and Ni**4a–c** are indeed shifted to lower energy compared to NiTPP and Ni**2d**, and that Ni**3** and Ni**4a–c** behave more like the very nonplanar porphyrins Ni**2b** and Ni**2c**. However, the magnitudes of the shifts in the absorption spectra of Ni**3** and Ni**4a–c** are quite different. This may be because the porphyrins are distorted from planarity in different ways and/or to different degrees. Alternatively, it may be because the porphyrins have substituents with different electron-donating characteristics. INDO/CI calculations show that the correct core conformation *and* substituents are necessary to reproduce the trends in optical spectra of Ni**1a**, Ni**1b**, Ni**2a**, and Ni**2b**.[35]

Raman spectra of Ni**3** and Ni**4a–c** also show quite clearly that these porphyrins exist in nonplanar conformations in solution. As Raman spectroscopy has previously been used to show that NiOEP is present as a mixture of both planar and nonplanar conformations in solution,[43] we attempted to determine if Ni**3** and Ni**4a–c** exist in multiple conformations in solution. Our results to date are inconclusive, but these studies are continuing.[44]

Conclusions

Dodecaphenylporphyrin (**3**) and the dodecaalkylporphyrins **4a–c** provide a unique opportunity to study many facets of porphyrin nonplanarity. We have investigated several aspects of the syntheses, structures, and spectroscopic properties of these porphyrins. Three of the key results obtained from our studies are as follows: (1) A very nonplanar saddle distortion is seen in the crystal structure of **3**, and a very nonplanar ruffled distortion is seen in the crystal structure of Ni**4c**. (2) These nonplanar distortions are correctly predicted by molecular mechanics calculations using a force field for nickel(II) porphyrins. (3) Variable temperature NMR studies indicate that the macrocycle conformations of **3** and Ni**4c** in solution are similar to those seen in the crystalline state.

Acknowledgment. Work performed at the University of California was supported by the National Science Foundation (CHE-90-01381, K.M.S.) and the Deutsche Forschungsgemeinschaft (Se 543/1-1, M.O.S.). Work performed at Sandia National Laboratories was supported by the U.S. Department of Energy (DE-AC04-76DP00789, J.A.S.). C.J.M. thanks the Fulbright Commission for the award of a travel scholarship. C.J.M. and L.D.S. thank the Associated Western Universities, Inc., for fellowships.

Supplementary Material Available: Details of the crystal structure determinations of **3** and Ni**4c** including lists of atomic coordinates, anisotropic thermal parameters, H-atom coordinates, bond lengths, bond angles, torsion angles, and least-squares planes (29 pages); observed and calculated structure factors for **3** and Ni**4c** (37 pages). Ordering information is given on any current masthead page.

---

[44] Sparks, L. D., Shelnutt, J. A.; Medforth, C. J.; Smith, K. M. Unpublished results.

Synthesis and Characterization of a Superoxo Complex of the Dicobalt Cofacial Diporphyrin [(μ-O$_2$)Co$_2$(DPB)(1,5-diphenylimidazole)$_2$][PF$_6$], the Structure of the Parent Dicobalt Diporphyrin Co$_2$(DPB), and a New Synthesis of the Free-Base Cofacial Diporphyrin H$_4$(DPB)

James P. Collman,[*,†] James E. Hutchison,[†] Michel Angel Lopez,[‡] Alain Tabard,[‡] Roger Guilard,[‡] Won K. Seok,[§] James A. Ibers,[§] and Maurice L'Her[⊥]

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, Université de Bourgogne, Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 33), Faculté des Sciences "Gabriel", 21100 Dijon Cedex, France, Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, and Université de Bretagne Occidentale URA CNRS 322, Faculté des Sciences, 6 Avenue Victor Le Gorgeu, 29287 Brest Cedex, France. *Received April 8, 1992*

Abstract: Chemical oxidation of the dicobalt cofacial diporphyrin Co$_2^{II/II}$(DPB), followed by exposure to dioxygen affords the bridged superoxo complex [(μ-O$_2$)Co$_2$(DPB)][PF$_6$]. This μ-superoxo complex has been implicated in possible mechanisms of four-electron dioxygen reduction by dicobalt cofacial diporphyrins but had not been isolated and fully-characterized previously. Although the superoxo complex is unstable with respect to loss of dioxygen, addition of 2 equiv of 1,5-diphenylimidazole yields [(μ-O$_2$)Co$_2^{III/III}$(DPB)(1,5-diphenylimidazole)$_2$][PF$_6$], a μ-superoxo complex that is stable toward loss of dioxygen. Analytically pure samples of the latter complex have been prepared, and their spectral and electrochemical properties are described. The crystal structure of the parent dicobalt cofacial diporphyrin Co$_2^{II/II}$(DPB) is reported. The Co–Co distance (3.726 (1) Å) and other structural features are compared to those of Co$_2$(FTF4) and of other known metallo-DPB structures. A new, improved total synthesis of the free-base porphyrin H$_4$(DPB) is presented. The combination of new reaction sequences, increased reaction scales, and improved product yields allows for large scale synthesis (gram quantities) of the free-base porphyrin needed to develop fully the coordination chemistry of the cofacial metallodiporphyrins.

The development of electrode materials that catalyze the four-electron reduction of dioxygen at or near the thermodynamic reduction potential (1.23 V vs NHE[1]) is important for fuel-cell technology and has been the subject of intense study. Although metallic platinum is an efficient fuel-cell cathode, its cost has prohibited routine use. Through the use of low loadings of platinum in solid polymer electrolytes, more economical, platinum-based fuel cells are presently being developed.[2] Still, there

---

[†] Stanford University.
[‡] Université de Bourgogne.
[§] Northwestern University.
[⊥] Université de Bretagne Occidentale.

[1] Abbreviations: DPB^{4-} = diporphyrinato biphenylene tetraanion, DPA^{4-} = diporphyrinato anthracene tetraanion, DPIm = 1,5-diphenylimidazole, EPG = edge-plane graphite, FeCp$_2$ = ferrocene, NHE = normal hydrogen electrode, DMSO = dimethyl sulfoxide, THF = tetrahydrofuran.

0002-7863/92/1514-9869$03.00/0

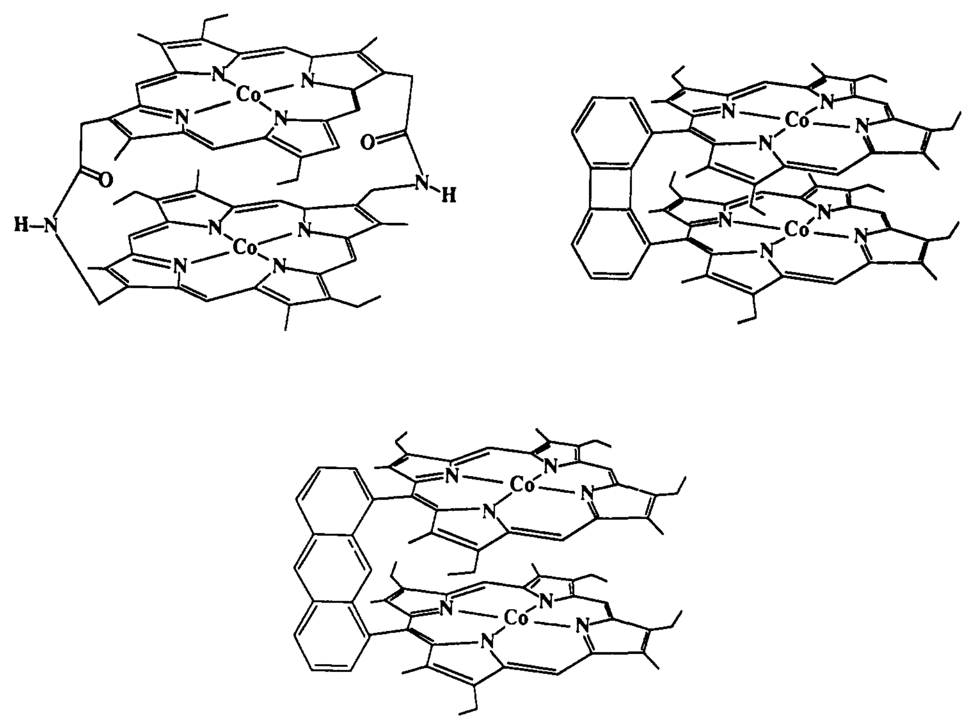

Figure 1. Cofacial dicobalt diporphyrins discussed in this paper: Co_3(FTF4) (upper left), Co_2(DPB) (upper right), and Co_2(DPA) (lower).

is interest in developing new electrode materials for dioxygen reduction and in understanding the mechanisms of multielectron transfers involved in dioxygen reduction. Co_2(FTF4)[3,4] and other cofacial metallodiporphyrins[4–7] (Figure 1) have been developed by several groups and have been shown to catalyze the four-electron reduction of dioxygen at moderately high potentials when the catalyst is adsorbed on edge-plane graphite that is in contact with dioxygenated, acidic aqueous solutions. Although considerable effort has been made to understand the mechanism of four-electron dioxygen reduction by cofacial metallodiporphyrins, the details of the catalysis remain unclear.

Initially it was believed that $Co_2^{II/II}$(FTF4) was the active catalyst and that dioxygen reacted with it to form the peroxo complex (μ-O_2)Co_2(FTF4), in which O_2 was bridging the two metals.[3] It was proposed that subsequent protonations and electron additions led to O–O bond cleavage and formation of water. Several variations of this mechanism have been suggested as the result of other studies.[4,6–11]

In nonaqueous solvents, $Co_2^{II/II}$(FTF4) is oxidized by one electron to produce either a mixed-valent cation ($Co_2^{II/III}$) or a porphyrin ring-centered radical cation, depending upon the solvent.[12] Whatever the nature of the cation, in benzonitrile its binding constant for dioxygen is 10^3, whereas the binding constant for $Co_2^{II/II}$(FTF4) is immeasurably small.[13,14] More detailed studies of Co_2(FTF4) adsorbed on EPG[1] suggested that the first surface oxidation of $Co_2^{II/II}$(FTF4) produces adsorbed [$Co_2^{II/III}$(FTF4)]X.[9] Because this oxidation occurs at the potential at which four-electron dioxygen reduction begins, the mixed-valence complex may be the active catalyst. Through the use of more rigorously purified Co_2(FTF4) adsorbed on EPG, it has been shown that a change in the product distribution (water vs hydrogen peroxide) occurring between 0.5 and 0.3 V (vs NHE) coincides with the $Co_2^{II/II}$–$Co_2^{II/III}$ redox couple.[11] Thus present evidence suggests that the active form of the catalyst is the mixed-valence complex [$Co_2^{II/III}$(FTF4)]X.

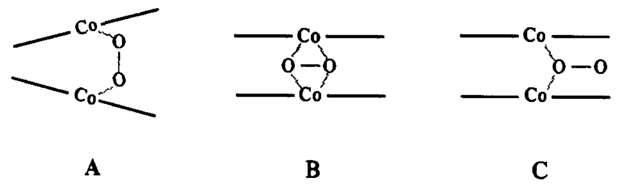

Figure 2. Dioxygen binding modes for Co_2(FTF4) proposed by Kim et al.[15]

In addition to these electrochemical studies of adsorbed and dissolved catalyst, structural studies of isolable complexes have been carried out in an attempt to establish a structural basis for the four-electron reduction mechanism. Although the crystal structure of Co_2(FTF4) is known,[15] the structure of its bridged superoxo complex [(μ-O_2)Co_2(FTF4)]X has not been determined. From the Co–Co separation in Co_2(FTF4) several orientations

---

(2) (a) Ticianelli, E. A.; Derouin, C. R.; Redondo, A.; Srinivasan, S. *J. Electrochem. Soc.* **1988**, *135*, 2209–2214. (b) Wilson, M. S.; Gottesfeld, S. *J. Electrochem. Soc.* **1992**, *139*, L28–L30.

(3) (a) Collman, J. P.; Marrocco, M.; Denisevich, P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem.* **1979**, *101*, 117–122. (b) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027–6036.

(4) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710–2718.

(5) Chang, C. K.; Liu, H.-Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725–2726.

(6) Liu, H.-Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 665–670.

(7) Ni, C.-L.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1987**, *91*, 1158–1166.

(8) Le Mest, Y.; L'Her, M.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E. R.; Bencosme, C. S. *J. Electroanal. Chem.* **1985**, *184*, 331–346.

(9) Ngameni, E.; Le Mest, Y.; L'Her, M.; Collman, J. P.; Hendricks, N. H.; Kim, K. *J. Electroanal. Chem.* **1987**, *220*, 247–257.

(10) Le Mest, Y.; L'Her, M.; Collman, J. P.; Kim, K.; Hendricks, N. H.; Helm, S. *J. Electroanal. Chem.* **1987**, *234*, 277–295.

(11) Collman, J. P.; Hendricks, N. H.; Leidner, C. R.; Ngameni, E.; L'Her, M. *Inorg. Chem.* **1988**, *27*, 387–393.

(12) (a) The site of the first oxidation of Co_2(DPB) and Co_2(FTF4) is highly dependent on reaction conditions. The first oxidation of the dicobalt diporphyrins dissolved in a noncoordinating solvent, e.g., dichloromethane, likely occurs on the ligand rather than on one of the metal centers. In the presence of dioxygen or other ligands, it is a cobalt center that is oxidized. (b) Le Mest, Y. Ph. D. Thesis, Université de Bretagne Occidentale, Brest, France, 1988. (c) Ngameni, E.; Laouénan, A.; L'Her, M.; Hinnen, C.; Hendricks, N. H.; Collman, J. P. *J. Electroanal. Chem.* **1991**, *301*, 207–226.

(13) Le Mest, Y.; L'Her, M.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E. R.; Bencosme, C. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1286–1287.

(14) Le Mest, Y.; L'Her, M.; Collman, J. P.; Hendricks, N. H.; McElwee-White, L. *J. Am. Chem. Soc.* **1986**, *108*, 533–535.

(15) Kim, K.; Collman, J. P.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4242–4246.

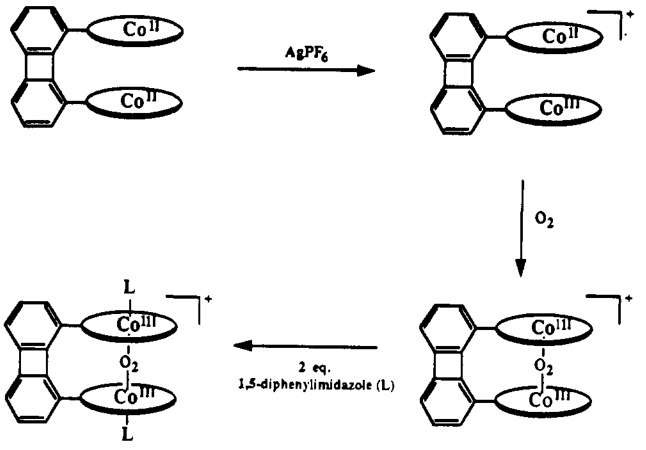

Figure 3. Preparation of the μ-superoxo complex $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$.

of the dioxygen bridge in $[(\mu\text{-}O_2)Co_2(FTF4)]X$ (Figure 2) have been suggested.[15] Resonance Raman studies[16] of a dioxygenated cofacial diporphyrin similar to $Co_2(FTF4)$ suggest that a sandwiched, bridged dioxygen complex (B in Figure 2) is most likely. However, these Raman studies were performed on dioxygen complexes formed in situ, and hence the exact nature of the species is uncertain. To date neither Raman nor X-ray crystallographic studies have been carried out on the isolated, fully-characterized, putative intermediate species $[(\mu\text{-}O_2)Co_2(FTF4)]X$.

In this paper we describe the isolation and full characterization of the stable superoxo complex of the cofacial diporphyrin $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ as well as the nonaqueous electrochemistry of this bridged superoxo complex. We report the structure of the parent cofacial metallodiporphyrin $Co_2^{II/II}(DPB)$. Additionally, we describe major improvements in the methods, yields, and scales of the syntheses leading to the free-base cofacial diporphyrin $H_4(DPB)$.

Results and Discussion

Synthesis of Analytically Pure $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$, a Stable, Bridged Superoxo Complex of Cofacial Dicobalt Diporphyrin. Although samples of μ-superoxo complexes of dicobalt cofacial diporphyrins have been prepared in situ for spectroscopic measurements, none have been isolated in pure form. The in situ preparation used most often involves addition of an axial ligand to a dioxygen-saturated solution of the dicobalt cofacial diporphyrin followed by oxidation with a "trace" of added iodine.[3,13,14,17]

$Co_2^{II/II}(DPB)$ reacts readily with dioxygen upon addition of 2 equiv of an imidazole ligand, such as 1,5-diphenyl- or 1,5-dicyclohexylimidazole, to form a complex that is likely to be the bridged peroxo complex. However, our efforts to isolate and characterize a pure sample of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2]X$ employing iodine oxidation were unsuccessful, and spectral titration studies with iodine suggest that it is easy to overoxidize the superoxo complex $[(\mu\text{-}O_2)Co_2^{III/III}(DPB)(L)_2]^+$.

An alternative approach is to prepare the cationic complex $[Co_2(DPB)]X$ from $Co_2^{II/II}(DPB)$ by bulk electrolysis.[10] Although subsequent treatment with dioxygen and an N-alkylimidazole affords the superoxo complex, removal of the backing electrolyte is difficult and no pure sample of the superoxo complex has been synthesized with this method.

The two synthetic approaches to the superoxo cation $[(\mu\text{-}O_2)Co_2(\text{cofacial diporphyrin})(L)_2]^+$ described above are unsatisfactory for several reasons. It is difficult to ascertain the success of these published methods because the products were seldom isolated and their purity was not tested. Preparations that use trace amounts of oxidant may also yield under- or over-oxidized complexes: overoxidation can result in loss of dioxygen. The size and concentration of the axial ligand used in the formation of μ-superoxo complexes are also important. Evidence from several sources suggests that all but the bulkiest ligands may gain access to the interior coordination sites of the cofacial metallodiporphyrins, $M_2(DPB)$.[8,18] We have avoided both of these problems through the use of 1 equiv of oxidant and 2 equiv of a very bulky axial ligand (Figure 3).

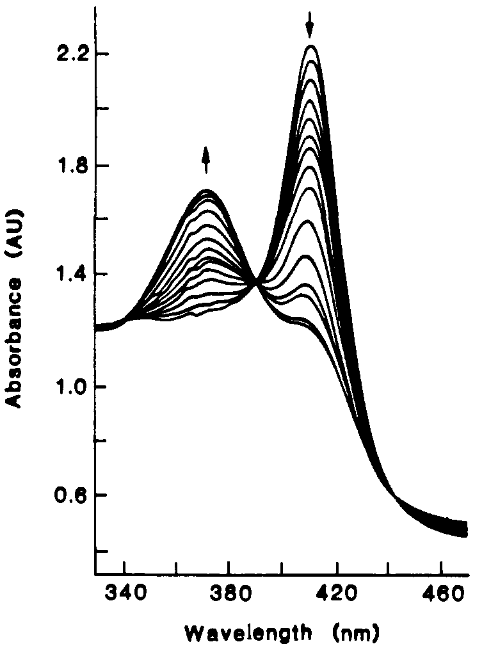

Figure 4. Deoxygenation of $[(\mu\text{-}O_2)Co_2(DPB)][PF_6]$ in dichloromethane upon exposure to the atmosphere.

Addition of 1 equiv of silver hexafluorophosphate to a toluene solution of $Co_2(DPB)$ resulted in the formation of a finely-dispersed precipitate that consists of $[Co_2(DPB)][PF_6]$ and silver metal. The precipitate was collected by filtration through a glass-fiber plug and was washed with toluene to remove any unreacted starting material. $[Co_2(DPB)][PF_6]$ was extracted from the silver by washing the plug with dichloromethane. Removal of the solvent yielded the product in 93% yield.

In dichloromethane, $[Co_2(DPB)][PF_6]$ binds dioxygen reversibly but weakly. When the solution is bubbled with dioxygen, $[(\mu\text{-}O_2)Co_2(DPB)][PF_6]$ is formed cleanly. If the solution is opened to the air, the complex slowly loses dioxygen. This lability of the bound dioxygen ligand indicates a rather low dioxygen binding affinity of the cationic complex (its binding constant is at most $K_{O_2} = 5$, whereas the same complex in benzonitrile has $K_{O_2} = 10^{1.9}$).[12] Both $[Co_2(DPB)][PF_6]$ and $[Co_2(FTF4)]X$ exhibit higher affinities for dioxygen in benzonitrile than in dichloromethane, presumably because benzonitrile acts as an axial ligand and stabilizes dioxygen binding.

The loss of dioxygen from $[(\mu\text{-}O_2)Co_2(DPB)][PF_6]$ can be followed by UV/vis spectroscopy, as shown in Figure 4. Isosbestic points at 388 and 442 nm suggest that the loss of dioxygen occurs cleanly; the isosbestic points are retained through several cycles of oxygenation/deoxygenation.

Addition of 2 equiv of 1,5-diphenylimidazole to $[(\mu\text{-}O_2)Co_2(DPB)][PF_6]$ results in the immediate formation of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ (Figure 3). It is no longer possible to deoxygenate $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ by passing an inert gas through the solution. This superoxo complex, when crystallized from chloroform/methanol, is analytically pure, gives a molecular cation in the mass spectrum, and exhibits a 15-line ESR spectrum (Figure 5). If an excess of axial ligand is used, initially the superoxo complex is formed but over time the Soret band in the UV/vis spectrum shifts to the red. This is consistent with re-

---

(16) Proniewicz, L. M.; Odo, J.; Gōral, J.; Chang, C. K.; Nakamoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 2105–2110.

(17) Chang, C. K. *J. Chem. Soc., Chem. Commun.* **1977**, 800–801.

(18) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1992**, *114*, 8074.

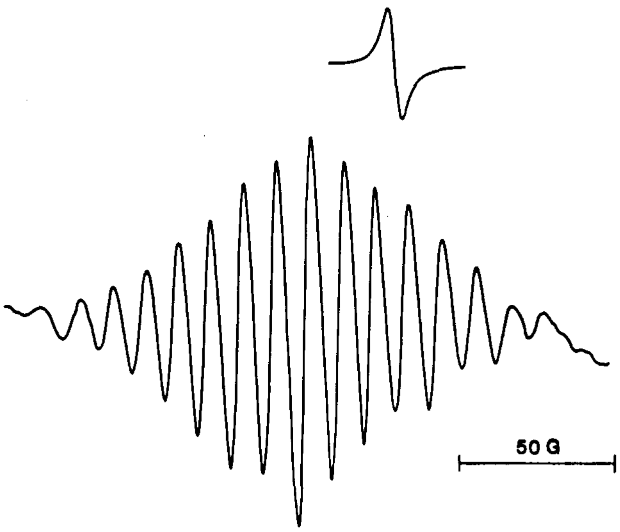

Figure 5. ESR spectrum of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ in dichloromethane at room temperature (vs DPPH).

Table I. Redox Values for Relevant Cobalt Porphyrin Complexes[a]

$[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$[b]	$E_{pc} = -1.75$V (4 electrons)		$E_{pa} = +0.31$V (1 electron)	
porphyrin	(I–I ↔ I–II)	(I–II ↔ II–II)	(II–II ↔ II–III)	(II–III ↔ III–III)
$Co_2(DPB)$[c]	−1.90	−1.71	0.00	+0.165
$Co_2(FTF4)$[c]	−1.78	−1.52	−0.04	+0.17
porphyrin		(I) ↔ (II)		(II) ↔ (III)
Co(TPP)/benzonitrile[d]		−1.288		+0.056
Co(TPP)/benzonitrile[e]		−0.858		0.486
Co(TPP)/pyridine[f]		−1.030		−0.214

[a] Potentials in volts vs $FeCp_2^{+/0}$ unless noted. (II) ↔ (III) denotes the redox couple Co(II)(porphyrin)/Co(III)(porphyrin). All redox processes are one-electron transfers except where noted. Oxidations to Co(III) may involve oxidation of the porphyrin ring instead of the metal.[12] [b] Platinum working electrode, in dichloromethane/$[(n\text{-}Bu)_4N][PF_6]$. Scan rate = 100 mV/s. [c] Platinum working electrode, in benzonitrile, vs $FeCp_2^{+/0}$.[10] [d] Platinum working electrode, benzonitrile, measured vs SCE[54] and converted to vs $FeCp_2^{+/0}$ for comparison to the cofacial systems using a value for $FeCp_2^{+/0}$ in benzonitrile of +0.43 V.[10] [e] Same as for *b*, except for vs SCE.[54] [f] Platinum working electrode, in pyridine, vs SCE.[54]

placement of the dioxygen ligand by imidazole ligands to form six-coordinate cobalt centers.

Electrochemistry of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$. The electrochemical properties of the bridged superoxo complex under dinitrogen in dichloromethane/$[(n\text{-}Bu)_4N][PF_6]$ were studied by both cyclic voltammetry and rotating disk voltammetry. The electrochemical data obtained for $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ are summarized together with results for cofacial and monomeric porphyrins in Table I.

The resting state of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ is the μ-superoxo complex in which both metals are taken to be in the Co^{III} state and the unpaired electron is shared between the two dioxygen atoms. The dioxygen complex can be oxidized by one electron ($E_{pa} = +0.31$ V vs $FeCp_2$ at 100 mV/s). The ratio of i_{pa}/i_{pc} varies with scan rate and approaches 1 (0.94) at about 500 mV/s (Figure 6). The nature of this wave suggests that a chemical reaction follows the initial oxidation. We suspect that this chemical step involves the loss of dioxygen because the dication $[Co_2^{III/III}(DPB)(DPIm)_2]^{2+}$ should have a low affinity for dioxygen. There are additional oxidations more positive on the forward scan that likely involve the porphyrin ligands of $[Co_2^{III/III}(DPB)(DPIm)_2]^{2+}$.

When the electrode is scanned to reducing potentials, a large, irreversible wave is observed at −1.75 V (E_{pc} vs $FeCp_2^{+/0}$) (Figure 7) instead of the expected one-electron reduction to the μ-peroxo complex. In the rotating disk experiment, this cathodic wave has

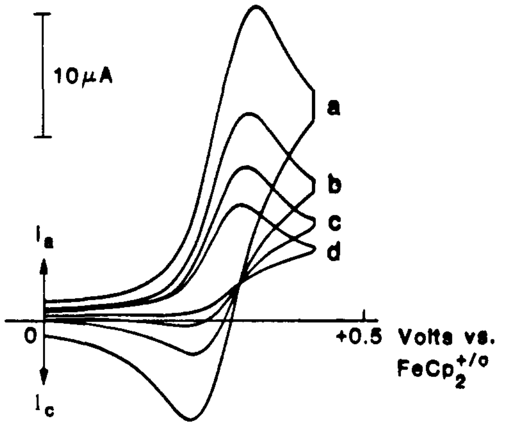

Figure 6. Scan rate dependence of the first oxidation of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ in dichloromethane/$[(n\text{-}Bu)_4N][PF_6]$ at a platinum working electrode for (a) 500 mV/s, (b) 200 mV/s, (c) 100 mV/s, and (d) 50 mV/s.

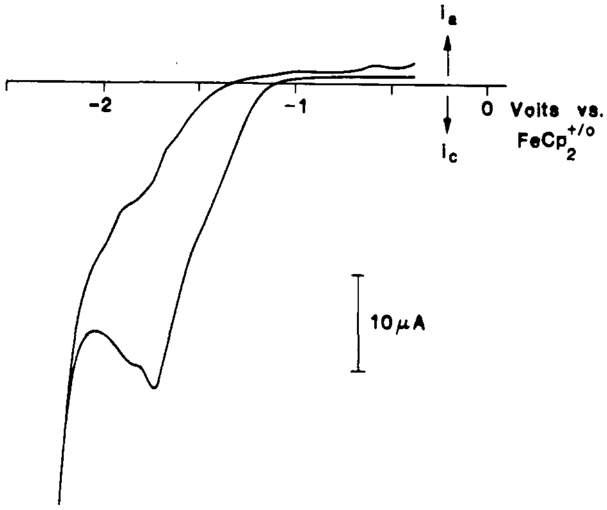

Figure 7. Reduction of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ at a platinum working electrode in dichloromethane/$[(n\text{-}Bu)_4N][PF_6]$. Scan rate = 100 mV/s.

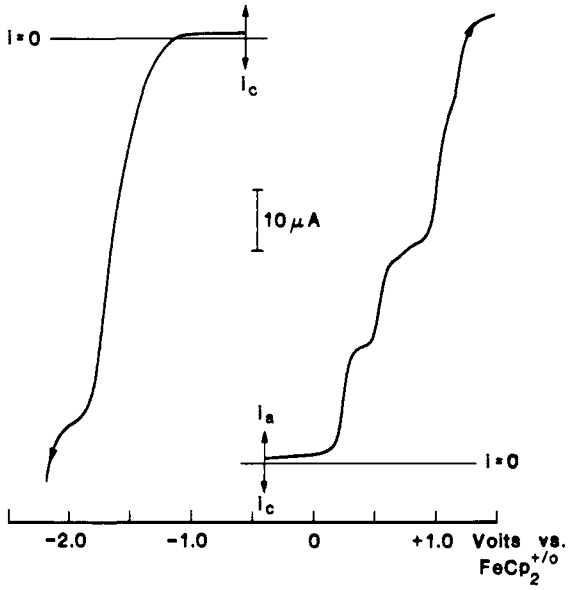

Figure 8. Rotating disk voltammograms of the oxidations and reductions of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ in dichloromethane/$[(n\text{-}Bu)_4N][PF_6]$ at a platinum working electrode. Scan rate = 5 mV/s. Rotation rate = 100 rpm.

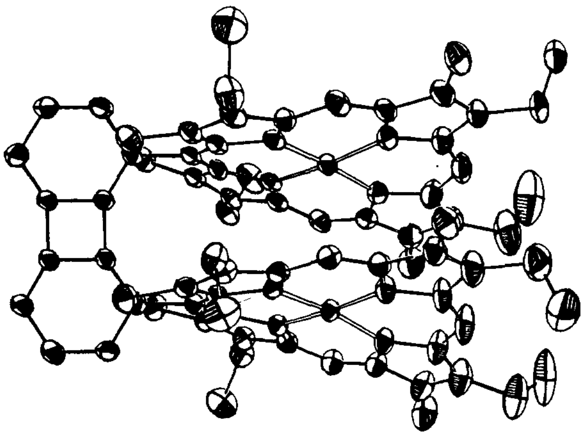

Figure 9. View of the structure of Co_2(DPB). The 50% probability ellipsoids are shown. Hydrogen atoms have been omitted for the sake of clarity.

3.8 times the limiting current of the first oxidation wave (Figure 8).

Some of the possible combinations of chemical steps that might accompany this electrochemical behavior are (1) liberation of unreduced O_2 and formation of a Co^0–Co^I diporphyrin, (2) production of H_2O_2 and a Co^I–Co^{II} diporphyrin, or (3) liberation of H_2O and production of a Co^{II}–Co^{III} diporphyrin. At this potential (−1.75 V), the resulting porphyrin should be the Co^I–Co^I or Co^I–Co^{II} complex because the reduction of Co^{II} to Co^I in Co_2(DPB) generally occurs near this potential. Moreover, it is known that the Co^{II}–Co^I redox couple is not affected by the presence of *N*-alkylimidazole.[8] The fate of the superoxo ligand as a result of this reduction remains unknown. Liberation of H_2O_2 (the protons being obtained from protic impurities in the solvent) seems most likely. This would be consistent with the results obtained by Geiger and Anson,[19] who showed by rotating ring-disk voltammetric experiments on another type of macrocyclic cobalt complex that a μ-peroxo ligand was reduced and H_2O_2 was liberated. Because the formation of H_2O_2 would leave the diporphyrin formally in the Co^I–Co^{II} state, it is puzzling that no oxidation wave is seen on the return scan; if the porphyrinic product is Co^I–Co^{II} or Co^I–Co^I, then substantial reoxidation waves should be observable.

Based on this survey of the nonaqueous electrochemical properties of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$, we find that in the absence of an added proton source or additional dioxygen reduction of the superoxo ligand with concomitant formation of H_2O does not occur. It may be that protonation of the superoxo ligand is the required first step in a series of proton and electron additions. A more complete understanding of the mechanism of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ reduction in the presence of a proton source or additional dioxygen will require more detailed electrochemical studies.

Structure of Co_2(DPB). The structure of $Co_2^{II/II}$(DPB) is shown in Figure 9. The atom numbering scheme used to describe the DPB ligand follows that of Fillers et al.[20] Selected bond lengths and angles are presented in Table II. Additional metric data are given in Table SI of the supplementary material.

The structure of Co_2(DPB) is similar to that of Cu_2(DPB) reported by Fillers et al.[20] The Co–Co distance (3.726 (1) Å) is slightly shorter than the analogous Cu–Cu distance (3.807 Å). The magnitude of the slippage (24.9°) between the two rings is identical in the two compounds. The two porphyrin rings in each dimeric unit are essentially in van der Waals contact; the mean interplanar distance is 3.381 (7) Å in the cobalt complex.

The Co–Co distance is longer than that found in Co_2(FTF4) (3.417 (4) Å)[15] and shorter than the Co–Al distance in CoAl(OEt)(DPB) (4.370 (1) Å).[21] The Co–Co distance in the μ-superoxo cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ is 4.56 Å.[22] In order for the Co_2(DPB) fragment to form a μ-superoxo complex having a geometry similar to this pentammine cobalt cation, either there must be significant distortion of the porphyrin rings to accommodate a longer Co–Co distance or dioxygen must bind in a conformation more perpendicular to the Co–Co axis as in structures B or C in Figure 2.

Table II. Selected Bond Distancs (Å) and Bond Angles (deg) for Co_2(DPB)

atoms	porphyrin 1	porphyrin 2
	Distance	
Co(1)–Co(2)	3.726 (1)	
av N–C_a	1.381 (7)	1.386 (7)
av C_a–C_b	1.444 (7)	1.448 (8)
av C_b–C_b	1.347 (7)	1.351 (8)
av C_a–C_m	1.380 (7)	1.373 (7)
av Co–N	1.965 (4)	1.962 (5)
	Angle	
av N–Co–N	90.2 (2)	90.1 (2)
slip angle[a]	24.9	

[a] The "slippage" is the component of the lateral displacement of one metal center with respect to the other parallel to the 24-atom least-squares plane of the porphyrin. The slip angle is defined as $\sin^{-1}$ (slippage/metal–metal distance).

Although the structure of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ is of great interest, our efforts to prepare single crystals of the μ-superoxo complex have been unsuccessful. Raman studies of $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$ have been performed, but no differences were observed between the $^{18}O_2$ and $^{16}O_2$ complexes.[23]

An Improved Synthesis of the Biphenylene-Bridged Cofacial Diporphyrin. Chang and Abdalmuhdi first reported the synthesis of the biphenylene-bridged diporphyrin H_4(DPB)[24] as well as a singly-bridged anthracene cofacial diporphyrin H_4(DPA).[25] These cofacial diporphyrins have some advantages over the previously known doubly-bridged, amide-linked diporphyrins. For example, there are no stereoisomers and the single bridge allows for a greater range of possible binding geometries for bridging ligands. Additionally, the metalated derivatives of these two new cofacial diporphyrins and their analogues have a rich coordination chemistry,[26-28] and progress toward their development as soluble transition-metal-based catalysts has recently been reported.[5-7,29-31]

Unfortunately, the syntheses that have been reported for both H_4(DPB) and H_4(DPA) are lengthy and the overall yields are low. Many steps of the earlier procedures for preparing the diporphyrins[5,6,24,25,32] and their precursors suffered from poor yields, scale limitations, and inconvenient or dangerous procedures. In light of the increased interest in developing catalysts based on these cofacial diporphyrins, we sought improved methods for preparing them.

Our improved synthesis of H_4(DPB) is a convergent synthesis that involves three major branches. In the first branch, the 1,8-biphenylenedicarboxaldehyde bridge (**7**) (Figure 10) that joins the two porphyrin rings is constructed. The products of the other

---

(19) Geiger, T.; Anson, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 7489–7496.

(20) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417–424.

(21) Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Brandes, S.; Hutchison, J. E.; Collman, J. P. *J. Am. Chem. Soc.*, the following paper in this issue.

(22) Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 178–179.

(23) Piffat, C.; Spiro, T. G.; Hutchison, J. E.; Collman, J. P. Unpublished results.

(24) Chang, C. K.; Abdalmuhdi, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 164–165.

(25) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388–5390.

(26) Collman, J. P.; Kim, K.; Garner, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1711–1713.

(27) Collman, J. P.; Kim, K.; Leidner, C. R. *Inorg. Chem.* **1987**, *26*, 1152–1157.

(28) Collman, J. P.; Garner, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 166–173.

(29) Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S.; Lewis, N. S.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1990**, *112*, 8206–8208.

(30) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794–2796.

(31) Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 3595–3596.

(32) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177–3184.

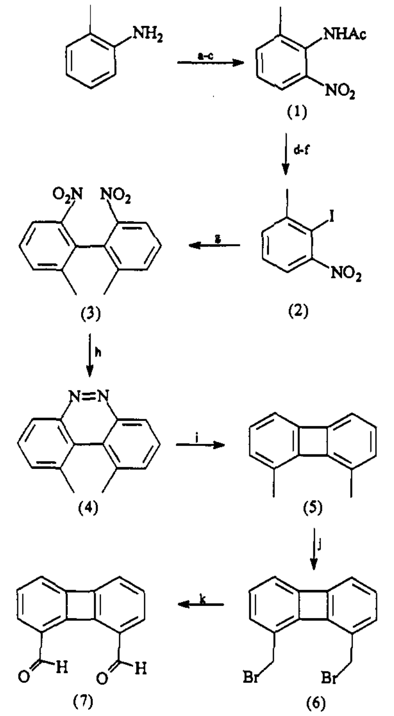

Figure 10. Synthesis of the 1,8-biphenylenedicarboxaldehyde. Reagents: (a) acetic anhydride; (b) concentrated nitric acid, <18 °C; (c) Witt/Uterman separation; (d) concentrated hydrochloric acid, reflux; (e) sodium nitrite; (f) potassium iodide, 0 °C; (g) copper powder, dimethylformamide, reflux; (h) lithium aluminum hydride, benzene/diethyl ether (1:1), reflux; (i) vacuum pyrolysis (800 °C, 0.6 Torr); (j) NBS, carbon tetrachloride, reflux; (k) tetrabutylammonium dichromate, chloroform, reflux.

two branches, the α-free pyrrole benzyl ester **8** and the dipyrrylmethanedialdehyde **9**, comprise the porphyrin macrocycle of the cofacial diporphyrin. Condensation of these three intermediates leads to the free-base cofacial diporphyrin H_4(DPB) (Figure 11).

Synthesis of 1,8-Biphenylenedicarboxaldehyde. The synthesis of the biphenylenedicarboxaldehyde **7** is shown in Figure 10. Originally the synthesis of 1,8-dimethylbiphenylene (**5**) was analogous to the method of Logullo et al.[33] This single-step conversion of 2-amino-3-methylbenzoic acid (a very expensive, but commercially available, starting material) yields the dimethylbiphenylene. The reaction is dangerous owing to potential explosions, and the formation of a mixture of the 1,5- and 1,8-dimethyl isomers is inconvenient. The separation of the two isomers is possible only after conversion of the methyl groups to the aldehydes followed by difficult column chromatography. Moreover, the yield is low (18% for the mixture of the two dimethyl isomers).

An improved synthesis of 1,8-dimethylbiphenylene based upon thermal extrusion of dinitrogen from a benzo[*c*]cinnoline[34] has been described by Wilcox et al.[35] It requires five steps starting from 2-methyl-6-nitroacetanilide (Figure 10); the key and final step is the pyrolysis of 1,8-dimethylbenzo[*c*]cinnoline. Our attempts to increase the scale of this pyrolysis to more than 5 g according to the literature procedure resulted in a marked decrease in yield. After adjustment of several experimental parameters (apparatus geometry and size, pyrolysis and sublimation temperatures, reactor pressure, and reaction time), we found a procedure that allows pyrolysis of 50 g of dimethylbenzo[*c*]cinnoline in 8 h in 47% yield versus a yield of 53% for the pyrolysis of a 5-g sample.[35]

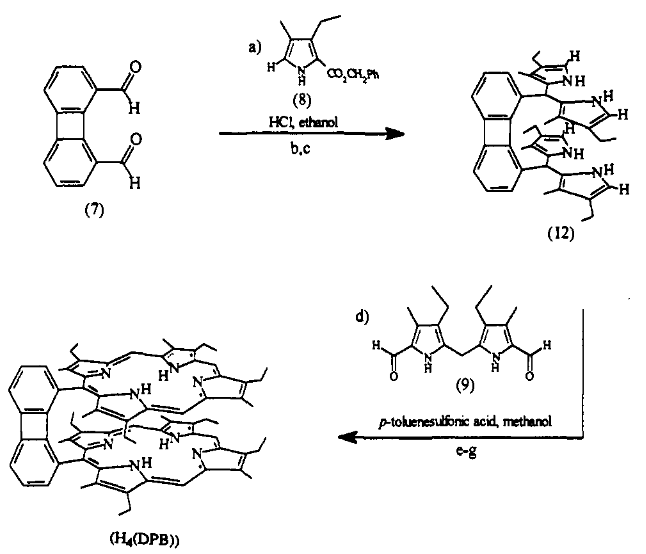

Figure 11. The final coupling steps in the synthesis of the biphenylene-bridged cofacial diporphyrin (H_4(DPB)). Reagents: (b) 10% palladium on carbon, 1 atm of dihydrogen, THF, triethylamine; (c) ethanolamine, reflux; (e) tetrachloro-1,2-benzoquinone; (f) zinc(II) aetate, methylene chloride/methanol, reflux; (g) 6 N hydrochloric acid.

Although the synthesis of 1,8-dimethylbiphenylene via the dimethylbenzo[*c*]cinnoline intermediate requires more steps than the benzyne coupling reaction, significant improvements were obtained: the starting material is cheap, the steps are simpler, the reactions can be carried out on a large scale, and the overall yield of 1,8-dimethylbiphenylene is higher (24% of the *pure* 1,8-isomer compared to 18% of a mixture of 1,8- and 1,5-isomers).[33] Because only the 1,8-isomer is produced, the labor-intensive isomer separation is avoided. Furthermore, the potential risk of explosion is eliminated.

Chang obtained the biphenylenedicarboxaldehyde **7** from the DMSO oxidation of the bis(bromomethyl)biphenylene **6**, a preparation originally described by Wilcox and co-workers.[36] The DMSO oxidation requires a long reaction time (96 h) and results in a poor yield (34% based on reacted starting material, 33% of the starting material was recovered). After surveying a number of oxidizing agents, we found that treatment of the dibromide **6** with tetrabutylammonium dichromate followed by column chromatography on silica provides the dialdehyde **7** in good yield (70%).

Synthesis of the α-Free Benzyl Ester Pyrrole 8 and the Dipyrrylmethanedialdehyde 9. The α-free ethyl ester pyrrole 2-(ethoxycarbonyl)-3-ethyl-4-methylpyrrole was prepared from ethyl isocyanoacetate[37] and 3-acetoxy-2-nitropentane[38,39] by the method of Barton and Zard.[40] Transesterification by the method of Badger et al.[41] gave the benzyl ester pyrrole. The benzyl ester was used because its conversion to the carboxylic acid by hydrolysis in subsequent steps is more convenient.

The dipyrrylmethanedialdehyde 5,5′-bis(benzyloxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrrylmethane was prepared by the method of Johnson et al.[42-44] Hydrogenolysis

---

(33) Logullo, F. M.; Seitz, A. H.; Friedman, L. *Org. Synth.* **1968**, *48*, 12-17.

(34) MacBride, J. A. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1219-1220.

(35) (a) Wilcox, C. F., Jr.; Lassila, K. R.; Kang, S. *J. Org. Chem.* **1988**, *53*, 4333-4339. (b) Kanoktanaporn, S.; MacBride, J. A. H. *J. Chem. Res.* (*M*) **1980**, 2901-2910.

(36) (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohman, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2532-2533. (b) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889-2895.

(37) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183-190.

(38) Sprang, C. A.; Degering, E. F. *J. Am. Chem. Soc.* **1942**, *64*, 1063-1064.

(39) Tindall, J. B. *Ind. Eng. Chem.* **1941**, *33*, 65-66.

(40) Barton, D. H. R.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1098-1100.

(41) Badger, G. M.; Jones, R. A.; Laslett, R. L. *Aust. J. Chem.* **1964**, *17*, 1157-1163.

(42) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416-3424.

(43) Johnson, A. W.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1958**, 4254-4257.

of the bis(benzyl ester) in THF with 10% Pd/C gave the dipyrrylmethanedicarboxylic acid[45] that when refluxed in ethanolamine gave 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane. Formylation[46] of this product with DMF and *p*-nitrobenzoyl chloride gave 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyl-2,2′-dipyrrylmethane in good yield.

Final Porphyrin Coupling Reaction. Perhaps the most significant improvement to the synthesis is the increased yield for the final porphyrin coupling step. Because we had trouble obtaining the yield reported in the original synthesis[24,32] (13%; our best yield using this method was 7%), we varied the reaction conditions until we found a procedure that provides a 23% yield of H_4(DPB).

The condensation reaction of the bis(dipyrrylmethane) **12** with the dipyrrylmethanedialdehyde **9** (Figure 11) was carried out in the dark in methanol in the presence of *p*-toluenesulfonic acid.[47] The zinc-metalated diporphyrin was easily isolated from the reaction mixture by column chromatography on silica. The free-base was then regenerated with dilute hydrochloric acid and was purified by flash chromatography.

The most notable modifications were the increase of the reaction time (48 h instead of 5 h) and the use of *p*-toluenesulfonic acid instead of perchloric acid. The increase in yield results primarily from the method of addition and the purity of the *p*-toluenesulfonic acid.

We described above a synthesis of H_4(DPB) from commercially-available starting materials that involves lower cost, less labor, and improved yields compared with previous synthetic methods. In addition, many of the reactions that have previously been "bottlenecks" in the preparation have now been scaled up considerably.

Experimental Section

Materials. *N*-Bromosuccinimide was recrystallized from water and dried under high vacuum for several hours prior to use. $[(n\text{-Bu})_4N]_2[Cr_2O_7]$ was prepared from $K_2Cr_2O_7$ and $[(n\text{-Bu})_4N][Br]$ as described in the literature.[48] It appears that the commercially available $[(n\text{-Bu})_4N]_2[Cr_2O_7]$ is not as effective as the freshly prepared oxidant. *p*-Toluenesulfonic acid was recrystallized from hydrochloric acid[49] and stored over P_2O_5. $[(n\text{-Bu})_4N][PF_6]$ was prepared by mixing equimolar, aqueous solutions of $(n\text{-Bu})_4N[OH]$ and HPF_6. The precipitated PF_6^- salt was washed with water, recrystallized twice from ethanol, and dried for 2–3 days under vacuum at 100 °C. $AgPF_6$ (Aldrich) was used without purification; however, fresh material results in higher yields. Methanol used in the final porphyrin coupling step was dried over 3-Å molecular sieves and degassed by bubbling with argon for 30 min. Solvents for use in the drybox were distilled from blue or purple sodium benzophenone ketyl solutions (benzene, toluene, and tetrahydrofuran), from P_2O_5 (dichloromethane and chloroform), and from $NaOCH_3$ (methanol). All other reagents and solvents were used as received.

Physical Measurements. ^1H NMR spectra were recorded on either a JEOL FX 100, a Nicolet NT-300, or a Bruker WM 400 Fourier transform spectrometer. All chemical shifts are reported relative to TMS. Electronic absorption spectra were measured on either a Hewlett-Packard 8452A or a Cary 219 UV–vis spectrophotometer. Mass spectrometry (LSIMS, tetraglyme) was done at the Mass Spectrometry Facility of the University of California, San Francisco.

All electrochemical measurements were made in dichloromethane solutions with $[(n\text{-Bu})_4N][PF_6]$ as a backing electrolyte. A 2-mm Pt disk was used as the working electrode. An $Ag/AgNO_3$ reference electrode was used, and all potentials were measured versus the ferrocene/ferricenium couple by adding ferrocene at the end of each experiment. A special small volume cell[10] was used for all cyclic voltammetric and rotating disk electrochemical experiments. A PAR 173 potentiostat/galvanostat, a PAR 175 universal programmer, and a Hewlett-Packard 7046B *X*–*Y* recorder were used to make all electrochemical measurements.

Table III. Crystal Data and Data Collection Procedures for Co_2(DPB)

formula	$C_{78}H_{76}Co_2N_8$
fw; amu	1219.4
space group	$P\bar{1}$
a, Å	12.496 (2)
b, Å	13.010 (2)
c, Å	20.925 (3)
α, deg	77.26 (1)
β, deg	79.59 (1)
γ, deg	64.75 (1)
V, Å^3	2987
Z	2
t, °C	−120[a]
density (calcd), g/cm^3	1.355
crystal shape	{0 0 1}, (0.055),[b] {0 1 0}, (0.152), {1 0 1}, (0.210), {1 1 0}, (0.217)
crystal volume, mm^3	0.0139
radiation	Cu Kα (λ = 1.5406 Å) β-filtered
μ, cm^{-1}	49.57
transmission coeff	0.236–0.609
detector aperature	2.7 mm wide, 3 mm high, 17 cm from the crystal
take-off angle, deg	2.3
scan mode	ω
scan speed, deg/min	1.0–2.7
2θ limits, deg	$2 \leq 2\theta \leq 75$
bkg counts	0.25 of scan range on each side of reflection
standard reflection	6 in diverse regions of reciprocal space measured every 3.0 h of X-ray exposure
scan range	±1.1 in ω
data collected	$+h, \pm k, \pm l$
p factor for $\sigma(F_o^2)$	0.04
unique data with $F_o^2 > 3\sigma(F_o^2)$	7639
no. of variables	775
$R(F)$ $(F_o^2 > 3\sigma(F_o^2))$	0.071
error in observation of unit wt, e	2.04

[a] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Sotorem, Z. I. deVic, 31320 Castanet-Tolosan, France. [b] The numbers in parentheses are the distances in mm between Friedel pairs of the preceding form.

X-ray Crystallography. Single crystals of Co_2(DPB) were obtained by vapor-diffusion of methanol into a chloroform solution at 5 °C. A red crystal of the substance was mounted in the cold stream (−120 °C) of an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined by least-squares refinement of 25 reflections. Crystallographic details are given in Table III. Data collection was performed at −120 °C. No systematic change was observed in the intensities of six standard reflections that were measured every 3 h of X-ray exposure. Intensity data were collected by previously described procedures.[50]

The structure was solved by a combination of Patterson and direct methods.[51] An analytical absorption correction was made. Idealized hydrogen atom positions (C–H = 0.95 Å, H–C–H = 109.5°) were either calculated (non-methyl) or obtained from a least-squares adjustment of the observed positions (methyl) and were added as fixed contributions to the structure factors. The final anisotropic refinement on F_o involved 7639 observations and 775 variables. The final positional and thermal parameters (Table SII) and structure amplitudes (Table SIII) are available as supplementary material.

Preparation of Compounds. 2-Methyl-6-nitroacetanilide (1). This compound was prepared as described in the literature[52] using 1.2 mol of 2-methylaniline. The cream-colored product that precipitated upon addition of the reaction mixture to water was collected by vacuum filtration, washed with ice water, and partially dried by suction.

The product was isolated by stirring the combined crude products of two nitrations in 9.33 L of Witt-Uterman solution[53] (7 L of H_2O, 0.78 kg of KOH, and 1.55 L of 95% ethanol) for 45 min. The resulting solution was vacuum-filtered to remove the unwanted 2-methyl-4-nitro-

---

(44) Kleinspehn, G. G. *J. Am. Chem. Soc.* **1955**, *77*, 1546–1548.

(45) Abraham, R. J.; Jackson, A. H.; Kenner, G. W.; Warburton, D. *J. Chem. Soc.* **1963**, 853–862.

(46) Chong, R.; Clezy, P. S.; Liepa, A. J.; Nichol, A. W. *Aust. J. Chem.* **1969**, *22*, 229–238.

(47) Cavaleiro, J. A. S.; Rocha Gonsalves, A. M. d'A.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1771–1781.

(48) Santaniello, E.; Ferraboschi, P. *Synth. Commun.* **1980**, *10*, 75–81.

(49) Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Longmans, Green and Co., Ltd.: London, 1956; p 552.

(50) Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3715–3721.

(51) The direct methods program used was DIRDIF. Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th., E. M.; Prick, P. A. J. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon: Oxford, 1982; p 516.

(52) Howard, J. C. *Organic Syntheses Coll. Vol. IV*; Wiley: New York, 1963; p 42–45.

(53) Wepster, B. M.; Verkade, P. E. *Rec. Trav. Chim.* **1949**, *68*, 77–87.

acetanilide isomer. The orange-red filtrate was acidified with 932 mL of glacial acetic acid. The precipitated product was collected by filtration, washed thoroughly with water, and dried in a vacuum oven at 60 °C to yield 542.1 g (60%) of yellow powder. The ^{1}H NMR spectrum is the same as that described in the literature.[35]

2-Iodo-3-methylnitrobenzene (2).[35] In a 6-L reactor equipped with two reflux condensers and a mechanical stirrer were introduced **1** (542.1 g, 2.79 mol) and concentrated HCl (2.7 L). The suspension was heated carefully (to avoid foaming) with stirring to dissolve the yellow powder. The resulting orange solution became deep orange after 7 h at reflux. The solution was cooled to 5–10 °C with an ice-water bath. An orange precipitate formed. A solution of $NaNO_2$ (241.1 g, 3.49 mol) in 875 mL of H_2O was added dropwise from a dropping funnel slowly enough so that the temperature remained between 8 and 10 °C. When the addition was complete, the solution was stirred for an additional 30 min and poured slowly into a stirred solution of KI (926 g, 5.58 mol) in 3.5 L of ice water. During the addition, yellow gas (nitrogen and iodine) was evolved and a thick, dark-brown foam developed. At the end of the addition, $NaHSO_3$ (aqueous solution, $d = 1.24$, ca. 165 mL) was added until the iodine color dissipated. The peach-colored product was recovered by filtration, washed thoroughly with water, and dried under vacuum to yield 715.2 g (97.4%). The ^{1}H NMR spectrum is the same as that described in the literature.[35]

6,6′-Dimethyl-2,2′-dinitrobiphenyl (3).[35] Under a nitrogen flow, a 6-L reactor was charged with 2-iodo-3-methylnitrobenzene (**2**) (715.2 g, 2.72 mol), dry DMF (distilled and dried over 4-Å molecular sieves, 3 L), and Cu powder (716 g). The mixture was heated to reflux with stirring. After 4 h an additional portion of Cu (716 g) was added and the reflux was continued for 2 h. The hot mixture was vacuum filtered through Celite (200 g). The inorganic material was washed with ether (2 × 1.1 L) in order to remove all the organic product. Ether was removed from the washings by rotoevaporation. The remaining residue and initial filtrate were combined and poured into 22 L of water. The resulting milky precipitate coagulated on standing. After filtration and partial drying by suction, the grey solid was recrystallized from 4 L of 95% ethanol to give light orange crystals of **3**. The mother liquor was concentrated to provide more product, total yield, 322 g (87%). The ^{1}H NMR spectrum is the same as that described in the literature.[35]

1,10-Dimethylbenzo[*c*]cinnoline (4).[35] A 20-L reactor equipped with a large reflux condenser, mechanical stirrer, dropping funnel, and N_2 inlet was charged with fresh $LiAlH_4$ (217.5 g, 5.73 mol) and anhydrous ether (4.88 L). A solution of 6,6′-dimethyl-2,2′-dinitrobiphenyl (**3**) (322 g, 1.18 mol) in dry benzene (4.88 L) was added dropwise so as to maintain a gentle reflux. The addition was complete after ca. 4 h. Decomposition of excess $LiAlH_4$ was achieved by the careful addition of water (220 mL), 15% aqueous NaOH (220 mL), and water (660 mL). The granular inorganic residue was removed by gravity filtration. Air was bubbled through the stirred orange filtrate in order to ensure complete oxidation of the hydrazo group. The solvent was rotoevaporated to provide pure **4** as a brown-yellow solid (241.1 g, 97.9%). The ^{1}H NMR spectrum is the same as that reported in the literature.[35]

1,8-Dimethylbiphenylene (5).[35] The pyrolysis of **4** was performed in a quartz tube in a horizontal tube furnace heated to 800 °C. The system was evacuated with a mechanical vacuum pump. 1,10-Dimethylbenzo[*c*]cinnoline (4, 6.24 g) was placed in a 100-mL two-necked round-bottomed flask along with a magnetic stirbar. One neck of the flask was connected to the quartz pyrolysis tube by a vacuum distillation adapter wrapped with heating tape. The other neck was fitted with a ground-glass stopper. The receiving end of the quartz tube was connected to a 100-mL two-necked round-bottomed flask (cooled with liquid N_2 during the pyrolysis) with another vacuum distillation adapter. The vacuum was applied to the second neck of the collection flask. Two liquid N_2-cooled traps were placed between the receiving flask and the vacuum pump. The oven was heated to 800 °C, the apparatus was evacuated, and the heating tape was set to 195 °C. The solid **4** was stirred and heated with an oil bath. The pyrolysis commenced when the oil bath reached about 170 °C. The oil bath temperature stabilized at 200 °C about 10 min after the reaction had begun. After an additional 35 min, the oil bath was removed, and the system was vented in order to add more **4** for another pyrolysis. The pyrolysates from eight 6.24-g samples (total 49.92 g, 0.24 mol) of **4** were recovered from the pyrolysis apparatus with dichloromethane. The dark solid obtained upon removal of the solvent (41.4 g) was dissolved in heptane and purified by flash column chromatography (10- × 5-cm, SiO_2, heptane). The column was eluted with heptane until all of the desired product had been removed. The heptane was removed in vacuo. Recrystallization from 74 mL of methanol (−20 °C) yielded pale yellow flakes (20.56 g, 47.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): CH_3 2.18 (s, 6 H); 2,7- and 4,5-biphenylene 6.46 (d, 2 H) and 6.53 (d, 2 H), 3,6-biphenylene 6.63 (dd, 2 H).

1,8-Bis(bromomethyl)biphenylene (6). A mixture of 1,8-dimethylbiphenylene (**5**) (10.28 g, 57 mmol), *N*-bromosuccinimide (22.6 g, 127 mmol), benzoyl peroxide (0.5 g), and carbon tetrachloride (250 mL) was stirred and refluxed for 5 h. Additional benzoyl peroxide (0.5 g) was added each hour. Insoluble material was removed from the hot mixture by gravity filtration, and most of the solvent was evaporated. Heptane was added to induce precipitation. The precipitate was collected by filtration on a frit, washed with heptane, and dried. A first recrystallization from 120 mL of chloroform (−20 °C) followed by concentration of the filtrate to yield more crystals gave **6** as beige needles (8.24 g, 42.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): CH_2Br 4.43 (s, 4 H), H-biphenylene 6.60 (d, 2 H) and 6.75 (m, 4 H).

1,8-Diformylbiphenylene (7). 1,8-Bis(bromomethyl)biphenylene (**6**) (10 g, 29.6 mmol) and tetra-*n*-butylammonium dichromate (82.94 g, 118 mmol) were dissolved in $CHCl_3$ (430 mL) and refluxed for 3 h. The cold mixture was filtered through a silica gel pad. The silica was washed with ether until no more product was eluted (as monitored by TLC, SiO_2, dichloromethane, $R_f = 0.45$). The solvent was removed in vacuo, and the crude material was purified by flash chromatography (5- × 25-cm, SiO_2, dichloromethane) to give 4.35 g (70.6%) of bright yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): CHO 10.32 (s, 2 H), 2,7-biphenylene 7.27 (d, 2 H), 3,6-biphenylene 7.23 (dd, 2 H), 4,5-biphenylene 6.86 (d, 2 H).

1,8-Bis(5,5′-bis(benzyloxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrrylmethyl)biphenylene (10). 1,8-Diformylbiphenylene (**7**) (6.25 g, 30 mmol) and 2-(benzyloxycarbonyl)-3-ethyl-4-methylpyrrole (**8**)[37–41] (29.27 g, 120 mmol) were dissolved in absolute ethanol (300 mL, degassed by bubbling with argon for 20 min) that contained concentrated HCl (5.9 mL). The solution was stirred and heated at reflux under argon for 3.5 h. It was then allowed to cool with stirring to room temperature and was next placed in a freezer. The resultant brown-red precipitate was filtered, washed with cold methanol, and dried (31.26 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): NH 8.28 (br s, 4 H), phenyl-H 7.33 (m, 20 H), 3,6-biphenylene 6.70 (t, 2 H), 4,5-biphenylene 6.64 (d, 2 H), 2,7-bipenylene 6.05 (d, 2 H), CH_2Ph 5.25 (d, 8 H), CH 4.76 (s, 2 H), CH_2CH_3 2.66 (q, 8 H), CH_3 1.44 (s, 12 H), CH_2CH_3 1.02 (t, 12 H).

1,8-Bis(4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrrylmethyl)biphenylene (12). The hydrogenolysis of the tetrabenzyl ester **10** (61.32 g, 53 mmol) was carried out in a 3-L filter flask containing THF (2.2 L), triethylamine (24.3 mL), and 10% Pd/C (12.15 g) under H_2 (1 atm). The consumption of H_2 stopped after 2 h. The mixture was stirred under H_2 for an additional 3 h and filtered through Celite to remove the catalyst. The Celite was washed with ethanol until only catalyst remained. The combined filtrate and washings were rotoevaporated to yield 1,8-bis(5,5′-dicarboxy-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrrylmethyl)biphenylene (**11**) as a pale yellow powder.

The tetracarboxylic acid **11** was taken up in 600 mL of ethanolamine and heated to reflux under argon for 1.5 h. The hot solution was poured with stirring into 6 L of ice water and allowed to stand for 30 min. The yellow precipitate was collected by vacuum filtration, washed with water, and dried under vacuum over P_2O_5 (32.3 g, 99%). The yellow solid **12** was stored under an inert atmosphere at −18 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): NH 7.35 (br s, 4 H), 3,6-biphenylene 6.66 (t, 2 H), 2,7- or 4,5-biphenylene 6.55 (d 2 H), 5-pyrrole 6.34 (s, 4 H), 2,7- or 4,5-biphenylene 6.26 (d, 2 H), CH 4.93 (s, 2 H), CH_2CH_3 2.39 (q, 8 H), CH_3 1.61 (s, 12 H), CH_2CH_3 1.16 (t, 12 H).

1,8-Bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]biphenylene (H_4(DPB)). Under argon, a suspension of **12** (4.88 g, 8 mmol) and 5,5′-bis(benzyloxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrrylmethane (**9**)[42,43,45,46] (4.82 g, 16.8 mmol) in dry methanol (1.3 L) was stirred for 1 h. A solution of *p*-toluenesulfonic acid (3.56 g) in methanol (20 mL) was added dropwise to the stirred suspension via a cannula over a 2-h period. The resulting dark-red solution was stirred in the dark for 48 h. To the solution was added *o*-chloranil (tetrachloro-1,2-benzoquinone, 3.56 g), and the stirring was continued for 3 h. A saturated, aqueous $NaHCO_3$ solution (1.2 L) was added to precipitate the organic products. The precipitate was collected by filtration through Celite. It was then washed with water until the pH of the water was 7, and it was next dissolved in dichloromethane. The solution was washed with brine, and the volume was reduced to ca. 600 mL. A saturated solution of zinc acetate in methanol (60 mL) was added, and the solution was heated at reflux for 1 h. After the solvent was removed, the residue was taken up in dichloromethane and chromatographed on silica gel (7.5- × 17-cm). The first band eluted by dichloromethane was collected. The eluent was concentrated (to ca. 200 mL) and vigorously stirred with 6 N HCl (16 mL) for 15 min. The solution was neutralized with 10% aqueous sodium carbonate (36 mL), and the mixture was stirred for 15 min. The organic phase of this mixture was separated,

---

(54) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484–3489.

washed with water, dried ($MgSO_4$), and evaporated. The residue was redissolved in dichloromethane and flash chromatographed on silica gel (230-400 mesh, 5- × 25-cm). A band eluted first with 5% MeOH-CH_2Cl_2 solution. A second fraction was collected with 10-20% MeOH-CH_2Cl_2 solution. The product was eluted with 20-70% MeOH-CH_2Cl_2 solution. Partial evaporation of the solvent removed mainly dichloromethane to yield pure H_4(DPB) as purple microcrystalline powder (2.0 g, 23%). The ^1H NMR spectrum is the same as that reported in the literature.[24]

Co_2(DPB). In a dinitrogen drybox, a solution of 107 mg of free-base DPB, 364 mg of anhydrous cobalt(II) chloride, and 15 drops of 2,6-lutidine in 125 mL of THF was stirred and refluxed for 20 h. The resulting mixture was filtered through a column of neutral, activity I alumina (1- × 15-cm) to remove unreacted cobalt chloride. The solvent was removed under vacuum to yield Co_2(DPB) as a blood-red powder. Crystallization from dichloromethane/methanol yields analytically pure Co_2(DPB). Anal. Calcd for $C_{76}H_{76}N_8Co_2$: C, 74.86; H, 6.28; N, 9.19. Found: C, 74.83; H, 6.05; N, 9.04. Crystals for X-ray analysis were grown by slowly diffusing methanol into a chloroform solution of Co_2(DPB) at 5 °C. UV/vis (dichloromethane, nm): 382 (Soret), 530, 559 (lit.[10] 382, 530, 558 nm).

$[Co_2(DPB)][PF_6]$. In a dinitrogen drybox, 19.5 mg of Co_2(DPB) was dissolved in 15 mL of benzene with vigorous stirring. A THF solution of $AgPF_6$ (360 μL of a 4.31×10^{-2} M solution (21.8 mg in 2 mL of THF)) was added dropwise to the stirred solution. The mixture was stirred for 4 h after the final addition of oxidant. The reaction mixture was filtered through a glass-fiber plug in a pipette to remove precipitated silver metal and the oxidized product. The plug was washed with several milliliters of benzene to remove any unreacted starting material. The product was collected by washing the plug with dichloromethane until the washings remained colorless. Subsequent removal of the solvent under reduced pressure yielded 20.3 mg (93%) of $[Co_2(DPB)][PF_6]$. UV/vis (dichloromethane, nm): 372 (Soret), 524, 552 (lit.[10] 372 (Soret), 540 nm).

$[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$. 1,5-Diphenylimidazole (360 μL of an 8.33×10^{-2} M solution in dichloromethane) was added to a dioxygen-saturated solution of 20.3 mg of $[Co_2(DPB)][PF_6]$. The solvent was evaporated away under a stream of dioxygen. Recrystallization from chloroform/methanol yielded analytically pure $[(\mu\text{-}O_2)Co_2(DPB)(DPIm)_2][PF_6]$. Anal. Calcd for $C_{106}H_{100}Co_2F_6N_{12}O_2P$: C, 69.31; H, 5.49; N, 9.15. Found: C, 69.43; H, 5.31; N, 9.08. UV/vis (dichloromethane, nm): 334, 410 (Soret), 534, 568. MS: LSIMS (tetraglyme) 1692 (cluster) $[M^+ - PF_6]$.

Acknowledgment. We thank Kimoon Kim and Michele McMahon for contributions to the development of the improved synthesis of the free-base diporphyrin. We thank the National Science Foundation, the National Institutes of Health (Grants GM-17880 to J.P.C. and HL-13157 to J.A.I.), and the CNRS for financial support.

Supplementary Material Available: Table SI, additional bond distances and angles for Co_2(DPB), Table SII, final positional and thermal parameters for Co_2(DPB), and improved, large scale procedures for the preparation of compounds **8** and **9** (19 pages); Table SIII, structural amplitudes for Co_2(DPB) (31 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Novel Cobalt Aluminum Cofacial Porphyrins. First Crystal and Molecular Structure of a Heterobimetallic Biphenylene Pillared Cofacial Diporphyrin

Roger Guilard,*,[1a] Michel Angel Lopez,[1a] Alain Tabard,[1a] Philippe Richard,[1a] Claude Lecomte,[1b] Stéphane Brandes,[1a] James E. Hutchison,[1c] and James P. Collman[1c]

Contribution from the Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Associé au C.N.R.S. (URA 33), Faculté des Sciences "Gabriel", Université de Bourgogne (Dijon), 6, boulevard Gabriel, 21100 Dijon, France, Laboratoire de Minéralogie et Cristallographie, Associé au C.N.R.S. (URA 809), Université de Nancy I, B.P. 239, 54506 Vandoeuvre les Nancy, France, and Department of Chemistry, Stanford University, Stanford, California 94305.

Received April 8, 1992

Abstract: The synthesis of the novel family of heterodinuclear complexes (DP)CoAl(OR) (where DP^{4-} is the tetraanion of the diporphyrin biphenylene DPB or the diporphyrin anthracene DPA, and R = CH_3, CH_2CH_3, or $CH_2C_6H_5$) is reported. These complexes were obtained by selective metalation of the cofacial diporphyrins with cobalt and aluminum. Each (DP)CoAl(OR) complex was characterized by mass spectrometry and UV-vis, IR, ESR, and ^1H NMR spectroscopies. Unusually large paramagnetic shifts were observed for the protons on axial ligands bound to aluminum and for the porphyrinic N-H protons of the monocobalt DPB and DPA complexes. Analysis of the paramagnetic shifts indicates that the main contribution to isotropic shifts arises from a through space (or dipolar) interaction of an unpaired electron on cobalt(II). Structural data were deduced from the ^1H NMR study. In addition, the molecular structure of the cobalt(II) aluminum(III) ethoxide diporphyrin biphenylene (DPB)CoAl(OCH_2CH_3) was determined by X-ray diffraction. This is the first crystal structure of a heterobimetallic cofacial diporphyrin. (DPB)CoAl(OCH_2CH_3) ($C_{78}H_{81}N_8OCoAl\cdot C_7H_8$) crystallizes in the triclinic system, space group $P\bar{1}$. Its lattice constants are as follows: a = 13.095 (4) Å, b = 16.836 (3) Å, c = 16.986 (3) Å, α = 87.47 (1)°, β = 70.40 (3)°, γ = 85.90 (2)°, V = 3516 Å^3, Z = 2, $R(F)$ = 5.30%, $R_w(F)$ = 5.27%, GOF = 2.5 for 6800 reflections with $I \geq 3\sigma(I)$. No metal-metal interaction occurs (Co-Al = 4.370 (1) Å), and both porphyrin moieties are slipped by α = 29.8°. Finally, the tedious synthesis of the (DPA)H_4 free-base porphyrin has been extensively modified, and several new reaction steps are presented leading to significant increases in both scale and yield.

Many efforts of our groups have been devoted to the study of metalloporphyrins with metal-metal bonds[2-12] in order to investigate the major factors which affect the metal-metal interactions.[7,8,13] In these compounds most of metal-metal bonds

---

[1] (a) Université de Bourgogne (Dijon). (b) Université de Nancy I. (c) Stanford University.

[2] Barbe, J.-M.; Guilard, R.; Lecomte, C.; Gerardin, R. *Polyhedron* **1984**, *3*, 889-894.

0002-7863/92/1514-9877$03.00/0