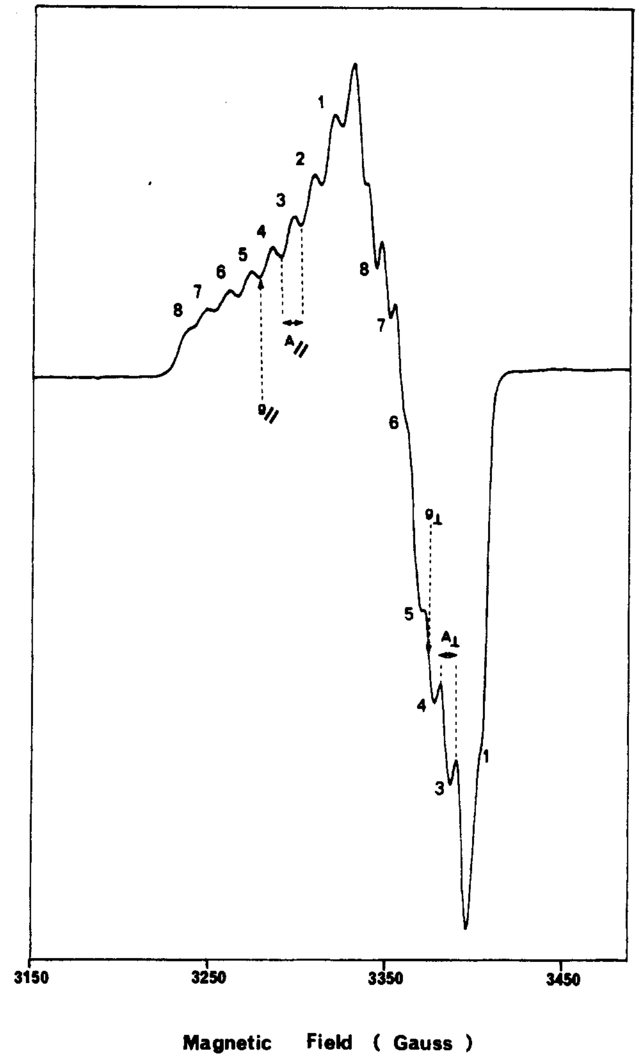

Figure 6. ESR spectrum of porphyrin **8b** in frozen aerated toluene ($T = 100$ K).

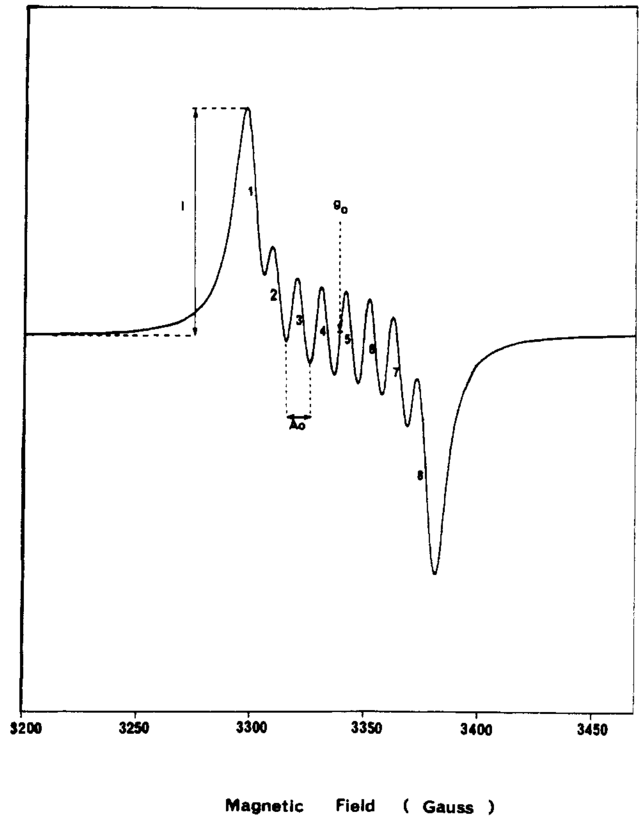

Figure 7. ESR spectrum of porphyrin **8b** in fluid aerated toluene ($T = 250$ K).

we have measured the intensity of the ESR signals of all these complexes at various temperatures. Complexes of CoTTP with *n*-butylamine and *N*-methylimidazole gave the more intense signals at all temperatures, which shows that they bind O_2 more strongly than the "looping-over" porphyrins **6b** and **8b**. As the temperature increases, the signal becomes less intense, the line width remaining constant. This decrease is, for the main part, due to a

$$\mathrm{L{-}Co^{III}(TTP)O_2^{\bullet -}} \rightleftarrows \mathrm{L{-}Co^{II}TTP} + O_2$$

shift of the equilibrium toward the right with increasing temperature leading to a Co(II) species, which shows no spectrum in isotropic media. In Figure 9 are plotted the logarithms of the

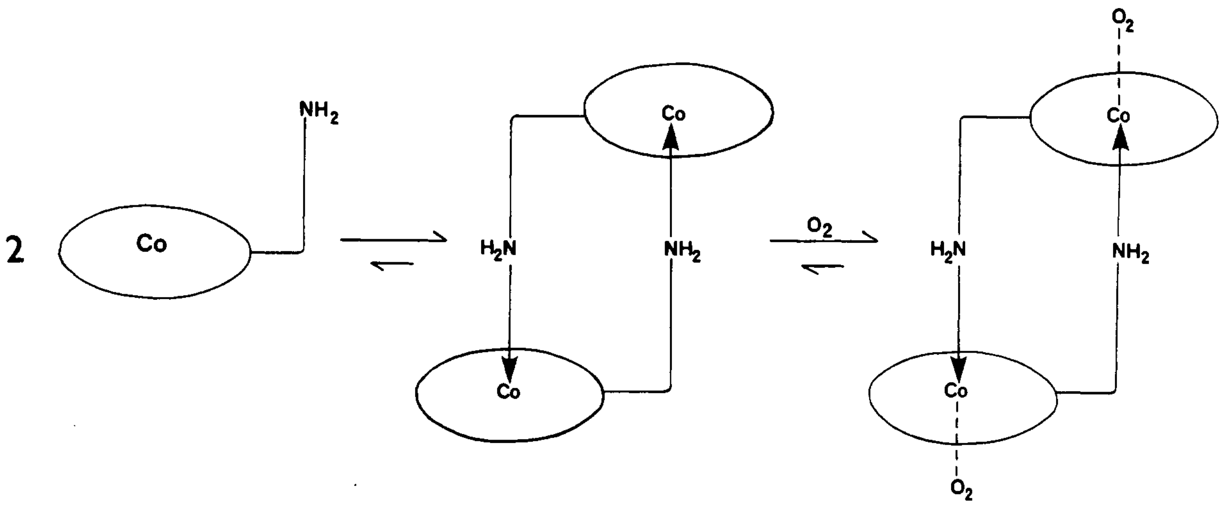

Figure 8. Dimerization of cobalt(II) looping-over porphyrins.

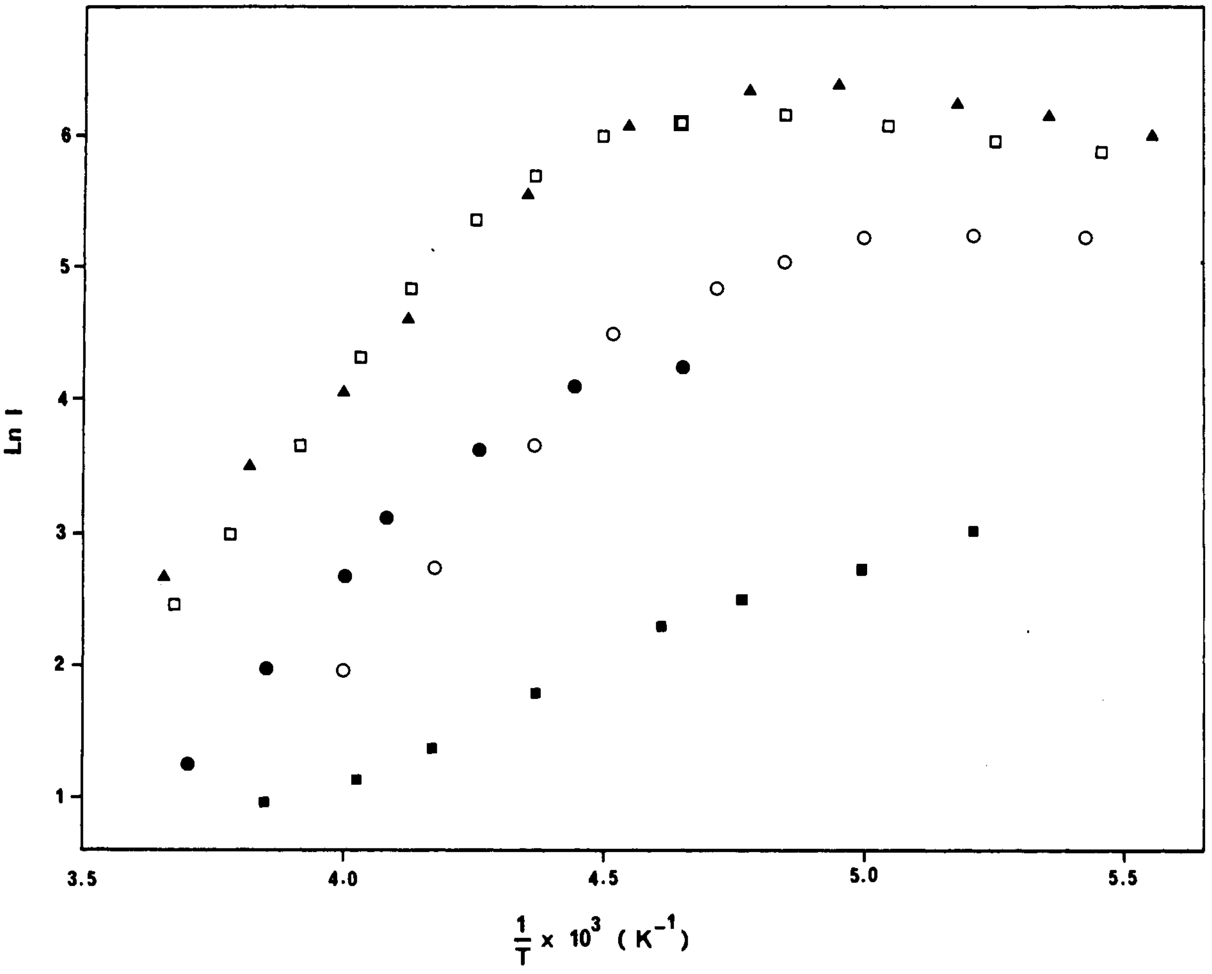

Figure 9. Plots of ln I vs $1/T$ for different cobalt(II) porphyrins, in fluid toluene from $T = 180$ to $T = 270$ K. I is the intensity of the low-field peak (cf. Figure 7). [porphyrin] = [added ligand] = 5×10^{-3} M. Key: (▲) CoTTP + N-MeIm; (□) CoTTP + $nBuNH_2$; (○) CoTTP + py; (●) **6b**; (■) **8b**.

spectral intensities vs $1/T$. This variation of intensity is completely reversible, ruling out the possibility of irreversible oxidation in a cobalt(III) complex.

In presence of O_2, the meta substituted porphyrin **12b** manifests a different behavior from that of the ortho-substituted compound **8b**. At 250 K and 5×10^{-3} M, product **12b** does not have a superoxide spectrum in contrast to product **8b**. However doubling the concentration of **12b** leads to the appearance of the spectrum of the complexed superoxide. This indicates that the dimeric form corresponding to intermolecular complexation is present at a higher concentration.

E. Catalytic Efficiency of the Cobalt "Looping-Over" Porphyrins in the Oxidation of 2,6-Di-*tert*-butylphenol. Oxidation of 2,6-di-*tert*-butylphenol by O_2 was chosen for two reasons.

(1) The rate of this reaction is strongly dependent on the structure of the catalysts.

(2) It yields only two oxidation products: 2,6-di-*tert*-butyl-1,4-benzoquinone and 2,6,2′,6′-tetra-*tert*-butyl-4,4′-diphenoquinone.

Except in the presence of an additional ligand, such as pyridine, CoTTP is a very poor catalyst for the oxidation of phenols by O_2.[2b] To estimate the catalytic efficiency of the cobalt(II) "looping-over"

Table IV. Half-Reaction Times and Yields of the Oxidation of 2,6-Di-*tert*-butylphenol by Different Catalytic Systems in Toluene (T = 296 K), under O_2 (1.1 atm)

catalytic system[a]	reaction half-time,[b] h	% yield after 24 h tot.[c]	BQ[d]	DBQ[e]
CoTTP	>24	2		
CoTTP–N-MeIm[f]	17	80	100	0
CoTTP–nBuNH$_2$[f]	3.3	100	100	0
5b		0		
6b	6	100	95	5
7b	>24	10		
8b	24	50	100	0
12b	>24	21		
CoTTP–NEt$_3$[a]	>24	20		
CoTTP–nBuNH$_2$–NEt$_3$[f]	0.3	100	100	0
CoTTP–*N*-MeIm–NEt$_3$[f]	1.3	100	100	0
6b–NEt$_3$	1.6	100	100	0
8b–NEt$_3$	0.8	100	100	0

[a] NEt$_3$ = triethylamine. [b] Time corresponding to the consumption of half of the theoretical volume of dioxygen. [c] Percent based on phenol. [d] BQ = benzoquinone. [e] DBQ = dibenzoquinone. [f] [porphyrin] = [added ligand] = 5×10^{-3} M.

porphyrins, we have measured the rate of consumption of molecular oxygen by a CH_2Cl_2 solution containing the phenol and the porphyrinic catalyst in a ratio 10:1. Even though the rate law of these oxidation reactions is probably not first order in the two reactants, O_2 and phenol, we have used the half-time of the reactions as a crude estimate of the relative reaction rates. The oxidation half-times thus measured are reported in Table IV. These data demonstrate the following:

The presence of a fifth ligand greatly increases the efficiency of CoTTP, whether it is added to the solution or covalently bound to the porphyrin ligand.

In the absence of a base (NEt$_3$), the "looping-over" porphyrins can be either less or more efficient catalysts than the corresponding CoTTP–L system. For example, complex **6b** was more efficient than CoTTP–1MeIm, whereas a faster oxidation was observed with CoTTP–*n*BuNH$_2$ than with complex **8b**.

The length of the tether bearing the ligand plays a crucial role. Complex **6b** is a very active catalyst whereas complexes **5b** and **7b**, which differ from **6b** by just one $-CH_2-$ on the chain, have practically no catalytic activity.

When the ligand-bearing chain is in the "meta" position of the phenyl ring, e.g. **12b**, very low catalytic efficiency is observed.

These results clearly indicate that the presence of a fifth ligand, either imidazole or $-NH_2$, considerably enhances the catalytic efficiency of the porphyrin, provided it can bind *intramolecularly* to the metal.

This is in complete agreement with the results previously reported concerning the use of cobalt(II) Schiff bases as catalysts:[2a] five-coordinate ligands proved to be much better catalysts than four-coordinate ones.

By reference to the mechanism which was previously proposed for the phenol oxidation[2b] the possible roles of the extra ligand may be the following: (1) to facilitate the binding of O_2 to cobalt; (2) to increase the stability of the (quino)dioxycobalt complex, which is a probable intermediate,[13] and thus to facilitate the reaction between the cobalt–dioxygen adduct and the phenoxy radical; (3) to act as a base that by abstracting a proton to phenol, converts the latter to the phenolate anion, which is easier to oxidize.

To test this assumption, we also performed the oxidation in the presence of 1 equiv of a noncoordinating amine, triethylamine NEt$_3$. The results reported in Table IV show that under these conditions, faster oxidation reactions occur. Depending on the complex, the reaction half-times are decreased by factors ranging from 4 to 30. These significant rate accelerations can be best explained by the conversion of the phenols in the more oxidizable phenolate anion by triethylamine. Consequently, the tethered ligand remains for a large part unprotonated and is free to bind to cobalt. To explain the large variation in rate increase observed in the presence of NEt$_3$, it will be necessary to determine the concentrations of the various species in equilibrium.

The large differences of rates observed with the various imidazole-attached porphyrins are quite remarkable: only complex **6b** catalyzed the oxidation of 2,6-di-*tert*-butylphenol efficienctly, the other complexes **5b**, **7b**, and **12b** being very poor catalysts. This variation must be due to the different affinities of these complexes toward oxygen: complex **6b** readily forms a more stable O_2 adduct than **5b** and **7b** do; **12b** binds O_2 but only at higher concentrations. The length of the tether thus plays a determinant role in the oxygen-binding properties of the complex. It appears that, in complex **6b**, the imidazole group can adopt an adequate geometry with respect to the cobalt–porphyrin moiety which must be required for efficient binding of O_2 whereas in complexes **5b** and **7b** the tether length is not as suitable. Goff[7c] had previously observed that, in the case of the corresponding iron(III) "looping-over" porphyrins, the binding of imidazole occurred with less tension with a 4-CH_2 chain (corresponding to **6b**) than with a 3-CH_2 chain (corresponding to **5b**). Our results suggest that axial imidazole tension can efficiently control the chemical properties of imidazole-attached metalloporphyrins.

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Registry No. **1b**, 127571-63-5; **2b**, 127571-64-6; **3b**, 127571-65-7; **4b**, 127571-66-8; **5b**, 127571-67-9; **6b**, 127571-68-0; **7b**, 127571-69-1; **8b**, 127571-70-4; **10b**, 127571-71-5; **11b**, 127571-72-6; **12b**, 127571-73-7; DMSO, 67-68-5; *N*-MeIm, 616-47-7; nBuNH$_2$, 109-73-9; NEt$_3$, 121-44-8; di-*tert*-butylphenol, 128-39-2.

Supplementary Material Available: Tables showing the analytical and visible data for the synthesized porphyrins and ESR parameters of the four-, five-, and six-coordinated forms of cobalt porphyrins (10 pages). Ordering information is given on any current masthead page.