bonds from H_2 and a CO_2 equivalent can occur under mild conditions at a rate that can be regarded as fast as measured against the catalyzed H_2O/H_2 exchange process taken as a benchmark.

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for support of this research. We also acknowledge support from the Camille and Henry Dreyfus Foudation. C.J.S. was supported as a Postdoctoral Fellow by the Swiss National Science Foundation.

Registry No. Pd, 7440-05-3; CO_3H^-, 71-52-3; HCO_2^-, 71-47-6; H_2, 1333-74-0; C, 7440-44-0; H_2O, 7732-18-5.

Electroreduction of Oxygen by Pillared Cobalt Cofacial Diporphyrin Catalysts

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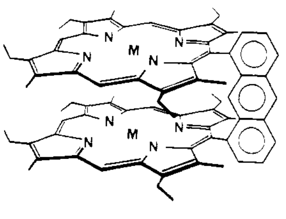
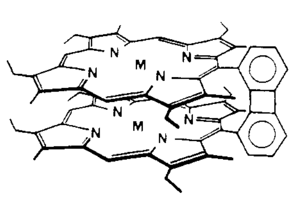
It has been shown that a graphite surface coated with a binuclear CoCo cofacial diporphyrin enables the reduction of dioxygen to occur via a 4-e pathway at potential near that of a platinum electrode.[2-4] Until now, the only macrocyclic complex capable of mediating the direct 4-e path of dioxygen reduction is a binuclear cobalt diporphyrin linked via two diametrically positioned four-atom amide chains (Co–Co-4 or Co_2FTF4).[3,4] Under identical experimental conditions, the majority of other similar compounds with different linking chains yielded predominantly H_2O_2. Collman and Anson[3] have attributed this unique reactivity to the ability of the dicobalt porphyrin to form a μ-peroxo complex as well as proper matching of formal redox potentials between metal and O_2. Work in our laboratory emphasized the fact that other dicobalt porphyrins can form the μ-peroxo species just as well and that the conformation of the O_2-intercalated complex may be critical.[4,5] Since it is difficult to test any theory with only one working datum point, the search for other electrocatalytically effective systems becomes a necessity. Ideally, one needs a wide range of diporphyrins whose redox potentials, interplanar distance, and conformation can be manipulated under strict control. This turns out to be practically impossible for the amide-linked dimers owing to the tendency for them to adopt a "slipped" conformation, i.e., the two rings are laterally displaced.[6-8] Changing the length or the constituents of the linkage would inevitably introduce variation in the degree of slippage, in addition to the vertical ring separation. We have therefore sought other designs to circumvent this problem.

1,8-Anthryldiporphyrin **1a** and 1,8-biphenylenediporphyrin **2a** were synthesized in a rational and stepwise manner.[9] The best method we now use affords diporphyrins in nearly 20% yield from readily obtainable dipyrrylmethanes.[10] The unique feature of this system is that the two porphyrin rings are anchored onto a rigid pillar such that the steric confines built into the system would prevent the two rings from rocking sideways to create a large lateral slippage. However, the two rings are still capable of bending back and forth along the ridge of the spacer groups.[9] Such flexibility presumably would make these two diporphyrins ideal binuclear systems for trapping substrate between the metals. Indeed, the $Co^{II}Co^{II}$ dimers readily form the μ-peroxo species[5] with dioxygen. Figure 1 shows the highly symmetric patterns of the EPR spectra of the oxidized μ-superoxo dimers. Previously, we have noticed a curious correlation[4] between the shape of the $Co–O_2–Co$ EPR signal and the electrocatalytical ability to mediate the 4-e reduction of O_2 on graphite surface; the well-resolved hyperfine lines would suggest these two dicobalt diporphyrins to be very good catalysts.



1a, M = 2H
b, M = Co^{II}



2a, M = 2H
b, M = Co^{II}

Rotating ring–disk voltammograms have been obtained at a graphite electrode coated with **1b** and **2b** in an oxygen-saturated 0.5 M aqueous trifluoroacetic acid solution.[11] As shown by Figure 2 and the compiled data in Table I, the result of O_2 reduction obtained in the present study is comparable to those of Co–Co–4 or Co_2FTF4. These four compounds clearly distinguish themselves as a special group from all other porphyrins and diporphyrins in terms of $E_{1/2}$ for O_2 reduction as well as the ring current. Furthermore, the rotating disk voltammograms of **1b** and **2b** exhibit a maximum ($\sim$+0.4 V) in the limiting current. This has been observed previously only with Co–Co–4 or Co_2FTF4. In the present systems the disk current decreases and then rises as the potential is scanned to more negative regions. The ring current follows the disk current, although not quantitatively. A possible explanation for this phenomenon is that the pillard dimers lose some of their activity toward the 4-e reduction of O_2 at more negative potentials but have significant catalytic activity toward the reduction of H_2O_2 at these potentials.[12]

The redox potentials of the surface-adsorbed dicobalt porphyrins consist of two well-separated waves (Table I), believed to be the Co^{II}/Co^{III} couple for the first and the second ring, respectively. Although the reduction of O_2 seems to begin near the foot of the second wave (less positive one),[3] a comparison of E_f^s for all porphyrins in Table I and previously published data failed to show any apparent correlation between the catalytic behavior and the redox potential. The metal–metal distance as well as the overall dimer conformation is likely more important in determining the catalytic response. The enigma as pointed out earlier is that there are many CoCo diporphyrins, including Co–Co–5 and "slipped" Co–Co–4,[4] all capable of forming intercalated peroxo and superoxo complexes, but only Co–Co–4 or Co_2FTF4 with a certain distance can bring about the 4-e process. To add to this puzzle, we now

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[10] In addition to the (dimethoxymethyldipyrryl)methene condensation described in ref 11, we also discovered that the MacDonald-style 2 + 2 dipyrrylmethane coupling can be successful if the reaction is conducted with 0.4% $HClO_4$ in methanol (Chang, C. K.; Abdalmuhdi, I. *Angew. Chem.* **1984**, *96*, 154).

[11] The ring–disk electrode (Pine Instrument Co. model AFDT06 PG/Pt) used for all measurements reported here is identical with those used previously in our laboratories and in Pasadena. Before coating, the electrode was first polished briefly on a wheel using silicon carbide paper (Sears 320) and cleansed with water and methylene chloride in an ultrasonic bath. The electrode was then soaked in a methylene chloride solution containing the dicobalt complex ($\sim$2 mM) for 15 min to effect adsorption. This method yielded superior results and was very reproducible.

[12] By use of 1 mM H_2O_2, **1b** catalyzes the reduction of H_2O_2 at ca. +0.13 V (Liu, H. Y.; Anson, F. C.; Chang, C. K.; Abdalmuhdi, I., manuscript submitted).

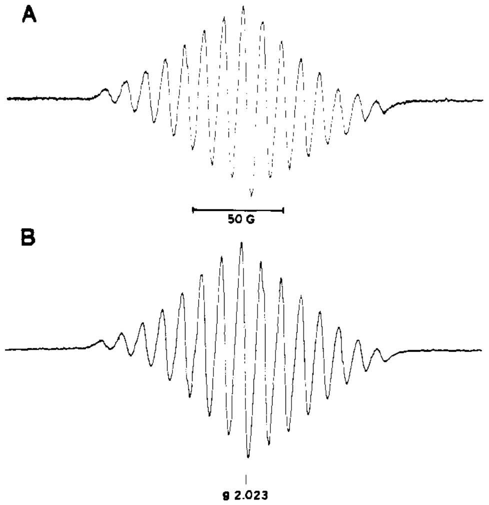

Figure 1. EPR spectra of μ-superoxo complexes of **1b** (A) and **2b** (B). Spectra was obtained by reacting the bis Co^{II} dimers with dioxygen at 23 °C in CH_2Cl_2 containing 0.1 M *N*-tritylimidazole and a trace amount of iodine.

Table I. Electrocatalytic Properties of Cobalt Porphyrin-Adsorbed Electrodes

Co porphyrins	E_f^s, V[a]	$E_{1/2}$, V[b]	% H_2O_2[c]
Co–Co–4[d]	0.69, 0.36	0.45	<5
1b	0.63, 0.33	0.43	<8 (4)
2b	0.64, 0.34	0.46	<8 (4)
Co_2FTF4[e]	0.61, 0.27	0.47	<1
CoTPP[f]	0.66	0.27	>60

[a] Formal potential for surface-confined redox couple, obtained from CV in 0.5 M HTFA (vs. SCE). [b] Half-wave potential for oxygen reduction at rotating disk electrode, evaluated at rotation rate of 100 rpm (vs. SCE). [c] Percentage of formation of hydrogen peroxide evaluated from % $H_2O_2 = -i_R/(Ni_D)$ where i_R and i_D are ring and disk limiting current, respectively, and N (=0.182) is the collection coefficient. At a fixed potential, e.g., +0.3 V, the current ratios yield % H_2O_2 given in the parenthesis. The number of electrons involved during the reduction of dioxygen for 1b and 2b is ca. 3.7–3.8, as calculated from the Levich equation. [d] Present study; these data deviate slightly from those in ref 4 due to different procedures used for the pretreatment of graphite electrode.[11] [e] See ref 3. [f] Liu, H. Y. Ph.D. Dissertation, Michigan State University, East Lansing, 1982.

have two compounds whose interplanar distance can differ as much as 1 Å,[13] yet both are effective catalysts for the 4-e reduction of O_2. It is perhaps the inherent flexibility of the pillard system that allows the complex to assume the optimum metal–metal distance as well as an overall conformation best suited for the reduction. We previously proposed that protonation and cleavage of the O–O bond of the Co–O–O–Co complex would be facilitated if it is in a cis configuration.[4,14] Considering the steric constraints in the pillared system and the dimers' "chomping" action, it seems highly probable that the peroxo complex is indeed in a cis configuration. Another difference between the pillared dimers and the previous amide system is the ease with which intramolecular bis Fe–(μ-oxo) complexes can be obtained: the Fe–Fe-5 or longer amide-linked diporphyrins preferentially form *intermolecular* Fe–O–Fe whereas the pillared analogues yield the internal oxo bonds easily. If one assumes that during O_2 reduction a protonated $Co–O–OH^+–Co$ would have to rearrange to $Co–O^+(OH)–Co$ according to well-studied binuclear peroxo Co^{III} examples,[15] then the flexibility of the pillared system is clearly of great importance. It remains to be seen as to what effect a polar group (e.g., the amide bond in Co–Co-4) near the edge of porphyrin may have in facilitating the protonation and reductive cleavage of $Co–O_2–Co$.

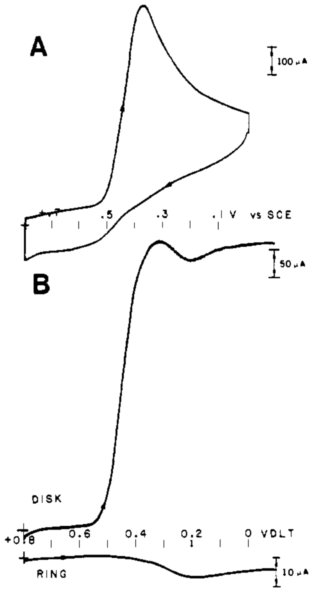

Figure 2. (A) Cyclic voltammogram obtained for an oxygen-saturated solution in 0.5 M trifluoroacetic acid at pyrolytic graphite disk (area = 0.47 cm^2) coated with **1b**. (B) Rotating ring–disk voltammograms in the same solution, using the same electrode; rotating speed = 100 rpm; disk current shown above, and ring current below, the *x* axis. All potentials are referenced against SCE.

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(13) X-ray crystallographic studies have been carried out on a Ni–Ni anthryldiporphyrin and a Cu–Cu biphenylene diporphyrin. While the structures are in final refinements, it is unmistaken that the two porphyrins lay perfectly parallel to each other, with interring distances of roughly 4.6 and 3.7 Å, respectively (Reidel, T.; Fillers, J. A.; Tulinsky, A.; Chang, C. K., unpublished results).

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Low-Temperature Synthesis of Plutonium Hexafluoride Using Dioxygen Difluoride

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We report the unprecedented low-temperature synthesis of plutonium hexafluoride by the action of dioxygen difluoride (O_2F_2) on plutonium fluorides, oxides, and oxyfluorides at room temperature and below. This development has technological significance because direct synthesis of PuF_6 has only been achieved previously by high-temperature fluorination[1] (typically >300 °C, at which temperature PuF_6 decomposition is extremely rapid) and by microwave or photolytic generation of fluorine atoms (a low-efficiency process).[2] The potency of O_2F_2 is illustrated by the following experiments:

(1) A sample of plutonium hexafluoride was photolyzed in a quartz U-tube using a 450W Hg lamp to form plutonium tetrafluoride (98 mg, 0.31 mmol). O_2F_2 (3.7 mmol) was condensed

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