

Reactivity toward Dioxygen of Dicobalt Face-to-Face Diporphyrins in Aprotic Media. Experimental and Theoretical Aspects. Possible Mechanistic Implication in the Reduction of Dioxygen

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Abstract: The reactivity toward dioxygen of two series of dicobalt cofacial diporphyrins in solution in an aprotic solvent is described. Some of these compounds are efficient electrocatalysts for the four-electron reduction of dioxygen when adsorbed on a graphite electrode immersed in aqueous acid. Their electrochemical and spectroscopic (UV–vis, EPR) behavior in solution shows that, contrary to what is observed with cobalt monomers, the neutral [PCo^{II}Co^{II}P] (1) (P stands for a porphyrin ring) form does not react with dioxygen. Uniquely the one- and two-electron-oxidized forms of the dimer, [PCo^{III}Co^{II}P]⁺ (1⁺) and [PCo^{III}Co^{III}P]²⁺ (1²⁺), respectively, reversibly bind dioxygen, giving two complexes, 2 and 3, at room temperature and in the absence of a good axial ligand. The stability constants of the two O₂ complexes have been measured spectrophotometrically and/or electrochemically, and prove to be remarkably high. As a whole, the present O₂ binding processes appear unprecedented as basically different in many respects from the process classically described in the case of cobalt monomers. Extended Hückel molecular orbital (EHMO) calculations, based on the crystal structure of the Co₂FTF4 dimer in its uncomplexed form (Co–Co distance 3.42 Å), show that, in the absence of very important deformations of its structure, the only possible geometry for the O₂ complex of the two-electron-oxidized derivative [PCo–O₂–CoP]²⁺ (3) is the μ-η²:η²-peroxo structure. The calculated corresponding electronic diagram affords a rationale for most of the experimentally observed properties. Specifically, the O₂ complex of the one-electron-oxidized form [PCo–O₂–CoP]⁺ (2), the reduced form of complex 3, should be considered as a species in which the O₂ moiety is further reduced, at least partially, as compared to its peroxo state in 3, i.e., consequently in an oxidation state intermediate between peroxo (–1) and oxo (–2). Preliminary results indicate that this species reacts with one proton, while the two-electron-oxidized O₂ complex 3 is resistant to protonation. The possible implications of these specific properties of the dicobalt dimers in the four-electron reduction mechanism of O₂ are discussed, and structural and mechanistic similarities with bioinorganic dinuclear sites appear significant.

Dicobalt cofacial diporphyrins^{1–5} are among the very few molecular electrocatalysts^{6–8} able to promote the direct reduction of dioxygen to water by a four-electron mechanism in an acidic medium. Mononuclear derivatives under the same conditions reduce dioxygen to hydrogen peroxide by a two-electron process.⁹ Understanding the catalytic cycle by which this four-electron reduction of O₂ proceeds and the properties critical for the catalyst's efficiency is a challenge of relevance to electrocatalysis for catalyst design and improvement as well as to bioinorganic reduction of O₂ by dinuclear systems such as cytochrome *c* oxidase,¹⁰ non-heme diiron sites,¹¹ copper oxidases,¹² etc. However, the exact mechanism for this catalysis

has yet remained elusive in spite of the amount of related research.^{2–5,13,14} Actually, the four-electron reduction process is only observed when the dicobalt dimers are adsorbed on an edge plane graphite electrode (EPGE) immersed in aqueous acid. Under these conditions, the redox exchanges, their sites on the molecule, the complexation of O₂, and protonation steps are

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practically impossible to determine. The proposed mechanisms were at first based on the electrochemical response of the EPG electrode interpreted in terms of the well-known properties and reactivity toward O_2 of monomeric porphyrins in nonaqueous solvents.¹⁵ It was also shown that very small modifications in the structure of these dicobalt dimer derivatives could induce a partial to total loss of their efficiency (Figure 1).^{1-3,13} Minor structural differences in the series cannot account for crucial differences in the absorption modes. This indicates that the adsorption mode does not determine on its own the efficiency of the catalysts, but that the efficiency is controlled by their structures and the resulting properties and reactivity toward O_2 . Hence, the actual properties of these compounds could constitute a new basis, alternative to those of the cobalt monomers used so far, for the interpretation of the EPGE response, and provide a new insight into the catalytic cycle.

We have undertaken a study of the electrochemical and spectroscopic properties of the dicobalt compounds in aprotic solvents. The goal was to emphasize any difference in their behavior and reactivity toward dioxygen in comparison with those of the monomeric cobalt porphyrins,¹⁵ as well as differences between the dimers in the series. It appeared that their cofacial configuration perturbed their electrochemical properties so strongly that they could not be interpreted on the basis of the juxtaposition of two independent monomers.¹⁶⁻¹⁸ From an electrochemical point of view, it was shown that the dimers must be considered as a single entity, from which or to which electrons are abstracted or added, and that, even in a moderately

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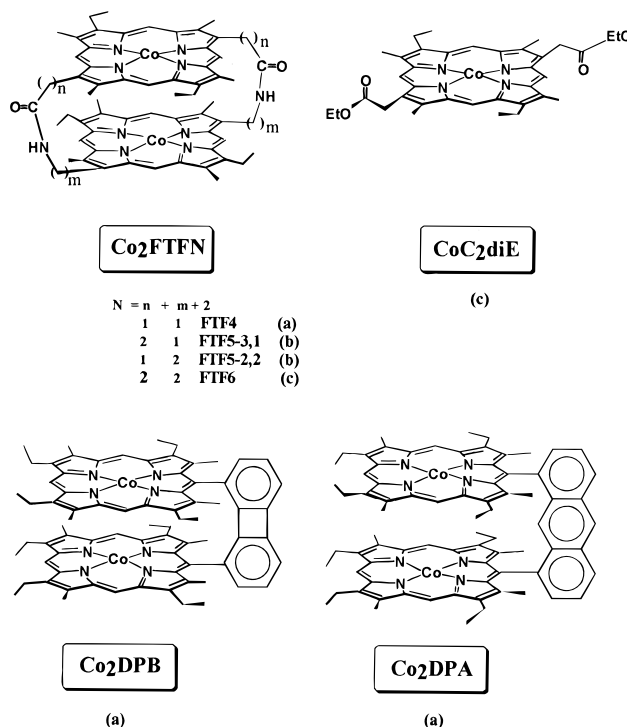
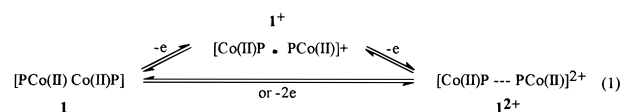


Figure 1. Representation of the dicobalt cofacial dimers examined in the present study: FTF n series and Pacman (DPA + DPB) series; (group 1) FTF6, DPA; (group 2) FTF4, FTF5-2,2, FTF5-3,1, DPB. When these dimers are adsorbed on EPGE in an aqueous acid medium,^{1-3,13} they (a) reduce O_2 to H_2O at a ca. 100% yield, (b) reduce O_2 to a mixture of H_2O and H_2O_2 , and (c) reduce O_2 to H_2O_2 .

coordinating medium such as benzonitrile (PhCN), the sites for the first oxidation process of the dicobalt dimers are the π -ring¹⁹ (eq 1), either through sequential one-electron processes, when



the porphyrins are very close to each other (group 2 compounds: FTF4, FTF5-2,2, FTF5-3,1, DPB), or through a one-step two-electron process when they are farther apart (group 1 compounds: FTF6, DPA) (see Figure 1).²⁰ The cobalt(II) atoms are oxidized to cobalt(III) only in a subsequent process. Under the same conditions, in the case of monoporphyrins, the cobalt(II) is oxidized at the first process.¹⁸ These specific properties of the dimers were proposed to result from a so-called "cofacial" effect of interactions, combination of π -ring- π -ring and cobalt-cobalt interactions of the two cobalt porphyrin moieties: this effect was explicated previously in terms of molecular orbital calculations.¹⁸ Preliminary results^{21,22} also evidenced a unique behavior of this family of compounds with regard to O_2 binding comparatively to monomers. However, this behavior could not be understood before the electronic properties of the dicobalt dimers were understood.¹⁸ So far the characterization of the

(19) Throughout the present paper, P designates the π -rings of the porphyrins. The dot designates an electron delocalized over the two π -rings, and the three dashes are the equivalent of a weak π - π bond obtained by pairing of two electrons (see ref 17). In the following the formal redox states of the cobalt will be omitted unless the issue of the electron repartition is specifically addressed.

(20) As in previous papers,^{17,18} we designate (i) by *process* the global abstraction of two electrons from the dimer, corresponding to one electron for each monomeric unit constituting the dimer, and (ii) by *step* each of the individual electrochemical reactions. Each process can thus take place either in two one-electron steps or in one two-electron step, not excluding that they may be intermingled.

dioxygen complexes of these dimers could be carried out neither by their crystal structures²³ nor by Raman studies.²⁴

The outcome of the oxidation pathway under N₂ evidenced by these dimers in benzonitrile (PhCN) (eq 1) is that, even in their oxidized forms, the dimers remain potentially reactive toward O₂ as still bearing cobalt(II). The purpose of the present report is the description of the reactivity toward O₂ of the two series of dimers shown in Figure 1, and for one example, Co₂-FTF4, the reactivity toward protons of the O₂ complexes. Extended Hückel molecular orbital (EHMO) calculations, based on the Co₂FTF4 structure,²⁵ advocate for a $\mu\text{-}\eta^2\text{:}\eta^2$ configuration for the O₂ complexes (Griffith-bridged coordination mode):^{9a,26} this electronic structure affords a theoretical basis for the unique O₂ reactivity of these dimers as compared to monomers.^{21,22} The possible implication of these properties in the O₂ four-electron reduction process is discussed, and comparison is made with some relevant biological dinuclear sites.

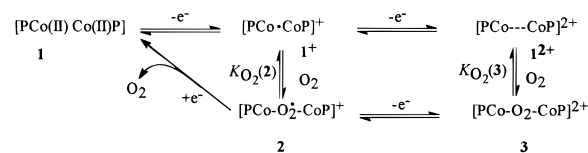
Experimental Section

Since the compounds used in the present work are obtained at very low yields after long synthetic routes, the available quantities for electrochemistry were very low (a few milligrams for each). This means that each experiment had to be performed on a very small fraction (0.2–0.3 mg) dissolved in minute volumes (ca. 300 μL) of solvent. Furthermore, the solubility of these compounds is low (<ca. 7×10^{-4} M). For these reasons, some of the quantitative measurements were obtained with a limited precision. Owing to the extreme sensitivity of these dimers to traces of oxygen and water, all experiments were carried out in a dry nitrogen atmosphere box with carefully deoxygenated solvents and chemicals.

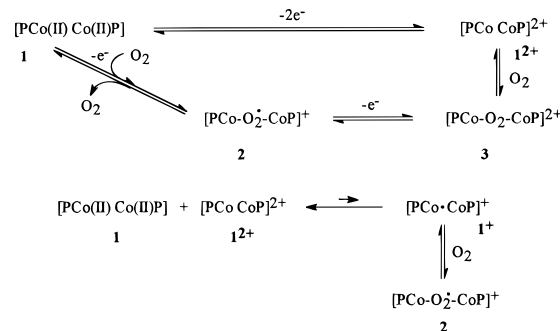
Chemicals. The synthesis, purification, and characterization of the diporphyrins of the FTFN series^{1,3} and the DPX (X = A or B) "Pacman" series³ have been described in detail elsewhere. All were synthesized at Stanford. The solvent (mainly benzonitrile (PhCN)) and the supporting electrolyte (tetrabutylammonium hexafluorophosphate (Bu₄NPF₆)) were purified as previously described.¹⁶ Solutions of the supporting electrolyte were prepared in the drybox, stored on molecular sieves (Linde 4 Å), and twice percolated through an activated (400 °C under vacuum for 48 h) neutral alumina (Merck) column. The oxidized forms of the derivatives were generated electrochemically: thus, all the spectra were recorded in the presence of the supporting electrolyte. To record the spectra, solutions were transferred from the electrochemical cell to EPR tubes or to UV-vis cuvettes and sealed prior to removal from the drybox. For measurements of the stability constants of the O₂ complexes, saturation of the solutions by O₂/N₂ mixtures were conducted in the drybox by bubbling directly in the electrochemical or UV-vis cells or EPR tubes. Gas mixtures were prepared either by mixing known volumes of gas in a flask (for low $p(\text{O}_2)$) or by using a mixing pump (Digamix, H. Wösthoff). In any case pure O₂ or mixtures were dried over freshly activated molecular sieves before introduction in the box in a Schlenk flask.

Apparatus. The drybox was manufactured by Jaram. The nitrogen flow was continuously purified by passage through molecular sieves at ambient temperature and divided copper BTS catalyst (BASf) at 100 °C. The electrochemical cell was specifically designed to fit the rotating disk electrode (EDI Tacussel) for a minimum volume of solution in the main compartment. The auxiliary and reference (ferrocenium/ferrocene (Fc⁺/Fc)) electrodes were in separate compart-

Scheme 1. Oxidation Pathways for Group 2 Dimers in the Presence of O₂¹⁹



Scheme 2. Oxidation Pathways for Group 1 Dimers in the Presence of O₂¹⁹



ments connected to the main one through ground joints terminated by frits (Vycor tips from PAR). For voltammetric measurements, a platinum disk ($\varnothing = 2$ mm) was employed, and the electrolyses were performed with the same electrode, but rotated, equipped with a 4 mm diameter disk. For the purpose of comparison, the formal potential of Fc/Fc⁺ versus SCE is 0.43 V measured in the same medium (PhCN, 0.2 M Bu₄NPF₆). A Model PAR 173 potentiostat equipped with a PAR 179 digital coulometric unit, was monitored by a PAR 175 programmer. The chart recorder was a T-2Y SEFRAM ENERTEC. UV-vis spectra were recorded on a CARY 219 spectrophotometer from Varian. A JEOL FE3X apparatus was used for the EPR spectroscopy. Spectra were recorded from solutions ($V = 40$ μL) at a concentration close to 5×10^{-4} M in quartz tubes with a power of 1 mW and frequency close to 9.2 GHz.

Results

Reactivity toward Dioxygen. The reactivity toward O₂ of the dimers in the different redox states depicted in eq 1 has been monitored by UV-vis and EPR spectroscopies of their electrochemically generated solutions under N₂ in benzonitrile (PhCN). The influence of O₂ on their electrochemical behavior is described below, and the thermodynamic stability constants of the O₂ complexes were determined. In the case of cobalt(II) monomer it has been shown that the presence of a donor axial ligand such as a nitrogenous base, usually designated by L, is a prerequisite for O₂ binding.¹⁵ Thus, the effect of the presence of such a ligand L, *N*-methylimidazole (*N*-MeIm) in the solvent, has been examined. The O₂ binding pathways emphasized by these results are depicted in Scheme 1 for group 2 dimers and Scheme 2 for group 1 dimers.¹⁹

Spectroscopy. The neutral derivatives [PCo^{II}Co^{II}P] (1) of the dimers of both group 1 and group 2 do not reversibly bind O₂. In the pure solvent, after several hours, a very slight evolution of the UV-vis and EPR spectra of this species is observed indicative of an irreversible oxidation to complex 2 via 1⁺. In the presence of *N*-MeIm the same oxidation/O₂ complexation reaction is instantaneously observed.²⁷ The low-temperature EPR spectrum of 1, in the presence of *N*-MeIm, observed under N₂, characteristic of exchange-coupled dicobalt systems^{2b,16} shown in Figure 2a (spectrum 1), disappeared in the presence of 1 atm of O₂ to give rise instantaneously at low temperature to an anisotropic signal (Figure 2b) corresponding to a 15-line spectrum at room temperature.^{21,28} If only a very small amount of O₂ is introduced into the solution, the intensity of the signal of the initial solution decreases and is replaced by

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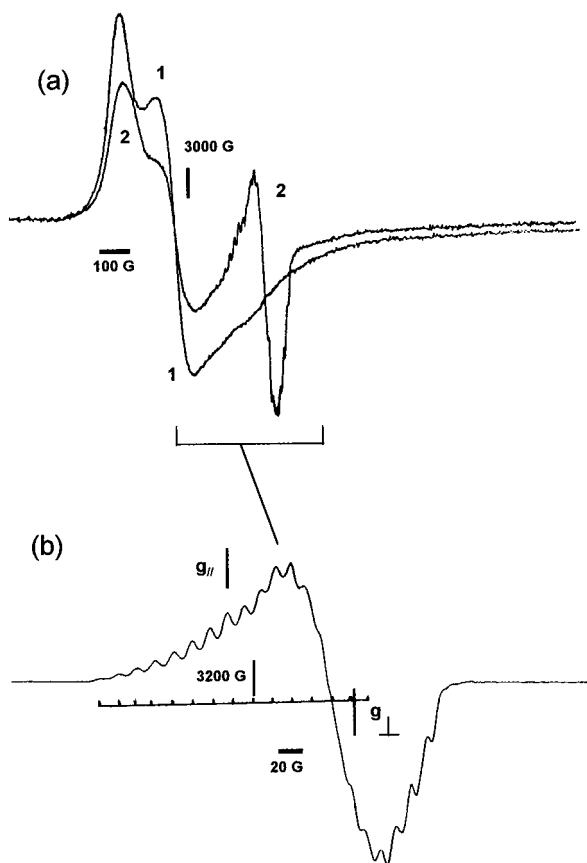


Figure 2. EPR spectra of frozen (130 K) solutions of the diporphyrin $\text{Co}_2\text{FTF4}$ in PhCN, in its neutral form $[\text{PCo}^{\text{II}}\text{Co}^{\text{II}}\text{P}]$, in the presence of *N*-MeIm (*N*-MeIm/Co ratio ca. 20): (a) spectrum 1, under N_2 ; spectrum 2, after adding a trace of O_2 ; (b) under O_2 , $p(\text{O}_2) = 1$ atm.

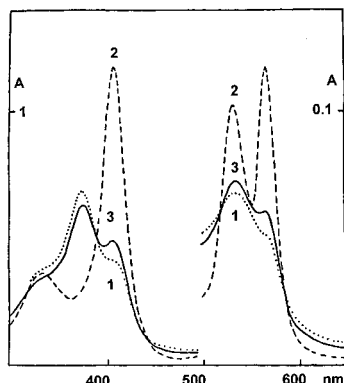


Figure 3. UV-vis spectrophotometry of solutions of the $\text{Co}_2\text{FTF4}$ diporphyrin, in its one-electron-oxidized form $[\text{PCo}\cdot\text{CoP}]^+$, in PhCN, 0.2 M Bu_4NPF_6 , $C \approx 4 \times 10^{-5}$ M: (1) under N_2 ; (2) under O_2 ; (3) after bubbling N_2 .

ca. an equivalent amount (in terms of integration) of the 15-line anisotropic signal. This evolution shown in Figure 2a indicates that no diamagnetic intermediate is involved.

The one-electron-oxidized form of group 2 complexes, 1^+ , reacts immediately and reversibly with O_2 in pure PhCN, giving the complex $[\text{PCo}-\text{O}_2^-\text{CoP}]^+$, **2**. As shown in Figure 3 in the case of $\text{Co}_2\text{FTF4}$, the broad UV-vis bands observed for these derivatives under N_2 , close to the spectrum of π -radical cations,^{17,29a} are replaced, in the presence of O_2 , by new sharp

(27) The presence of H_2O and traces of aqueous acid increases the rate of the oxidation + O_2 complexation reaction. Under protic conditions (H^+ or H_2O) this is probably due to an increased oxidizing power of O_2 by stabilization of its reduced forms which was not scrutinized. In the presence of an axial donor ligand on cobalt(II), it is ascribable to the lowering of the oxidation potential of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ by stabilization of the Co^{III} redox state.

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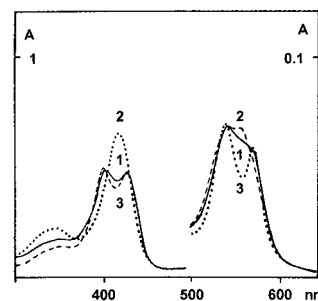


Figure 4. UV-vis spectrophotometry of solutions of the Co_2DPA diporphyrin, half-electrolyzed at a potential on the first oxidation wave (mixture $[\text{PCo}\cdot\text{CoP}] = [\text{PCo}-\text{CoP}]^{2+}$), in PhCN, 0.2 M Bu_4NPF_6 , $C \approx 4 \times 10^{-5}$ M: (1) under N_2 ; (2) under O_2 ; (3) after bubbling N_2 .

bands, in both the Soret and visible parts of the spectra. This change is reversible, and bubbling N_2 or Ar in the solution completely restores the original spectrum. The spectra of the oxygenated derivatives of all the group 2 compounds are very similar with λ_{max} (nm) (ϵ (10^{-3} L·mol $^{-1}$ ·cm $^{-1}$)) \approx 407 (140), 531 (12), and 565 (13). By EPR, the addition of O_2 in solutions of $[\text{PCo}\cdot\text{CoP}]^+$ generates at room temperature a 15-line spectrum as previously reported.²¹ The corresponding low-temperature anisotropic spectrum is similar to that shown in Figure 2b. The spectra obtained for all the derivatives of group 2 are very similar, [$g_{\text{iso}} = 2.02$ ($A_{\text{iso,Co}} = 12-14$ G), $g_{\parallel} = 2.09$ $g_{\perp} = 2.00$ ($A_{\parallel,\text{Co}} = 15-17$ G)], and the presence of *N*-MeIm modifies the characteristics of the spectra only slightly. This kind of spectrum is usually ascribed to a μ -superoxodicobalt configuration $[\text{PCo}^{\text{III}}-\text{O}_2^-\text{Co}^{\text{III}}\text{P}]^+$ in which the dioxygen is bridged between the two cobalt atoms and the unpaired electron is partly delocalized on the two cobalt nuclei ($I = 7/2$).^{2b,3a,b,21,23,24,28}

Concerning the one-electron-oxidized solutions of the less interactive group 1 compounds $\text{Co}_2\text{FTF6}$ and Co_2DPA , the situation is different as these solutions correspond to a 1:1 mixture of the neutral and two-electron-oxidized forms **1** and 1^{2+} .¹⁶ As shown in Figure 4, in pure PhCN, the presence of O_2 in solution has an effect similar to that for group 2 derivatives. It induces an instant transformation of the original UV-vis spectrum into one very similar to that of group 2 oxygenated derivatives. This process is reversed by bubbling N_2 . The observation is similar in the presence of *N*-MeIm. EPR demonstrates that the formulation of the oxygen complexes is different for the two derivatives. In the case of the Co_2DPA dimer, the spectrum is the typical 15-line signal at room temperature and that of Figure 2b at low temperature, quite similarly to that of group 2 complexes. Conversely in the case of the $\text{Co}_2\text{FTF6}$ dimer, the room temperature spectrum of the oxygenated complex displays eight equivalent lines and at low temperature the corresponding anisotropic signal. The characteristics of the spectra are the same as for the spectra discussed above, except that $A_{\parallel,\text{Co}} = 36$ G. This kind of spectrum corresponds to nonbridged superoxo complexes,¹⁵ in which O_2 interacts with only one cobalt atom: this indicates that the two cobalt centers of the $\text{Co}_2\text{FTF6}$ derivative are too far apart for a bridged-oxygen conformation. As $\text{Co}_2\text{FTF6}$ and Co_2DPA are structurally similar in terms of the Co-Co distance in their uncomplexed forms, the formation of a bridged species in the case of Co_2DPA can be explained by a closing process of the two rings allowed by the single linking bridge between the two porphyrins.

Unprecedentedly, it was found that the two-electron-oxidized form of the complexes, 1^{2+} , also reversibly binds dioxygen,

(29) (a) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Part C, p 53. (b) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Part B, p 197.

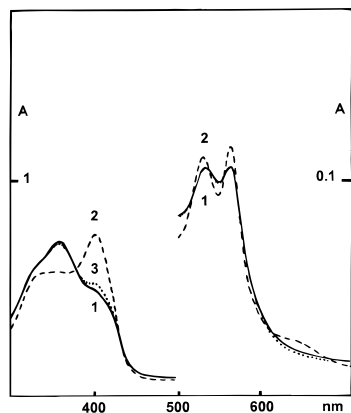


Figure 5. UV-vis spectrophotometry of solutions of the Co₂FTF4 diporphyrin, in its two-electron-oxidized form [PCo--CoP]²⁺, in PhCN, $C \approx 4 \times 10^{-5}$ M: (1) under N₂; (2) under O₂; (3) after bubbling N₂.

leading to [PCo-O₂-CoP]²⁺, **3**. On the basis of our previous assignment of this derivative as an isoelectronic dicobalt(III) configuration [PCo^{III}Co^{III}P]²⁺, O₂ binding could not be explained.²² The reversible formation of the O₂ complex **3** is evidenced by UV-vis spectrophotometry (Figure 5) in the case of the Co₂FTF4 dimer. The characteristics of its spectrum are λ_{\max} (nm) (ϵ (10⁻³ L·mol⁻¹·cm⁻¹)) = 400 (~70), 532 (~8), 564 (~8), and 650 sh. The wavelengths of these bands are closer to those generally observed for cobalt(III) derivatives, but their intensities are decreased by a factor of ca. 2 as compared to cobalt(II) or cobalt(III) derivatives.¹⁸ A weak shoulder is observed at 650 nm which suggests a π -cation radical.^{29a} O₂ binding to [PCo--CoP]²⁺ is also evidenced by EPR. The original two-electron-oxidized **1**²⁺ species is EPR silent under N₂. Saturation of the solution with O₂ generates a one-line spectrum with $g = 2.004$ (LW = 9 G) typical of a porphyrin π -cation radical.^{29b} Its intensity decreases on bubbling N₂, and re-increases by saturating on O₂.³⁰ In the presence of added H₂O or of *N*-MeIm in the solution of **1**²⁺, no O₂ binding is observed.

Electrochemistry under O₂. The specific reactivity toward dioxygen of the dicobalt porphyrin dimers in their different redox states is also supported by the voltammetric behavior of these compounds. As in most of the usual solvents, it was verified that in pure PhCN the electrochemical behavior of cobalt monoporphyrins is absolutely not modified in the presence of O₂ in the absence of a strong donor ligand (L). Conversely, even in the absence of L, the cyclic voltammograms (CV) of the dimers are completely transformed in the presence of O₂. The transformation is totally reversible, and N₂ bubbling restores the original CV. Figure 6 shows the effect of O₂ ($p(\text{O}_2) = 1$ atm) on the cyclic voltammogram of the first oxidation process²⁰ of the Co₂FTF4 dimer. The O₂ effect is qualitatively the same for each compound of group 2. The second and third oxidation processes of these dimers are very little affected by the presence of oxygen and are not displayed in Figure 6. Electrochemical data are reported in Table 1. Under N₂, cyclic voltammetry of the dicobalt cofacial dimers, for their first oxidation process, displays two discrete one-electron reversible steps ascribed to the oxidation of the π -rings of the porphyrins as outlined in eq 1.¹⁶⁻¹⁸ When the solution is saturated with dioxygen, the splitting between the two redox steps is largely increased. The first oxidation step occurs at a more negative potential and

(30) The intensity of the EPR signal, integrated against that of the π -cation radical of ZnTPP as previously described,¹⁷ gave inaccurate values between 1 and 2 equiv of electrons ($n = 1.3 \pm 0.6$). This may be due to the low stability of the complex **3**, reaction with H₂O, and a mixture of electronic configurations (e.g., a triplet state).

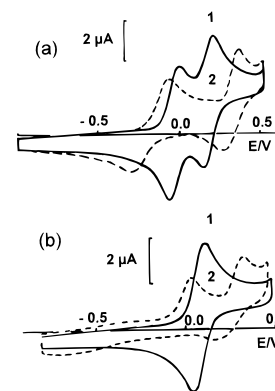


Figure 6. Cyclic voltammetry of the dicobalt diporphyrins: (a) Co₂FTF4 and (b) Co₂FTF6, in PhCN, 0.2 M Bu₄NPF₆ (Pt electrode; reference Fc⁺/Fc, 0.1 V/s); (1) (—) under N₂; (2) (- - -) under O₂, $p(\text{O}_2) = 1$ atm. After (2), (1) is integrally restored through N₂ bubbling.

Table 1. Electrochemical Data for the Dicobalt Porphyrin Dimers under O₂^a

porphyrin	$E_{\text{pa}}^b(2/1)^c/V$ ($\Delta E_p/mV$) ^d	$E'^c(3/2)^c/V$ ($\Delta E_p/mV$) ^d
Co ₂ FTF4	-0.12 (200)	0.34 (75)
Co ₂ FTF5-3,1	-0.10 (400)	0.26 (80)
Co ₂ FTF5-2,2	-0.03 (400)	0.34 (100)
Co ₂ FTF6	-0.04 (70)	0.25 (150)
Co ₂ DPB	-0.04 (600)	0.32 (80)
Co ₂ DPA	0.00 (700)	0.35 (100)

^a Obtained from cyclic voltammetry in PhCN + Bu₄NPF₆; platinum electrode; 100 mV/s; reference Fc⁺/Fc; $p(\text{O}_2) = 1$ atm. ^b E_{pa} = potential of the anodic peak. ^c As defined in Scheme 1. ^d $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$.

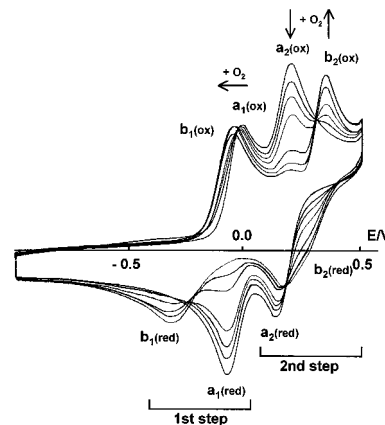


Figure 7. Variation of the cyclic voltammogram for a solution of Co₂FTF4 with the partial pressure of O₂ increasing from 0 to 0.05 atm. Peak a corresponds to the uncomplexed derivatives; peak b corresponds to the O₂ complexes (IPP = isopotential points; PhCN, 0.2 M Bu₄NPF₆; Pt electrode; reference Fc⁺/Fc, 0.1 V/s).

becomes electrochemically irreversible (non-Nernstian) with a very large peak-to-peak separation (e.g., $\Delta E_p = E_{\text{pa}} - E_{\text{pc}} = 300$ mV at 0.1 V·s⁻¹) dependent on the scan rate. Moreover, as shown in Figure 7, the anodic peak of the first step is gradually shifted negatively when $p(\text{O}_2)$ is increased (peaks: a₁(ox) → b₁(ox)) ($0 < p(\text{O}_2) < 0.05$ atm). Critically, the negative shift and broadening of the cathodic reverse peak (peaks: a₁(red) → b₁(red)) increases with the sweep rate. These observations indicate that the electrochemical oxidation step (E) **1** → **1**⁺ is followed by a chemical step (C), namely, O₂ binding by **1**⁺ to give complex **2** (EC process),³¹ and that on the reverse scan decoordination of O₂ is observed during the reduction of **2** to **1**.

The second oxidation step observed under N₂ is replaced under O₂ by a new fully reversible process, at a more positive potential as displayed in Figure 6 at $p(\text{O}_2) = 1$ atm, with $\Delta E_p \approx 60$ mV, normal potential, and $i_{\text{pa}}/i_{\text{pc}} (\sim 1)$, each independent

of the scan rate. This indicates that no chemical reaction is detected during the electrochemical oxidation of the O₂ complex **2**. Moreover, it is evidenced in Figure 7 that the variation of $p(\text{O}_2)$ leads for this second oxidation step to a simple interconversion between the redox system observed under N₂ (peaks a₂) and that observed at $p(\text{O}_2) = 1$ atm (peaks b₂). This result demonstrates the independence with respect to $p(\text{O}_2)$ of the redox potentials. Together with the observation of isopotential points (IPP),³² for both the anodic and cathodic peaks, this observation indicates that the oxidized form of complex **2** also corresponds to O₂ complex **3**. These observations unambiguously establish, as presented in Scheme 1,^{31c} that, in the case of group 2 dimers in agreement with the spectroscopic behavior, the neutral form of the dimers [PCo CoP] (**1**) does not bind O₂, while the one- and two-electron-oxidized forms [PCo•CoP]⁺ (**1**⁺) and [PCo---CoP]²⁺ (**1**²⁺) react reversibly with O₂ to give complexes **2** and **3** which interconvert reversibly.

Concerning group 1 dimers, as recalled in Figure 6b in the case of Co₂FTF6, under N₂ their first oxidation is a reversible one-step two-electron exchange.¹⁶ As expected from the spectroscopic results, the presence of O₂ in the solutions of this family of derivatives also has a pronounced effect on their voltammograms, still even in the absence of a strong donor ligand (L). It induces a very large splitting into two one-electron steps for this first oxidation process. The subsequent oxidation processes are not altered by the presence of oxygen. The voltammetric behavior of the two redox systems observed under O₂ is qualitatively the same as that described for group 2. The first system is clearly associated with a chemical reaction with broadened peaks and even larger peak to peak separation ($\Delta E_p \approx 500$ mV at $\nu = 100$ mV•s⁻¹), and dependence of the peak potentials on scan rate and $p(\text{O}_2)$. The second system is quasi-reversible, independent of ν and $p(\text{O}_2)$. The same observations are made with Co₂DPA. In accordance with the spectroscopic observations, these electrochemical results demonstrate that the presence of dioxygen has the same effect as with group 2 dimers, which implies a comproportionation reaction via the intermediate compound **1**⁺, stabilized as the oxygen complex **2** (Scheme 2).

The existence of O₂ binding for group 1 compounds illustrates once more the unprecedented properties of this family even for complexes showing weaker intramolecular interactions. Noteworthy is the fact that one of these two compounds, Co₂DPA, is an efficient catalyst for the four-electron reduction of O₂, and the other, Co₂FTF6, is not.¹⁻³ This observation is very significant as it is shown above by EPR that Co₂DPA gives a bridged O₂ complex, and Co₂FTF6 an unbridged one.

Determination of the Stability Constants of the O₂ Complexes. The stability constants of the dioxygen derivatives **2** and **3**, respectively, $K_{\text{O}_2(\mathbf{2})}$ and $K_{\text{O}_2(\mathbf{3})}$ (Scheme 1),^{31c} were determined in the case of group 2 compounds by spectrophotometric and electrochemical methods. In the case of group 1 compounds, the presence of more than two species in equilib-

(31) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamental and Applications*; John Wiley & Sons: New York, 1980. (b) Brown, E. R.; Large, R. F. In *Techniques of Chemistry; Physical Methods of Chemistry; Electrochemical Methods*; Weisberger, A., Ed.; Wiley-Interscience: New York, 1971; Vol. I, Part IIA, p 530. (c) Scheme 1 corresponds almost exactly to that proposed by Savéant et al. from similar observations as a model example. Thermodynamic treatment for the determination of the constants was made following the same procedure. Lexa, D.; Rentien, P.; Savéant, J. M.; Xu, F. *J. Electroanal. Chem.* **1985**, *191*, 253.

(32) An IPP (isopotential point) is the equivalent in voltammetry of an isobestic point in spectroscopy; it arises when one electroactive species undergoes a transformation to form another. The existence of an IPP implies that the transformation is quantitative and the sum of the reactants and products remains constant. If there are any side reactions involving either set of species, an IPP does not occur. See: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888 and references therein.

Table 2. Stability Constants^a of Complex **2**,^b $K_{\text{O}_2(\mathbf{2})}$ and Complex **3**,^b $K_{\text{O}_2(\mathbf{3})}$, of the Different Dicobalt Group 2 Dimers

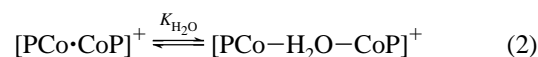
porphyrin	log $K_{\text{O}_2(\mathbf{2})}$		log $K_{\text{O}_2(\mathbf{3})}$
	spectrophotometry	potentiometry	voltammetry
Co ₂ FTF4	3.3 ± 0.3	3.0 ± 0.1	0.5 ± 0.2
Co ₂ FTF4 (H ₂ O) ^c	1.3 ± 0.4		
Co ₂ FTF4 (<i>N</i> -MeIm) ^d	3.0 ± 0.3		
Co ₂ FTF5-3,1	0.8 ± 0.1	0.8 ± 0.1	-1.4 ± 0.2
Co ₂ FTF5-2,2	2.0 ± 0.1	2.0 ± 0.1	-1.6 ± 0.2
Co ₂ DPB	1.9 ± 0.1		-0.8 ± 0.2

^a Values expressed in atm⁻¹, except those noted in footnote c, obtained in PhCN + Bu₄NPF₆, 0.2 M; 20 °C. ^b Complex **2** and complex **3** as defined in Scheme 1. ^c $K_{\text{O}_2(\text{H}_2\text{O})}$ in M•atm⁻¹, [H₂O] = 0.1 M. ^d Ratio *N*-MeIm/Co = 2, 5, 1000.

rium resulting from the comproportionation between the neutral species [PCo CoP] and the two-electron derivative [PCo---CoP]²⁺, observed under O₂, and formation of two dioxygen complexes, **2** and **3** (Scheme 2), precluded the determination of the constants.

(i) Spectrophotometry. In the case of the one-electron-oxidized form **1**⁺ of group 2 compounds, an increase of the partial pressure of O₂ in the gas saturating the solution generates a set of spectra corresponding to the conversion of the deoxy form into the oxy form **2** of complex **1**⁺. The observation of isobestic points reflects clearly the equilibrium between these two forms of the complex. The values of $K_{\text{O}_2(\mathbf{2})}$ calculated from these sets of spectra are reported in Table 2.³³

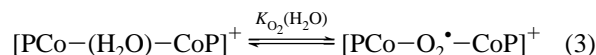
Similar experiments were performed on solutions of Co₂FTF4 in the presence of *N*-MeIm present at different ratios: *N*-MeIm/Co₂FTF4 = 2, 50, and 2000. Contrary to what is observed in the case of the cobalt monoporphyrins, the presence of the ligand and its concentration do not significantly affect the value of the constant in benzonitrile (Table 2). The presence of H₂O in the solvent considerably lowers the binding constant: $K_{\text{O}_2(\text{H}_2\text{O})} = 10^{1.3 \pm 0.4}$ M•atm⁻¹. Spectrophotometric titration indicates the ligation of H₂O by the one-electron-oxidized species **1**⁺ under N₂: $K_{\text{H}_2\text{O}} = 10^{1.3 \pm 0.1}$ M⁻¹ for the equilibrium



The value of this constant compared to that obtained under O₂ under anhydrous conditions

$$K_{\text{O}_2(\text{H}_2\text{O})}K_{\text{H}_2\text{O}} = 10^{2.6 \pm 0.5} \approx K_{\text{O}_2(\mathbf{2})}$$

indicates a competition between dioxygen and water for binding inside the cavity:



Incidentally this corroborates the assumption that the water molecule is bound inside the interporphyrin cavity.

(ii) Potentiometry. Given the kinetic perturbation associated with the first oxidation step under O₂, a direct determination of $K_{\text{O}_2(\mathbf{2})}$ from voltammetric measurements could not be considered. A suitable method is potentiometry of an electrogenerated equimolecular solution of the neutral and one-electron-oxidized species for different $p(\text{O}_2)$ ($0.1 < p(\text{O}_2) < 1$ atm). The relationship between the electrode potentials of this solution under a nitrogen atmosphere, $E_{\text{N}_2}(\mathbf{1})$, and under a given partial

(33) Optical density measurements were performed on each set of spectra of the isobestic set at λ_{max} of the Soret band of the oxy form of the complexes (400–410 nm range), where the absorbance variations are maximal. The data were computed with the "Micmac" program for nonlinear least-squares multiparametric refinement of Laouenan et al., which allows the direct determination of the equilibrium constants. See: Laouenan, A.; Suet, E. *Talanta* **1985**, *32*, 245.

pressure of dioxygen $p(\text{O}_2)$, $E_{p(\text{O}_2)}(1)$, is given by

$$\Delta E = E_{N_2}(1) - E_{p(\text{O}_2)}(1) = 0.059 \log(1 + K_{\text{O}_2}(2)p(\text{O}_2))$$

The values of $K_{\text{O}_2}(2)$ obtained by this method are presented in Table 2.^{34a} The good concordance with the spectrophotometric determination ensures their validity over the whole range of $p(\text{O}_2)$, inasmuch as the two methods relate to different physicochemical properties and operate in two complementary ranges, $p(\text{O}_2) = 0$ to 0.1–0.2 atm and 0.1 to 1 atm, respectively, for spectrophotometry and electrochemistry. This technique cannot be applied when H_2O or $N\text{-MeIm}$ is present in the solution as several redox systems become intermingled.

(iii) **Voltammetry.** The stability constant $K_{\text{O}_2}(3)$ can be obtained directly by voltammetric measurements.^{34b} It is shown above that the redox couple corresponding to the interconversion of the oxygen complex **2** into complex **3** is reversible, independent of $p(\text{O}_2)$, and not affected by kinetic effects. Therefore, the value of the constant can be directly derived from the normal potentials of the second oxidation step under N_2 , $E^{\circ}_{N_2}(2)$, and under O_2 , $E^{\circ}_{\text{O}_2}(2)$:

$$\log K_{\text{O}_2}(3) = \log K_{\text{O}_2}(2) - \frac{E^{\circ}_{\text{O}_2}(2) - E^{\circ}_{N_2}(2)}{0.059}$$

The values of $K_{\text{O}_2}(3)$ for the different derivatives (Table 2) appear significantly lower than those of complex **2**, and are discussed below.

Reactivity of the Oxygen Complexes toward Protons. The strong pH dependence of the O_2 electrocatalytic reduction process by dicobalt complexes, when adsorbed on EPGE, emphasized by Collman and Anson et al.,^{1,2,13} is proposed to be consistent with a protonation step of the O_2 complex prior to O–O cleavage. In the case of biological models, it is often proposed that an initial one-electron reduction (or nucleophilic attack) of the O_2 complexes is followed by protonation prior to the O–O bond cleavage.^{10–12,35} The reactivity of the O_2 complexes **2** and **3** toward protons was investigated for $\text{Co}_2\text{-FTF4}$, which is the most efficient catalyst, and for which a protonation step following oxygenation in electrocatalysis has been proposed.^{1,2,13} The added acid was an aqueous perchloric acid solution in PhCN.

Complex **2** reacts with one proton. On addition of protons to a solution of the complex, the initial UV–vis spectrum of complex **2** is converted into a new spectrum also with a clear isosbestic point in the Soret region. The product obtained by reaction with the proton displays a spectrum with λ_{max} (nm) (ϵ ($10^{-3} \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)) = 416 (160), 532 (12), 564 (13), and 670 (sh). Worthy of notice is the appearance of the weak shoulder band at 670 nm usually observed with π -radicals,^{29a} reminiscent of that observed, but at 650 nm in the case of the O_2 complex **3**. A similar observation is made by EPR. Addition of protons results in the concomitant disappearance of the 15-line spectrum and development of a 1-line spectrum typical of

a π -radical with $g = 2.004$, similar to that of complex **3**. The integration of this signal is not accurate and gives a number of spin n , $1 < n < 2$. Both by UV–vis spectrophotometry and by EPR spectroscopy, the transformation is complete for the addition of 1 equiv of proton/mol of complex. The “proton-evolved” species is different from a simple oxidation product of complex **2**: its UV–vis spectrum is different from those of complex **3** and of the oxidized form $\mathbf{1}^{2+}$ in anhydrous medium or in the presence of H_2O ,^{16–18} both by the position of the Soret and by molar absorptions, which are higher in this case by a factor of ca. 2. The O_2 complex **3** is not affected by the presence of protons since neither its UV–vis nor its EPR spectra are noticeably modified on addition of protons.

Preliminary voltammetric experiments confirmed the reactivity toward protons of the cobalt dimers, already detected by spectroscopy. Actually the presence of H_2O and aqueous acid modifies the electrochemistry of the cobalt dimers. A complete description would require a thorough re-examination in the presence of H_2O , H^+ , and O_2 . The addition of protons in substoichiometric quantity (0.2–0.5 equiv) to a solution of the neutral compound **1** in the presence of O_2 gives rise to complex **2** through a combined oxidation–complexation process by O_2 .²⁷ The addition of 1 equiv of proton leads to the same observation as that made above for complex **2** prepared electrochemically. The addition of an excess of H^+ in the presence of O_2 generates a catalytic reduction wave at the potential of the reduction wave of complex **2** after reaction with one proton, while an oxidation wave close to that of the $3/2$ redox process is still present. This behavior resembles that described in aqueous acid with the catalyst adsorbed on EPGE (condition of the O_2 to H_2O electrocatalysis).^{1,2,13} The product of the catalysis (H_2O versus H_2O_2) in the present aqueous/organic medium could not be determined.

Comparison of the Present O_2 Complexation Processes to That Observed for Cobalt Monomers. The present results highlight a remarkable behavior toward dioxygen of the dicobalt cofacial dimers compared with cobalt monomers.^{9,15} The generally accepted scheme for O_2 interactions with cobalt monoporphyrins and other macrocyclic derivatives involves dioxygen binding by neutral cobalt monoporphyrins ($\text{Co}^{\text{II}}\text{P}$) in the presence of a donor ligand (L) whereby a superoxo [$\text{LPCo}^{\text{III}}\text{O}_2^*$] or a μ -peroxo [$\text{LPCo}^{\text{III}}\text{---O---O---Co}^{\text{III}}\text{LP}$] derivative is formed. The latter may be oxidizable to a μ -superoxo derivative, [$\text{PLCo}^{\text{III}}\text{---O}^*\text{---O---Co}^{\text{III}}\text{LP}$]⁺, and further oxidation produces Co^{III} and O_2 . The formation of the μ -peroxo form in protic solutions very often leads to an irreversible oxidation of Co^{II} into Co^{III} with hydrogen peroxide release. Therefore, a reversible behavior for the oxygenation process necessitates in most cases the use of low temperature to stabilize the superoxo while preventing decomposition through the μ -peroxo. Thus, the oxygen reactivity of these dimeric complexes is unprecedented. (i) First of all, contrary to what is observed for Co^{II} monomers, the neutral form of the dimers [$\text{PCo}^{\text{II}}\text{Co}^{\text{II}}\text{P}$] does not give rise to O_2 complexation. UV–vis spectrophotometry, EPR spectroscopy, and electrochemistry clearly demonstrate this point. (ii) Instead it appears that it is the electron-deficient forms of the dimers [PCo^+CoP]⁺ and [$\text{PCo}^{\text{---}}\text{CoP}$]²⁺ that behave as oxygen carriers. This was especially surprising in the case of the latter, which is isoelectronic with a dicobalt(III) derivative (Scheme 1). (iii) These two derivatives strictly behave as true oxygen carriers; i.e., they can adsorb and desorb dioxygen, with no noticeable decomposition, even at room temperature. Moreover, the two cobalt centers participate in the oxygen binding reaction. This is remarkable if it is recalled that monomeric oxygen carriers often require low temperature to prevent decomposition through the action of a second cobalt atom in a

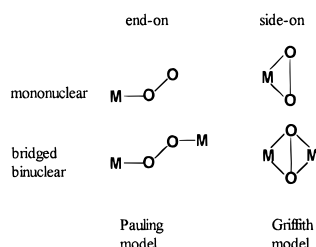
(34) (a) In pure PhCN, the values of $K_{\text{O}_2}(2)$ estimated by potentiometry were derived from the measurement of the electrode potential of an equimolar solution of the neutral and one-electron-oxidized species under N_2 (E_{N_2}) and under several measurements gas mixtures with different $p(\text{O}_2)$ ($E_{p(\text{O}_2)}$, with $0.1 < p(\text{O}_2) < 1$ atm). This is the range in which the potential variations are the largest. The estimated values of $K_{\text{O}_2}(2)$ are constant within this range, and the averages are presented in Table 2. (b) The constant $K_{\text{O}_2}(3)$ could not be determined by UV–vis spectrophotometry: the very high affinity of the [$\text{PCo}^{\text{---}}\text{CoP}$]²⁺ redox form of the dimers for H_2O precludes the preparation of pure solution of the oxygen complexes after somewhat long saturation of solutions by gas containing residual traces of water,¹⁶ and consequently the observation of isosbestic sets of spectra.

(35) (a) Solomon, E. I.; Hemming, B. L.; Root, D. E. In ref 12a. (b) Tyeklár, Z.; Karlin, K. D. *Ibid.* (c) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, 92, 521. (d) Sorrell, T. N. *Tetrahedron* **1989**, 45, 3.

Table 3. Comparison of $P_{1/2}^a$ for Dioxygen Binding to Dicobalt Face-to-Face Porphyrins, Cobalt Porphyrins, and Models of Hemoproteins

compound	conditions	$P_{1/2}^a/\text{Torr}$		ref
		complex 2	complex 3	
Co ₂ FTF4	PhCN, Bu ₄ NPF ₆ , 20 °C	0.4	240	<i>f</i>
Co ₂ FTF5-3,1	PhCN, Bu ₄ NPF ₆ , 20 °C	120	19 000	<i>f</i>
Co ₂ FTF5-2,2	PhCN, Bu ₄ NPF ₆ , 20 °C	8	30 300	<i>f</i>
Co ₂ DPB	PhCN, Bu ₄ NPF ₆ , 20 °C	10	4800	<i>f</i>
CoMb ^b	pH 7 (0.1 M phosphate buffer), 25 °C	51		36
CoTpivPP(<i>N</i> -MeIm) ^c	toluene, 25 °C	140		36
CoPPIXDME(<i>N</i> -Im) ^d	toluene, 25 °C	17 800		36
Mb ^e	pH 7–7.4, (0.1 M phosphate buffer), 25 °C	0.37–10		36

^a $P_{1/2} = 1/K_{O_2}$. ^b Sperm whale or horse myoglobin. ^c “Picket fence” porphyrin. ^d Cobalt(II) protoporphyrin dimethyl ester. ^e Myoglobin. *f* Present work.

Scheme 3

peroxo-bridged fashion.¹⁵ (iv) The oxygen complexation does not require the presence of a donor ligand (L) demonstrated to be a prerequisite in the case of the monomers,¹⁵ while the presence of base (*N*-MeIm) does not greatly modify their oxygen affinity as shown in Table 2. (v) Nevertheless, these derivatives have a remarkably high affinity for dioxygen as seen in Table 3, even at room temperature. In the case of complex 2 the affinity is higher than that of any other synthetic derivative, and only comparable to that reported for natural hemoglobin.³⁶ For complex 3, the stability remains on the same order of magnitude as that for cobalt monoporphyrins, still even in the absence of an axial donor ligand. (vi) From Scheme 1, it appears that, to account for a classical formulation of the oxygen complexes, namely, the μ -superoxo structure proposed formerly for complex 2 and a putative μ -peroxo form for complex 3, the binding of O₂ should involve very complex π -ring \leftrightarrow cobalt \leftrightarrow oxygen intramolecular electron transfers.^{21c} (vii) More puzzling is the fact that electrochemical interconversion of these two complexes would correspond to the formation of a μ -peroxo (O₂)²⁻ by the oxidation of the μ -superoxo (O₂)⁻. This would also require a structural rearrangement inducing important reorganizations of the MO levels if the same formalism is kept. This does not appear likely in view of the electrochemical reversibility of the redox process 2 \leftrightarrow 3. (viii) Finally the reactivity of complexes 2 and 3 toward protons is completely different from that of the cobalt monomers.

These considerations clearly demonstrate that a “classical” formulation of the O₂ complexes 2 and 3 does not apply at all. Actually, from the general picture proposed by Yeager,^{9a} O₂–metal bonding in oxygen complexes can be restricted to the two models often referred as the Pauling³⁷ (η^1 or end-on) or Griffith²⁶ (η^2 or side-on) models, which can be bridged or not (Scheme 3). In the former the bonding interaction takes place between the filled or half-filled d_{z^2} orbitals of the metal and the π^* orbitals of O₂. The Griffith model involves stronger and more complex interactions between the empty d_{z^2} orbitals of the metal with the π orbitals of O₂ and back-bonding from at least partially filled d_{xz} orbitals of the metal to the π^* orbitals of O₂. For cobalt and iron porphyrins the Pauling mode is the widely reported bonding interaction, referred as the classical

superoxo and peroxo complexes.¹⁵ This model is amply documented, and especially the preponderant role of the axial ligand corresponds to an activation of the d_{z^2} orbital not observed in the present case. Until recently there were very few examples of O₂ complexes in the Griffith mode of coordination and especially in the bridged μ - η^2 : η^2 configuration with the late transition metals.

Attempts to isolate the O₂ complexes of the present dimers as crystals for structural characterization have been so far unsuccessful²³ and their characterization in solution as by Raman not feasible due to the lack of the adapted equipment. Therefore, the possible electronic structures of the O₂ complexes have been considered from a theoretical aspect by means of calculations based on the X-ray structure of one of the dimers, namely, Co₂-FTF4.²⁵

Molecular Orbital Calculations. Assuming that the whole dioxygen unit is coordinated inside the cavity of the diporphyrin, the only possible coordination mode is the symmetrical side-on μ - η^2 : η^2 configuration. Indeed, the rather rigid skeleton of the face-to-face diporphyrin precludes any other geometry in which both oxygen atoms would be inside the cavity. We have analyzed the electronic factors susceptible to stabilize the conformation by the means of EHMO calculations.³⁸ The model for the diporphyrinic host, namely, [Co(N₄C₂₀H₁₂)₂]₂, was assumed to have the D_{4d} symmetry. It was generated from the idealization of the experimental structure of a Co₂FTF4 derivative,²⁵ by replacing the various substituents and links by hydrogen atoms. The two porphyrinic rings were considered planar, in a parallel and staggered orientation, with an interplane separation of 3.42 Å. The O–O unit was considered to bridge symmetrically the two metal atoms so that the overall symmetry of the model is C_{2v} . Unless specified in the text, the O–O distance is considered to be 1.45 Å, implying the four Co–O distances to be 1.86 Å. Standard atomic parameters^{38,39} were used throughout the calculations. It has been verified that a moderate change of the Co H_{ii} parameters³⁹ does not modify the general conclusions of our EHMO study (*vide infra*). It has also been determined that a moderate variation of the structural parameters (i.e., bending, staggering, or slippage of the rings; Co···Co or O–O distances, etc.) does not significantly change the qualitative EHMO results.

The frontier orbital diagram of the calculated model is shown in the middle of Figure 8. It is clear that its best closed-shell electron count corresponds to the +2 charge. For this [PCo–O₂–CoP]²⁺ model, a significant HOMO/LUMO gap of 0.63 eV is computed, separating the occupied bonding and nonbonding levels from the vacant antibonding ones. The MO diagram of this cationic complex can be conceptually derived from the interaction of the frontier orbitals of the formally charged

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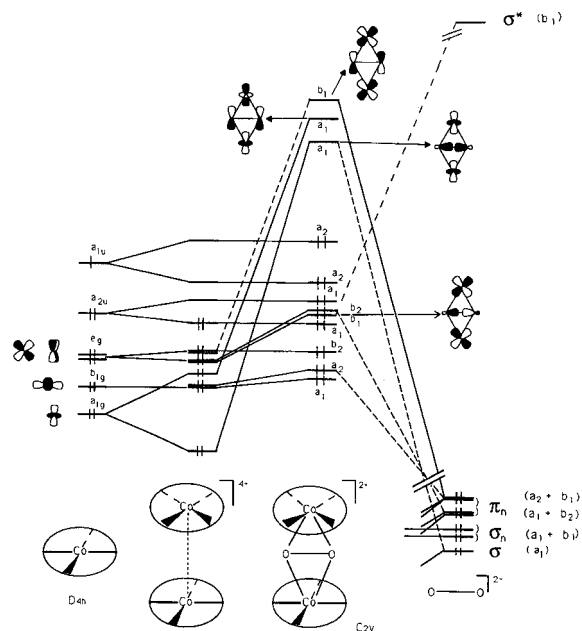


Figure 8. EHMO diagram for the oxygen complex **3**, $[\text{PCo-O}_2\text{-CoP}]^{2+}$, built on the basis of the interaction between the $[\text{PCo CoP}]^{4+}$ and O_2^{2-} fragments ($\text{O-O} = 1.45 \text{ \AA}$; $\text{Co-O} = 1.86 \text{ \AA}$; $\text{Co-Co} = 3.42 \text{ \AA}$).

$[\text{PCo CoP}]^{4+}$ and $(\text{O}_2)^{2-}$ fragment. The MO diagram of the peroxo unit is simple. In addition to its low-lying σ (bonding) and high-lying σ^* (antibonding) levels, it exhibits six mainly nonbonding levels which are the in-phase and out-of-phase combinations of the π -type and σ -lone pair orbitals. The frontier orbitals of the $[\text{PCo CoP}]^{4+}$ can themselves be easily derived from those of a CoP D_{4h} monomer, which are shown on the left side of Figure 8. Such a square-planar mononuclear D_{4h} unit has four 3d-type nonbonding levels, namely, $z^2(a_{1g})$, $x^2 - y^2(b_{1g})$, and xz and $yz(e_g)$. It also has two nonbonding porphyrinic levels of a_{1u} and a_{2u} symmetry. The ligand vs metal EHMO ordering of these levels in the CoP monomer (left of Figure 8) is certainly not correct. For example, recent DFT calculations on a NiP model lead to the following ordering: $z^2(a_{1g}) < xz, yz(e_g) < a_{2u}(P) < a_{1u}(P) < x^2 - y^2(b_{1g})$.⁴⁰ By modifying the EH parametrization, it is possible to reproduce a level ordering close to the one obtained by DFT theory. However, we have chosen not to change the standard parameters, although they lead to an overestimation of the energy of the a_{1u} and a_{2u} ligand levels, with respect to the Co levels. This aspect has been discussed recently.¹⁸ When two CoP units are brought together in a staggered D_{4h} conformation to form the diporphyrinic host, each of the monomer levels generates a bonding and an antibonding combination (Figure 8) which are weakly split since the two monomers are rather far apart (3.42 \AA). The largest splitting is found for the z^2 combinations, due to the better overlap afforded by these σ -type orbitals. When the $[\text{PCo CoP}]^{4+}$ unit interacts with the $(\text{O}_2)^{2-}$ fragment, only metal and oxygen orbitals which are lying in the CoOOCo plane (*i.e.*, σ -type) can interact significantly. As a consequence, only the z^2 - and xz -type combinations of $[\text{PCo CoP}]^{4+}$ are involved in the complexation. The z^2 in-phase and out-of-phase combinations interact strongly with the σ -bonding and in-plane π -bonding combinations of $(\text{O}_2)^{2-}$, respectively. The corresponding metal-centered antibonding combinations are the two lowest unoccupied a_1 levels of $[\text{PCo-O}_2\text{-CoP}]^{2+}$. Similarly, the out-of-phase xz combination interacts with the in-plane π -antibonding combination of $(\text{O}_2)^{2-}$, generating a vacant level of b_1 symmetry. On the other side, the occupied b_1 in-phase xz MO

interacts to stabilize the high-lying vacant σ^* orbital of $(\text{O}_2)^{2-}$. It is noteworthy that the σ -lone pairs of the $(\text{O}_2)^{2-}$ ligand are not significantly involved in the complexation. Their main lobes are pointing away from the cobalt atoms. Related bonding interactions have been shown to exist also in $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxodicopper(II)}$ ⁴¹⁻⁴⁴ and discussed in $\mu\text{-}\eta^2\text{:}\eta^2\text{-divanadium(III)}$ ^{45a} and -diiron^{11,45b} complexes.

To summarize, there are four 2-electron 2-orbital bonding interactions which are associated with the four Co-O bonds, but also with the O-O bond, since the σ and σ^* orbitals of $(\text{O}_2)^{2-}$ are involved in the complexation. Clearly, this is an electron-deficient, delocalized bonding. A localized bonding would imply the participation of the four peroxo lone pairs through sp^3 hybridization of oxygen, *i.e.*, a CoO_2Co butterfly arrangement. Such a geometry is not allowed by the rigidity of the diporphyrin. The computed Co-O overlap populations are significant (0.193). The O-O overlap population in the complex (0.298) is weaker than the corresponding value in the free $(\text{O}_2)^{2-}$ fragment (0.351). This is the result of the depopulation of $\sigma_{\text{O-O}}$ and of σ^* population under complexation (by 0.43 and 0.11 electron, respectively). The parallel between the electronic structures of the $[\text{PCo-O}_2\text{-CoP}]^{2+}$ model and of the $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxodicopper(II)}$ complexes of Kitajima, Moro-Oka, and co-workers is striking.⁴¹⁻⁴⁴ In both cases, the planar 8-electron 4-center delocalized bonding is, at least partly, favored by steric constraints. In both cases, two electrons and four orbitals (two σ -type and two π -type combinations) are provided by the dinuclear fragment for bonding. The two formally vacant σ -type metallic orbitals are destabilized by occupied peroxo levels, while the π -type ones behave differently. One is destabilized by a low-lying π -lone pair combination on oxygen, and the other one is stabilized by $\sigma^*_{\text{O-O}}$, housing the metal electron pair involved in the bonding. This different behavior of the π -type orbitals is responsible for the significant HOMO/LUMO gap computed for the copper complex.⁴¹⁻⁴⁴ Similarly, the computed HOMO/LUMO gap of $[\text{PCo-O}_2\text{-CoP}]^{2+}$ is significant. It is even most probably underestimated in our calculations, since the use of standard EH parameters tends to overestimate the energy of the porphyrin-localized HOMO, with respect to that of the nonbonding metallic levels (*vide supra*).

The one-electron reduction of this dicationic model leads to the partial occupation of an antibonding level, inducing instability. The partial occupation of the $\sigma^*_{\text{O-O}}$ orbital would correspond to some O-O elongation. However, this is a rather high-lying, not easily accessible level (Figure 8). The b_1 π -type antibonding Co-O orbital might be a better candidate for occupation. It is easily stabilized by shifting the O-O unit along the x axis, away from the symmetrical bridging position. EH calculations do not allow the full structural optimization of such a radical complex. However, the rough exploration of the

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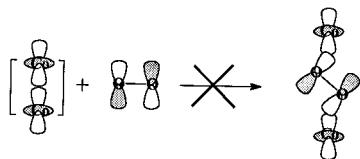
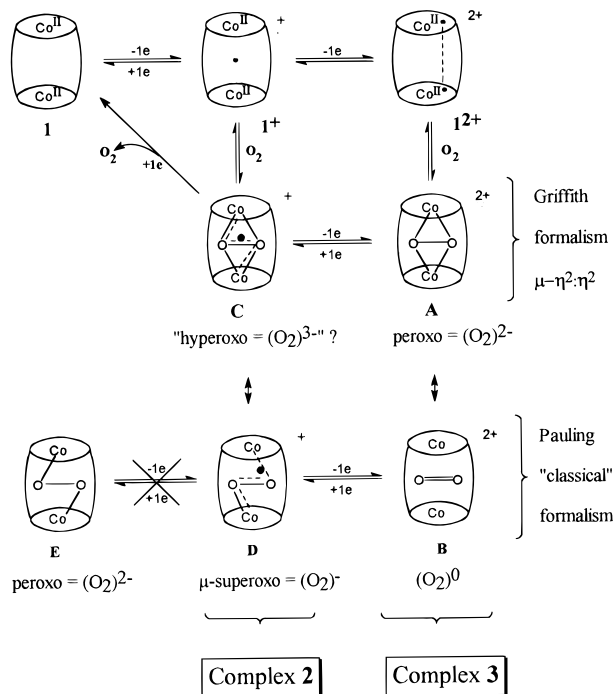
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Scheme 4

Scheme 5. Proposition for the Possible Formulations for the O₂ Complexes of the Dicobalt Cofacial Diporphyrins

potential energy surface associated with this distortion indicates that it is softer in the case of the monocation than in the case of the dication. For example, maintaining the O–O distance constant, the complete shifting of the peroxo ligand away from its symmetrical bridging position to a conformation in which one oxygen atom lies right in the middle of the Co–Co vector costs 0.3 eV to the monocation, but 0.9 eV to the dication. In this unsymmetrical position, the charges on the oxygen atoms are different. In the monocation they are -0.13 and -0.74 for the coordinated and uncoordinated atoms, respectively. This would render the latter more easily susceptible to proton attack.

Discussion

Electronic Structure/Properties Relationship. These EHMO calculations strongly support the bridged Griffith mode of binding for the O₂ complexes of this family of compounds, while it is clear that the Pauling mode of O₂ binding is not possible due to the proximity of the two metals with the two d_{z²} nearly colinear. This configuration, secured by the binucleating ligand, does not simply allow the minimum overlap between the two metal d_{z²} and the O₂ π* orbitals as shown in Scheme 4.

Moreover, the proposed electronic structure is in agreement with the very specific properties of the complexes **2** and **3** as compared to those of the classical complexes (i–viii). The two possible models for the O₂ binding by the dicobalt dimers are opposed in Scheme 5, using the simplified Lewis representation.

The μ-peroxo in the classical form E of the Pauling formalism is not observed; its formation as well as that of a μ-superoxo complex D would have necessitated the presence of an axial ligand L which is not the case. This formalism would also lead for complex **3** to form B which appears meaningless. Conversely, the electronic structure of the bridged Griffith mode of

coordination (Figure 8) indicates the stabilization of an O₂ complex **3** at the +2 oxidation state (form A). The MO diagram in Figure 8 shows that the z² orbitals are unfilled in this model which explains that the presence of the axial ligand L does not have any effect. All the three lowest unoccupied levels in complex **3** are cobalt–O₂ antibonding. As a consequence when two electrons are added (reduction of **3** to **1**), the cobalt–O₂ bonding interaction is considerably weakened; furthermore, it has also been shown previously that in the neutral form **1** the cobalt metallic orbitals are locked owing to the combination of the cobalt–cobalt and π–π interactions (“cofacial” effect).¹⁸ These observations explain that no O₂ binding occurs at the neutral redox state **1**, and account for the decoordination of O₂ observed by CV when complex **2** is reduced to **1** with no oxygenated intermediate detected.^{46–48} In this model of Co–O₂ bonding for **3**, it is also noteworthy that, among the four bonding interactions, one results in the population of the σ*_{O–O} antibonding level and one in the depopulation of the σ_{O–O} bonding orbital. Therefore, this results in a significant weakening of the O–O bond. This is particularly striking if one considers that the most prominent properties of these compounds is to reduce O₂ directly to H₂O through an efficient O–O bond cleavage mechanism. Moreover, the most active compounds in this process are those possessing the greater stability constant K_{O₂}(**3**) for complex **3**, viz., Co₂FTF4 and Co₂DPB (Table 2). This would indicate that the greater this constant is, the greater the Co–O₂ bonding interactions through the μ-η²:η² geometry and the weaker the O–O bond.

The orbital diagram proposed for the μ-η²:η²-O₂-dicopper complexes are quite similar to the diagram presented here.^{42–44} Interestingly it has been emphasized that these μ-η²:η²-dicopper complexes of O₂ are more acidic and electrophilic than the μ-η¹ complexes (Pauling binding mode).^{12,35,42} This property explains that this type of complex remains resistant to protonation, until a nucleophilic attack or an electrochemical reduction step of the O₂ moiety. Therefore, the Griffith geometry for complex **3** appears in total agreement with its resistance to protonation. This interpretation is also supported by the observation that complex **2**, the one-electron-reduced form of **3**, reacts with one proton.

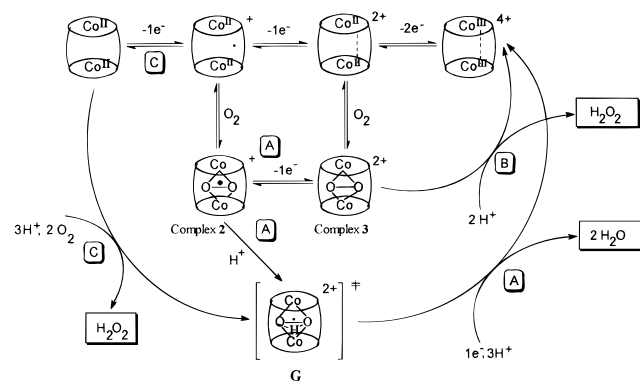
On the basis of experimental, geometric, and theoretical considerations, complex **2** cannot be considered as a classical μ-superoxo derivative D which is the oxidized form of the Pauling peroxo complex E which does not exist. As it is the reduced form of a peroxo complex **3**, complex **2** is best represented by formulation C (Scheme 5) in which the O₂ moiety is in a redox state intermediate between peroxo (–1) and oxo (–2).⁴⁹ This formulation is electronically equivalent to the [Fe₂O₂]³⁺ moiety proposed during the O₂ reduction cycle of non-heme diiron sites.¹¹ In form C of complex **2**, the electronic density and consequently the basicity of the O₂ moiety are enhanced as compared to those of complex **3**. The O₂ moiety in this form reduced beyond the peroxo stage could be

(46) An alternative to this dissociation of O₂ would have been the formation of a di-μ-oxo compound. In the case of cobalt, it is known that oxo derivatives are not stable.^{45,47} Actually such an intermediate species is proposed for the formation of oxo derivatives of early transition metals by reaction with O₂,⁴⁵ and suggested during the homolytic O–O bond cleavage in μ-η²:η²-Cu₂O₂ complexes,⁴⁸ and Fe₂O₂ complexes.¹¹

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(49) Such an oxidation state could tentatively be formally considered as a “hyperoxo” oxidation state of -1.5 , in which an extra electron, as compared to the peroxo state, is delocalized in the O–O bonding. The proposition of such an electronic structure could explain the particular shape of the EPR room temperature spectrum, different from that of the classical μ-superoxo compounds: possible interpretation of this particular shape has already been discussed.³

Scheme 6. Proposition of the Mechanism for the Reduction of O₂ by Dicobalt Cofacial Diporphyrins

protonated to give G (Scheme 6) in a transient step. This sequence is in agreement with the above-mentioned observation that the acidic $\mu\text{-}\eta^2\text{-}\eta^2\text{-O}_2$ complexes are protonated only after a reduction step.

Proposition of an Electrocatalytic Scheme for O₂ Reduction. The present results afford a new insight in the mechanism for the four-electron reduction of dioxygen by the dicobalt cofacial diporphyrins when adsorbed on an EPGE immersed in aqueous acid. So far the propositions of mechanism^{1-4,13,14} had been mainly based on the properties and classical model of O₂ complexes observed for the monomers in solution.^{9,15} Once it has been demonstrated that the properties of the dimers in solution are basically different from those of the monomers, we believe that the real properties of the dimers constitute a better basis for the interpretation of the O₂ reduction mechanism by the dimeric compounds.^{16-18,21-23} Even if the effect of the adsorption and immersion in aqueous acid on the behavior of the dimers, with regard to their behavior in organic solvent, are not yet clearly established,^{13,14} the fundamental properties of the dimers should be retained under whichever conditions. (i) Namely, structural parameters such as metal-metal or π -ring- π -ring distances should not be drastically modified. Moreover, it is shown that the presence of aqueous acid in the organic solvent does not affect the O₂ binding and reaction with proton. Thus, their remarkable properties and resulting specific reactivity toward O₂ emphasized here should also be at work during the O₂ electrocatalytic reduction. (ii) The adsorption process on EPGE has been demonstrated to be crucial for the observation of an efficient four-electron process.^{1,2,14} However, the adsorption mode of structurally very similar compounds is not likely to be different while their efficiency in the electrocatalysis is radically different, e.g., four-electron process for Co₂FTF4, and ca. three-electron for Co₂FTF5-2,2 and Co₂FTF5-3,1 (Figure 1).^{1-3,13} This observation demonstrates that the route for the O₂ reduction is determined by the intrinsic properties of the dimers. These considerations lead us to propose an alternative interpretation of the catalytic cycle for O₂ reduction based on the specific properties of the dimers evidenced in the present work, which appears yet more consistent with the observations made when the catalysts are adsorbed on the EPG electrode (Scheme 6).^{1-3,13}

It is shown that the redox states in which the dicobalt cofacial dimers behave as oxygen carriers are [PCo^{II}Co^{II}P]⁺ (**1**⁺) and [PCo^{II}Co^{II}P]²⁺ (**1**²⁺). It thus appears that the crude form of the catalyst would be the four-electron-oxidized derivative [PCo^{III}Co^{III}P]⁴⁺. Its two-electron reduction in the presence of O₂ leads to **1**²⁺ and formation of the μ -peroxo derivative complex **3** by complexation of O₂. This step could correspond to the prewave observed on the EPG electrode. The subsequent one-electron reduction of **3** to **2**, followed by protonation, leads to the transient species G (first protonation step). The proto-

nation step proposed on the basis of the present results is the equivalent of that proposed by Collman and Anson et al. on the basis of the strong pH dependence of the catalysis.^{1,2,13} It does not seem likely that the O-O bond cleavage has been realized at this stage. It is proposed that the last one-electron reduction step of this species, followed by protonations, is necessary for the O-O bond breakage and H₂O release This would correspond to the second and catalytic wave observed only in the presence of both H⁺ and O₂. This final step aims at the closing of the catalytic cycle with return to the four-electron-oxidized form (route A).

Interestingly, the present observations give a possible explanation concerning the catalyst's efficiency as for the path of the catalysis, H₂O (route A) versus H₂O₂ (route B in Scheme 6). The dimers of group 2 with the largest K_{O₂}(**3**) give the higher H₂O/H₂O₂ ratio. This is especially evident for the Co₂FTF4 derivative which is the best catalyst (see Figure 1 and Table 2). Co₂DPB₂ is also a fairly good catalyst, while the two Co₂FTF5 catalysts yield a mixture (ca. 1/1) of H₂O and H₂O₂.^{1,2} This apparent correlation could arise from the fact that the value of K_{O₂}(**3**) reflects the ability of the dicobalt dimers to transfer electron density onto the O₂ moiety, through a greater O₂-Co₂ orbital overlap in the bridged side-on configuration. This property could influence the route of O₂ reduction by two concurrent processes: the greater K_{O₂}(**3**), (i) the more efficient the Co₂-O₂ orbitals overlap in and the easier the O-O bond cleavage and (ii) the more stable the peroxo complex **3** and the more difficult the production to H₂O₂ by protonation. Consequently it is proposed that noticeable production of H₂O₂ is observed (route B plus route A) when the dicobalt arrangement in the dimers departs sufficiently from the subtle configuration responsible for the strong stabilization of the bridged Griffith O₂ configuration.

In the case of group 1 compounds, one dimer Co₂DPA effects the four-electron reduction of O₂ and the other Co₂FTF6 behaves as a monomer reducing O₂ to H₂O₂, while they display similar Co-Co distances (Figure 1). It is shown here that both compounds display a reactivity similar to that of group 2 compounds in regard to oxygen reactivity, but Co₂FTF6 gives an unbridged O₂ complex, and Co₂DPA a bridged one like group 2 compounds. This significant difference arises very likely by a closing of the two porphyrins allowed for Co₂DPA by the single anthracene linking bridge. Accordingly, for Co₂DPA it may be assumed that the critical geometry for the O₂ complex in regard to catalyst efficiency can be attained via this effect.¹

Another puzzling observation that the present results would explain is the noticeable production of H₂O₂ observed at the ring-disk electrode even for the most efficient catalysts when the potential is swept down to values more negative than the maximum current of the catalytic wave.^{1,2} It is shown in the present report that if the catalyst is reduced to the neutral form [PCo^{II}Co^{II}P], O₂ cannot be complexed inside the cavity of the diporphyrin. Thus, at a potential sufficiently cathodic to generate mostly this neutral form, the dimers should behave as a monomer, producing only H₂O₂: route C in Scheme 6.

Evidently, this proposition of mechanism does not pretend to be exclusive. For example, heterodimers of the same family, in which only one cobalt is present, the other being replaced by an acidic metal, have been synthesized.⁵⁰ Significantly some of these derivatives prove also to be efficient for the four-electron reduction of O₂. It has been shown in the present study that the formation of a $\eta^2\text{-O}_2$ complex results from the acidic character of the two cobalt porphyrins in their high oxidation

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state. This acidity signifies vacancy of the two d_{z^2} orbitals by combination of the oxidation state and cobalt–cobalt interactions through the O_2 moiety. This suggests that, in the presence of an “acidic” metal, a nonbridged η^2 complex might also be stabilized. While in nonbridged η^2-O_2 complexes the O–O bond is also proposed to be considerably weakened,⁴⁵ this type of coordination in the case of the heterodimers could favor an alternative route for the four-electron reduction of O_2 .

Concluding Comments. From experimental evidence attesting an unprecedented reactivity toward dioxygen of the dicobalt face-to-face diporphyrins, we propose the $\mu-\eta^2:\eta^2$ geometry (Griffith mode) as a reasonable structure for their oxygen complexes on the basis of molecular orbital calculations and by comparison with related dicopper systems. This mode of binding had never been evidenced until very recently in the case of transition metals.^{35,41} To our knowledge the electrochemical behavior of O_2 complexes in this mode of binding has not been reported. It appears that the corresponding calculated electronic structure rationalizes the observed properties which, on the other hand, were not consistent with the widely described classical Pauling mode of O_2 binding. From the present observations, it is proposed that the one-electron-reduced form of the peroxo $\mu-\eta^2:\eta^2-Co-O_2$ complex could be best described as a complex of an oxygen moiety reduced beyond the peroxo state.⁴⁹ The stabilization of such a structure would be the result of a cofacial effect of interaction in this family of compounds.⁵¹ This mode of metal– O_2 binding resulting in a consequent weakening of the O–O bond is proposed to be the factor favoring an efficient direct O_2 to H_2O reduction process.

Worthy of notice are strong similarities in regard to the structure/function relationship between the present dicobalt dimers and biological compounds or their models active in O–O bond cleavage in oxygenation or O_2 reduction. The most prominent is the metal–metal distance which is 3.5 Å in the dicobalt dimers. This is almost exactly the distance found in the only isolated and structurally characterized O_2 –dicopper synthetic complex in the $\mu-\eta^2:\eta^2$ mode of bonding and in oxyhemocyanin.⁴² A close distance is also found in the X-ray structure of cytochrome *c* oxidase, obtained in a resting oxidized form, i.e., noncomplexed by O_2 .¹⁰ As this distance is proposed to favor the Griffith type of bonding, which reciprocally induces a considerable weakening of the O–O bond, the comparison of these systems appears significant.

Another resemblance is the acidic/electrophilic character of this type of O_2 complex. For the present compounds, this is illustrated by the resistance of complex **3** to protonation and its ease of reduction: it is protonatable only after a one-electron reduction. The acidic and electrophilic character of the $\mu-\eta^2:\eta^2$ dicopper complexes as compared to the other mode of binding has also been pointed out, and it is proposed that the initial step of the O–O cleavage is a nucleophilic attack (followed by protonation).^{12,35,42} Although the O_2 complex of the cytochrome *c* oxidase has not yet been isolated, it is interesting to note that

(51) Le Mest, Y.; Saillard, J.-Y. Unpublished results. A more quantitative analysis of the influence of the cofacial effect on the stabilization of the proposed structure for the O_2 complexes would require a higher level of theory. Such calculations are in progress.

it is mostly proposed that a one-electron reduction step precedes its protonation before O–O bond cleavage,¹⁰ indicating likely an acidic/electrophilic character of the intermediate O_2 complex. Also the common mechanistic framework for the O_2 reduction process by some non-heme diiron sites¹¹ includes firstly one-electron reduction of the Fe_2-O_2 complex before protonation of the O_2 moiety.

The present propositions for the O_2 reduction cycle clearly fulfill thermodynamic requirements for an efficient catalyst for the four-electron O_2 reduction, assumed by Collman as the working hypothesis in the cofacial project,^{1,2} and later conceptually discussed in more general terms by Taube.⁵² These requirements were the bypass of the one- and two-electron routes through a bimetallic cooperative process, with a very stable peroxo intermediate, both thermodynamically and against protonation, and reducible at a quite positive potential. In fact the present propositions suggest that not only are the one- and two-electron routes bypassed, but also that a three-electron species seems to be sufficiently stabilized to permit the four-electron route to be followed almost exclusively for the most efficient catalysts.

Finally it must be acknowledged that the present model for the O–O bond cleavage is derived from the mechanism of Hoffmann et al. based on the properties of vanadium derivatives.⁴⁵ Should this mechanism for the bond breakage be considered as fundamentally similar for a number of bimetallic sites including those quoted above (i.e., by population of the σ^*_{O-O} and depopulation of the σ_{O-O} through the $\mu-\eta^2:\eta^2$ configuration of the (metal)₂– O_2 complex), it could thus find some generality. However, the driving force for the reaction would be different depending on the metals involved. In the case of vanadium or other early transition metals, it is the strong stabilization as terminal oxo derivatives,⁴⁵ while in the case of iron it would be the formation of the μ -oxo species $Fe-O-Fe$. In the present case of the dicobalt complexes, since oxo derivatives are unstable,⁴⁷ the driving force for the bond breakage would be the combined electronation/protonation reactions with liberation of H_2O , as could be the case for the cytochrome *c* oxidase cycle where the stabilization of the oxoiron should also influence the process.

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Supporting Information Available: EPR spectra for the O_2 adduct of the Co_2FT6 derivative and of the two-electron-oxidized form $[PCo---CoP]^+$ (**1**²⁺) of Co_2FTF4 and UV–vis isosbestic sets of spectra for the binding of O_2 by the one-electron-oxidized form **1**⁺ of the Co_2FTF5 diporphyrin and for the reaction of the O_2 complex **2** during the addition of protons (5 pages). See any current masthead page for ordering and Internet access instructions.

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