zation. After completion of the last reagent addition, the reaction mixture was left overnight at 65 °C. The pyridine was removed on the rotary evaporator. The residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove the small amount of insoluble polymer. Purification of the product was accomplished by chromatography on a 14 × 3.5 cm silica column. First, pure CH_2Cl_2 was used to elute a narrow pink band of unreacted *p*-nitrophenyl ester (**3**), followed by a bright yellow band of *p*-nitrophenol. $CH_3CN-CH_2Cl_2$ (10:90) then eluted a red-purple band, the FTF4, and a narrow band of dark-colored impurities remained at the origin. The solvent was removed under reduced pressure, and the product was recrystallized from $CH_2Cl_2-CH_3OH$; yield 60–65%. FTF dimers are highly light-sensitive and must be handled in the dark.

Treatment of Chloro-Contaminated FTF4 with NH_2NH_2 To Obtain Pure FTF4. Pure FTF4 may be obtained from the synthetic pathway depicted in Figure 2. Treatment of the FTF4 mixture **6** with NH_2NH_2 in pyridine reduces the chlorine in the meso position of the chlorinated contaminants, leading to pure FTF4 **6c**, as shown by HPLC analysis. The procedure is described below. Chloro-contaminated FTF4 (42.1 mg, ca. 43 mmol), 97% anhydrous hydrazine (9.8 mL, 300 mmol), and pyridine (33 mL) were combined, stirred for 15 min under an argon purge, heated for 6 h at reflux under argon, cooled to room temperature, and mixed with methylene chloride (50 mL) and water (100 mL). The resulting mixture was shaken in a separatory funnel to give a colorless aqueous layer, deep red-purple organic layer, and a *clean* interface between the two. The aqueous layer was washed with additional methylene chloride (25 mL), and the organic layers were combined, washed with water (6 × 100 mL), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product was dissolved in a minimum of methylene chloride and chromatographed on silica gel (10 × 2.3 cm). The product was eluted with CH_2Cl_2, followed by 10:90 $CH_3CN-CH_2Cl_2$ and crystallized from methylene chloride–ethanol to give pure FTF4 (25.8 mg, 61% recovery).

Small-Scale Cobalt Insertion into Fractions a, b, and c. In the drybox, the cofacial porphyrin dimer (less than 0.5 mg) was dissolved in a saturated solution of anhydrous $CoCl_2$ in THF (0.5 mL), toluene (0.75 mL), and 2,6-lutidine (20 drops from a pipette), and the solution was heated at reflux for 6.5 h. The reaction was monitored by visible spectroscopy after removal of $CoCl_2$ from each reaction aliquot. For each aliquot a pipette plugged with glass wool was loaded with neutral alumina (activity III) (ca. 1 cm) and wetted with THF (ca. 0.5 mL). The aliquot of the reaction mixture was added and washed through the alumina directly into the UV–vis cell with additional THF. Upon complete metallation, the mixture was cooled, more THF was added, and the reaction mixture was filtered through alumina (activity III) (ca. 2.5 cm) in a pipette. The solvents were removed under vacuum, leaving a thin film of dicobalt product on the flask's sides: UV–vis λ 380, 518 (sh), 556 nm.

Acknowledgment. This work derives from a collaborative effort that also includes the research groups of Professors M. Boudart and H. Taube (Stanford University) and Dr. H. Tennent (Hercules Inc. Research Center). We express our gratitude to Dr. C. J. Wright of Eastman Kodak Co. for analytical assistance with the mass spectral analyses. We wish to thank B. Brown, K. Gillette, and J. Sugarman for technical assistance. This work was supported by National Science Foundation Grants CHE77-22722 and CHE81-10545. We acknowledge use of the Stanford Magnetic Resonance Laboratory (a facility supported by NSF Grant GP23633 and NIH Grant RR00711) and FT IR facilities at Stanford (NSF CHE78-02070). C.S.B. thanks the Venezuelan Council for Scientific and Technological Research (CONICIT) for her doctoral scholarship. R.B.P. thanks the Science Research Council of Great Britain for his postdoctoral fellowship.

Registry No. 1, 85097-07-0; **2**, 85084-68-0; **3** (Ar = *p*-$NO_2C_6H_4$), 85097-08-1; **5**, 85048-73-3; **6a**, 85097-09-2; **6b**, 85097-10-5; **6c**, 85084-69-1; **6c** dicobalt derivative, 71253-24-2; *p*-nitrophenyl trifluoroacetate, 658-78-6; oxygen, 7782-44-7.

Mixed-Metal Face-to-Face Porphyrin Dimers

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Received August 9, 1982

Abstract: A strategy for the synthesis of heterobimetallic "face-to-face" dimeric porphyrins, using silver as a "protecting group" in one of the coordination centers, is presented. The synthesis and characterization of cobalt–silver, cobalt–iron, and cobalt–manganese derivatives of a cofacial porphyrin dimer with two four-atom amide bridges at transverse β-pyrrolic positions are described.

During the past several years, much attention has been given to transition-metal chelates of N_4 macrocycles as potential electrocatalysts for the cathodic reduction of dioxygen in fuel cells.[2–4] So far, many of these complexes have been found to catalyze this reduction to hydrogen peroxide. Catalysis of the four-electron reduction of O_2 to H_2O through H_2O_2 intermediates cannot be extensive at potentials much more positive than the reversible O_2/H_2O_2 couple ($E° = 0.68$ V).[4,5] For maximum efficiency, the four-electron reduction should proceed as closely as possible to the thermodynamic potentials for the O_2/H_2O couple ($E° = +1.23$ V).

Speculation on the mechanism of enzyme action of cytochrome *c* oxidase, which carries out the four-electron reduction of dioxygen to water without forming free H_2O_2, suggested that cofacial binary

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(1) (a) Stanford University (this paper was abstracted from the Ph.D. Thesis of C.S.B., Stanford University, 1982). (b) California Institute of Technology.

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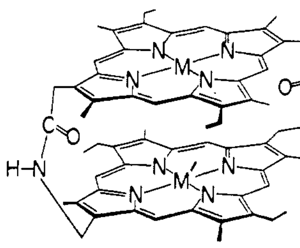

1 M = M' = 2H
2 M = M' = Co
3 M = Co, M' = 2H
4 M = Co, M' = Fe
5 M = Co, M' = Mn
6 M = Pd, M' = Co
7 M = M' = Ag
8 M = M' = Mn
19 M = 2H, M' = Ag
20 M = Co, M' = Ag

Figure 1. Homo- and heterometallo derivatives of FTF4.

cyclophane compounds might also catalyst this reaction.[6] Specifically, it was hoped to achieve an orientation of two cofacial metalloporphyrin rings such that the two metal centers could interact in a concerted fashion in binding and reducing dioxygen molecules. Toward this end, we prepared a systematic series of "face-to-face" porphyrin dimers[7,8] with different interporphyrin separations and examined the catalytic properties of some of their metal derivatives. This approach successfully led us to the synthesis of an effective catalyst for the cathodic reduction of O_2 to H_2O.[5] The catalyst is Co_2(FTF4) (**2**) adsorbed on a pyrolytic graphite electrode (see Figure 1). This catalyst reduces O_2 at potentials near +0.7 V vs. NHE in 0.5 M acid without the formation of free H_2O_2. At more negative potentials the catalyst can operate at turnover rates as high as 400 dioxygen molecules per catalyst site per second.[9] We have also been interested in finding a catalyst that would reduce dioxygen to water at more neutral pH levels than does Co_2(FTF4). The fact that multielectron redox enzymes have heterometallic active centers[11] suggested an approach to this problem. We therefore explored "mixed-metal" face-to-face porphyrin dimers (MM'(FTF4))[15] as possible catalysts for the reduction of O_2 to H_2O.

Additionally, mixed-metal porphyrins are important from a purely mechanistic point of view. Substitution of one of the cobalt centers of the electroactive Co_2(FTF4) by different metals may lead to an improved understanding of the coordination chemistry and of the role of the second metal during the catalytic cycle. In fact, these mixed-metal dimers are appealing candidates for mimicking the catalytic behavior of other heterometallic enzymatic centers such as that in nitrogenase. We speculate that such catalytic behavior may be found in spite of the lack of structural analogies between the synthetic catalyst and the heterometallic enzymes.

Our original target molecule was CoFe(FTF4) (**4**). It was hoped that it might catalyze an overall 4e reduction in the Co(II)/Fe(III) state. Co(II) monomeric porphyrins are known to bind O_2 and to catalyze effectively its 2e reduction to H_2O_2 over a wide range of pH values.[16] Catalase, a heme protein, is known to catalyze hydrogen peroxide disproportionation, presumably through oxidation to the formal Fe(V) state.[17] If both these reactions could be made to occur within the interporphyrin cavity, an overall 4e catalytic reduction of O_2 would be achieved. The Co–Mn complex (**5**) was designed with similar objectives in mind.

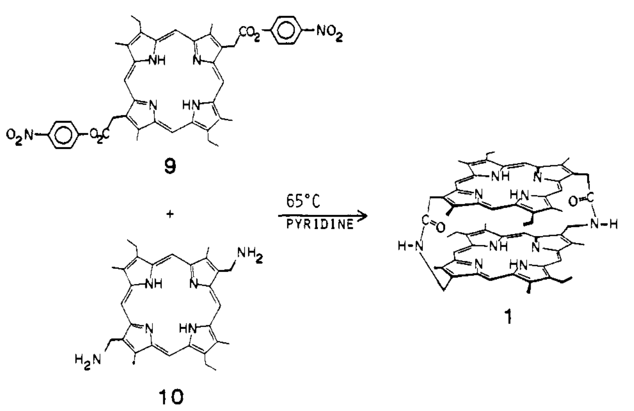

Figure 2. Preparation of the β-linked FTF4.

Very few cases of heterometallic cofacial macrocyclic complexes have been previously reported in the literature. Reed et al.[18] synthesized a heteronuclear Mn(II)/Co(II) porphyrin dimer as a spin model for the heme a_3/Cu_B active site of cytochrome oxidase. Elliott et al.[19] prepared a trimeric diiron(II)–heme—copper(II) complex as an alternate model to explain the "ESR-silent" heme a_3/Cu_B in cytochrome *c* oxidase.[12] Chang and coworkers reported the synthesis of the copper–iron[20,21] and the iron–magnesium[20] derivatives of their cofacial porphyrin dimer,[22] but the full characterization of these has not yet been published. "Mixed" copper–iron dimers have been reported also by Gunter et al.[23] as models for cytochrome *c* oxidase. No studies of the electrocatalytic behavior of any of these compounds have been reported.

In this paper, we present a general strategy for the synthesis of mixed-metal face-to-face porphyrin dimers. We report the syntheses of the H_2–Ag, Co–Ag, Co–H_2, Co–Fe, and Co–Mn derivatives of FTF4, together with their physical characterization. The electrocatalytic activity of these MM'(FTF4) complexes (Figure 1) in the reduction of molecular oxygen is described elsewhere.[8]

Results and Discussion

Synthesis. The free-base dimer FTF4 **1** is synthesized by the coupling of the monomeric diaminoporphyrin **10** with an equivalent amount of the di-*p*-nitrophenyl ester porphyrin **9** in pyridine (Figure 2).[5] The mixed-metal derivative of FTF4 may sometimes be prepared by simply coupling the metal complexes of the monomeric precursors or by reaction of one of the monometalated monomers with the free-base of the other porphyrin reagent. Insertion of the second metal into the monometalated dimer affords MM'(FTF4). This synthetic method was previously applied by

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(11) Cytochrome-*c* oxidase is the enzyme responsible for the reduction of O_2 to H_2O in the final step of cellular respiration. This enzyme has two hemes and two coppers in its active center.[12] Nitrogenase is a nonporphyrinic enzyme responsible for N_2-fixation processes. It catalyzes the 6e reduction of N_2 to NH_3. This enzyme has a iron-molybdenum cluster at the active site.[13,14]

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(15) "Mixed-metal" face-to-face porphyrins are abbreviated as MM'(FTF4) throughout this paper. M is always named first, and it refers to the metal center in the porphyrin ring on the carbonyl side of the dimer. M' is the corresponding metal on the amino side. FTF4 refers to the binary porphyrin ligand (**1**) as depicted in Figure 1.

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(20) Chang, C. K. *Adv. Chem. Ser.* **1979**, *No. 173*, 162.

(21) Ward, B.; Wang, C.; Chang, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 5236.

(22) Chang's cofacial porphyrin dimers differ from ours. The binary ligand reported in ref 20 has two *N*-*n*-butyl tertiary amide groups as bridging chains located at transverse 3,13 pyrrolic carbons. The other β substituents are 2,7,12,17-tetramethyl and 8,18-dihexyl groups in each porphyrin ring. The dimer in ref 21 is as in ref 20, but with secondary amide chains instead.

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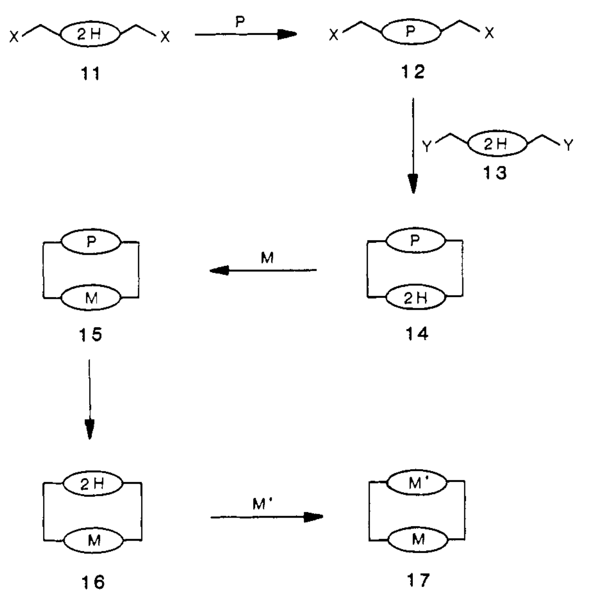

Figure 3. General method for the synthesis of MM'(FTF4).

Collman and Denisevich[5] in the synthesis of PdCo(FTF4) and NiCo(FTF4). This method was also used by Chang[20,21] to prepare his FeCu(FTF4).[22]

When both metals in the mixed-metal dimer prefer a hexacoordinate geometry and bind pyridine (which is the solvent of choice for the face-to-face coupling reaction), the above method does not work. Polymeric material is the only product we have obtained from such reactions. Even conducting the coupling between the metalated monomer and the corresponding free-base monomer in a noncoordinating solvent such as 2,6-lutidine does not improve the synthesis. This is probably because the amino groups of the C1 diamine monomer precursor bind to the metalloporphyrin in an axial position, thus interfering with the face-to-face coupling.

In these cases, an indirect route must be taken (Figure 3), in which one of the monomeric porphyrin precursors, **11**, is metalated with a tetracoordinate metal (P) that serves as a "protecting group". The coupling reaction of the monomers **12** and **13** is then carried out, and one of the metals (M) (the more kinetically robust) of the target heterobimetallic FTF4 is inserted. The protecting metal (P) is removed from the porphyrin dimer **15**, and the second metal is then inserted, thus affording the desired heterobimetallic fact-to-face complex, **17**.

The protecting metal must be tetracoordinate and easily introduced into the porphyrin ring. It should be sufficiently stable to withstand the coupling reaction conditions and the subsequent insertion of the second metal. At the same time, this masking metal must be labile enough to be removed under conditions that will not affect the other metal which has already been inserted into the porphyrin dimer.

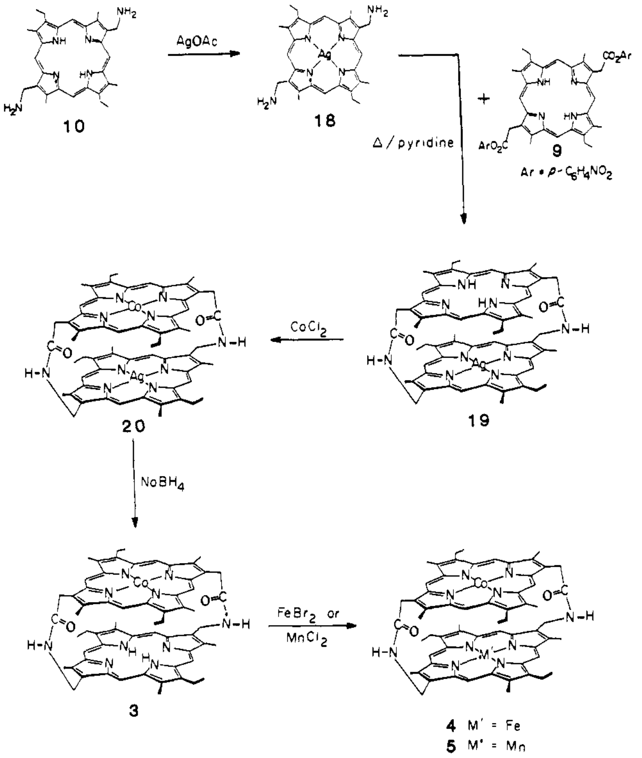

Figure 4. Schematic synthesis of Co–Mn and Co–Fe derivatives of FTF4.

From reports in the literature,[24] it appeared that silver(II) porphyrins might fulfill the above requirements; they were therefore investigated, and silver became the protecting metal of choice. The general strategy that was utilized in the present synthetic work is depicted in Figure 4. Silver is inserted into the C1 diaminoporphyrin **10** with silver acetate in glacial acetic acid.[25] As the silver complex of the diamino-substituted porphyrin monomer was found to be somewhat unstable, the best yields (up to 60%) for the H_2Ag(FTF4) (**19**) synthesis were obtained when freshly prepared silver diamine **18** was used.[26] Coupling with the free-base *p*-nitrophenyl ester porphyrin **9** yielded the monosilver face-to-face dimer **19**. This was then treated with anhydrous $CoCl_2$ in THF–toluene to give CoAg(FTF4) (**20**).

Gross et al.[24] found that silver derivatives of tetraphenyl and octaethylporphyrins demetalate when electrochemically reduced from Ag(II) to Ag(I). We therefore searched for chemical reducing agents capable of carrying out the silver demetalation step.

Silver demetalation was accomplished by treating the Co–Ag dimer **20** with $NaBH_4$ in THF–H_2O under an inert atmosphere. Silver(I), formed by borohydride reduction of silver(II), has a larger ionic radius and pops out from the porphyrin core. It is thus easily displaced from the ligand by an acid as weak as water.[27] Removal of excess $NaBH_4$ was accomplished with acetic acid. Upon addition of the acid, metallic silver precipitated from the solution and was removed by filtration through Celite.

The resulting monocobalt dimer **3** can then be metalated with the second metal of choice. CoFe(FTF4) (**4**) was obtained by treatment of the monocobalt dimer with $FeBr_2$ in THF–toluene.[28] CoMn(FTF4) (**5**) was generated from the reaction of CoH_2(FTF4) with anhydrous $MnCl_2$ in DMF.[29]

The above method for the synthesis of mixed-metal face-to-face porphyrins appears to be of general application. The relative stabilities of the metalloporphyrins, however, must be taken into account in order to avoid transmetalation.

Mass Spectra. For the CoFe(FTF4) (**4**) dimer, the spectrum obtained was the sum of 30 scans of the sample, with the emitter heating current at 24–27 mA (ca. 225 °C). The run covered the range 1000–1225 *m/e*. The parent peak ion was observed at *m/e* 1093.5 (the most abundant peak calculated for the molecular ion is *m/e* 1093.37). No other ions were observed. The peak distribution pattern fits that of the theoretical isotope distribution calculated for CoFe(FTF4).

The CoAg(FTF4) (**20**) spectrum was the result of 15 scans with the emitter heating current at 18–22 mA (175 °C) and 10 scans at 26–28 mA (ca. 225 °C). The peak parent ion was found at *m/e* 1144 (calcd 1144.34). Two other peaks were observed, one at *m/e* 1096 and the other at *m/e* 1040, which can be assigned

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Table I. Selected UV-Vis Spectral Data for "Face-to-Face" Porphyrin Dimers in Methylene Chloride[a] [λ_{max} nm (log ϵ)]

compound	Soret	IV	III, β	II, α	I[b,c]
H_4(FTF4) (1)	376 (12.26)	502 (8.98)	544 (8.99)	572 (8.73)	626 (7.80)
CoH_2(FTF4) (**3**)	380 (11.45)	505 (8.52)	538 (8.81)	569 (8.65)	622, 640 (7.40, 7.12)
Co_2(FTF4) (**2**)	382 (12.14)		524 sh	554 (9.68)	
H_2Ag(FTF4) (19)	386 (12.40)	510 (11.25)	548 (11.50)	572 (11.45)	640 (9.12)
Ag_2(FTF4) (7)	392 (12.49)		526 (9.13)	566 (9.63)	
CoAg(FTF4) (**20**)	384 (10.43)		520 (7.19)	558 (7.77)	
CoFe(FTF4) (4)	380		524 sh	552	
CoMn(FTF4) (5)	352 sh, 382	473	534	560	
Mn_2(FTF4) (8)	352 br	422 sh, 468	556	595 sh	

[a] Except for Co_2(FTF4), which was measured in benzonitrile. [b] Typical UV–vis spectra of porphyrins consist of an intense absorption band ca. 400 nm, known as the Soret band, and of four satellite bands (labeled as I, II, III, and IV) located in the region between 500 and 700 nm, approximately. The relative position and intensities of these bands depends upon the nature of the side chain in the porphyrin. [c] On metalation, the four bands in the spectrum of the free ligand in the visible region change to two bands (labeled as α and β). The Soret band is retained.[3c]

to the dicobalt **2** and monocobalt **3** face-to-face porphyrins, respectively. In each case, the isotopic distribution of the three signals matches that calculated.

The CoMn(FTF4) (**5**) spectrum was the result of summing 30 scans at 20–30 mA (ca. 225 °C). For this sample, peaks were observed at *m/e* 1092 (parent ion), 1096, 1088, 1037, and 1040 (in decreasing order of intensity), which would correspond to the Co–Mn (calcd parent ion, *m/e* 1092.37), dicobalt, dimanganese, monomanganese, and monocobalt derivatives of FTF4, respectively.

In order to try to establish the purity of this compound and to determine whether some demetalation and re/transmetalation had occurred in the probe of the mass spectrometer, we analyzed an equimolar mixture of pure Co_2(FTF4) (**2**) and pure Mn_2(FTF4) (**8**). If transmetalation were occurring in the probe of the mass spectrometer, a peak corresponding to CoMn(FTF4) might have been observed, but this was not the case. Only two peaks, attributable to dicobalt and dimanganese dimers, were observed. It is worth noting that even when an equimolar sample of these compounds was introduced into the spectrometer, the relative intensity of the peaks of Co_2(FTF4) and Mn_2(FTF4) was 3:1. This could be the result of Mn_2(FTF4) being either less soluble or less volatile. In any event, this result suggests that the relative intensities of the signals in the mass spectrogram do not reflect the relative concentration of the compounds in a mixture.

In the chemical-ionization mass spectrum of the monocobalt derivative, the parent ion was observed at *m/e* 1040 (100%). Two other peaks at *m/e* 983 (7%) and 1097 (29.1%), corresponding to the free-base and Co_2(FTF4), were also observed.

For the monosilver cofacial dimer, the mass spectrum showed two peaks, one at *m/e* 1090 ($M^+ + 1$, 100%) and the other at 985 ($M^+ + 2$, 60%), which correspond to the monosilver and the free-base FTF4, respectively.

Electrocatalysis of O_2 Reduction. Of the mixed-metal face-to-face porphyrin dimers reported in this paper, only CoAg(FTF4) exhibited unusual catalytic activity toward the four-electron reduction of O_2 to H_2O. It may be significant that CoAg(FTF4) was also the only heterobimetallic derivative in which the two metal centers are reduced at about the same potential in the porphyrin dimer.[8] The presence of a peak attributable to Co_2(FTF4) in the mass spectrum of CoAg(FTF4) made it conceivable that the electrocatalytic activity of CoAg(FTF4) might have arisen from a small amount of Co_2(FTF4). However, CoMn(FTF4), which is also derived from CoAg(FTF4) (Figure 4) and shows a peak corresponding to Co_2(FTF4) in its mass spectrum, exhibits no catalytic activity toward O_2 reduction in the potential range where Co_2(FTF4) is very active. Even slight contamination (~1%e by Co_2(FTF4) is readily detectable because this potent catalyst shifts the potential where O_2 is reduced by hundreds of millivolts.[5] Since the CoMn(FTF4) derivative produces no such shift, it could not be contaminated with Co_2(FTF4), and we infer the same to be true of CoAg(FTF4).

Electronic Spectra. UV-visible spectra of the free-base, monometallic and bimetallic FTF porphyrins are very characteristic. This can be seen in Figure 5, where a comparison of the electronic spectra of H_4(FTF4) (**1**), CoH_2(FTF4) (**3**), and Co_2(FTF4) (**2**) is presented. Electronic spectroscopy is a useful and practical method of monitoring the course of the mixed-metal FTF4 synthesis. This is accomplished by following the changes in the bands within the visible region, between 450 and 700 nm. Table I presents the λ_{max} for the Soret and visible absorption bands for the mixed-metal, monometallic, and some bimetallic FTF4 porphyrins. All these values were recorded in dry CH_2Cl_2 solutions.

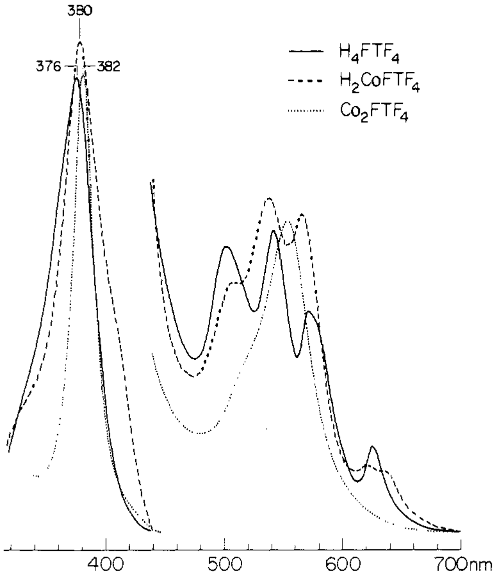

Figure 5. Comparison of UV–vis spectra of FTF4 (**1**), CoH_2(FTF4) (**3**), and Co_2(FTF4) (**2**).

ESR Spectroscopy. Electron spin resonance spectroscopy was utilized in the qualitative characterization of the mixed-metal and monometallic FTF4 porphyrins. Each of these systems exhibits a distinctive spectrum, the description and discussion of which constitute the subject of a forthcoming publication. This technique further demonstrates the purity of each heterometallic porphyrin.

Experimental Section

Reagents and Solvents. All reagents and solvents were of reagent-grade quality, purchased commercially, and used without further purification except where noted below. Dry solvents were refluxed (more than 6 h) with and distilled from CaH_2 (hexanes, methylene chloride, THF), magnesium methoxide (methanol), and P_2O_5 (toluene) under N_2. 2,6-Lutidine (Aldrich) was dried over molecular sieves and distilled under N_2 before use. Pyridine was dried over molecular sieves. *p*-Nitrophenyl trifluoroacetate (Aldrich) was dried under vacuum and stored in a drybox. Molecular sieves (Linde, $^1/_{16}$ in pellets, size 4 Å) were activated by heating (ca. 155 °C) under vacuum overnight.

Chromatography. Silica gel for column chromatography was obtained from Davidson Chemical, grade 62, 60–200 mesh. For TLC, commercially precoated silica and alumina plates from Analtech, Inc., were used. Alumina (Woelm, neutral) was activated by heating at 125 °C overnight under vacuum and then treating with water (6% by weight) to generate activity III material.

Physical and Spectroscopic Methods. Electronic spectra were obtained on a Cary 219 spectrometer in CH_2Cl_2 solutions. Pulsed Fourier transform ^1H NMR spectra of the free-base ligands were obtained on a Varian XL-100 by using a Nicolet Technological Corp. Model 1180 FT disk data system. Low-resolution field-desorption mass spectra determination of the heterobimetallic face-to-face porphyrins was carried at the Middle Atlantic Mas Spectrometry Laboratory, a National Science Foundation Shared Instrumentation Facility. The MS-50 from AEI/Kratos was calibrated with 1185 triazine, the base peak of which is at *m/e* 1066 and the last recorded peak is at *m/e* 1128. Chemical-ionization mass spectra of monosilver and monocobalt derivatives of FTF4 were recorded on a Ribermag R10-10B mass spectrometer with extended mass range to 1500 amu. The instrument was calibrated with tris(perfluorononyl)-*s*-triazine (M_r = 1485), with a base peak at *m/e* 1066 and the last observed at *m/e* 1466 (31%). The mass range recorded was 900–1400 amu. Samples were introduced with standard tungsten coil, with CH_4 as chemical reagent. The temperature of the source was 250 °C (coil at 0.25 mA). X-band ESR spectra were obtained on a Varian E-12 spectrometer.

Ag C1 Diamine 18. The reaction was carried out under dimmed light and argon atmosphere in a 50 mL, three-necked, round-bottom flask equipped with thermometer, argon inlet, and reflux condenser. The free-base C1 diamine (20 mg) (obtained as described in ref 31) was dissolved in glacial acetic acid (20 mL) and heated to 75 °C (higher temperatures decompose the metalated product). The silver insertion was monitored by electronic spectroscopy: the four bands of the free-base in the visible region (496, 532, 565, 620 nm) are replaced by the typical α,β bands of the silver porphyrin (524, 562 nm). After metalation had been completed (ca. 45 min), the reaction mixture was cooled down to room temperature and the solvent removed under reduced pressure. The solid was redissolved in CH_2Cl_2 and filtered through Celite. The solution was washed in a separatory funnel with 2 N aqueous NH_4OH, followed by H_2O until neutral. The organic layer was removed and dried over K_2CO_3, and the product was crystallized from CH_2Cl_2–CH_3OH: yield 85%; visible spectrum λ_{max} 409, 524, 562 nm.

H_2Ag(FTF4) (19). Silver C1 diamine (20 mg, 3.4×10^{-5} mol) and free-base *p*-nitrophenyl ester (26.6 mg, 3.4×10^{-5} mol) were added under an argon atmosphere to dry and degassed pyridine (400 mL), maintained at 65 °C. The reaction mixture was stirred for 2 h at this temperature. The reaction was monitored by TLC (silica) using 4% CH_3OH in CH_2Cl_2 as eluent: R_f silver C1 diamine, 0.1; H_2Ag(FTF4), 0.4; di-*p*-nitrophenyl ester, 0.9. After ca. 2 h, the reaction was complete. Isolation of the product was carried out by chromatography on a 5 × 1 in. silica column, eluted first with CH_2Cl_2 to remove unreacted *p*-nitrophenyl ester porphyrin (pink band) and *p*-nitrophenol (yellow) and then with 10:90 CH_3CN–CH_2Cl_2 to remove the monosilver face-to-face dimer. Any unreacted silver C1 diamine remains at the origin. The product was recrystallized from CH_2Cl_2–CH_3OH; yield 60% (23.50 mg). All manipulations were carried out under dimmed light: visible spectrum λ_{max} 416, 508, 542, 572 nm; MS, *m/e* 1090 (calcd 1089).

Cobalt Complexes. The insertion of cobalt into the porphyrin ring was carried out in the inert atmosphere box. A 10-fold excess of anhydrous $CoCl_2$ plus 2,6-lutidine (0.5 mL) was added to a THF–toluene (enough to dissolve the porphyrin) (1:3) solution of the free-base porphyrin. The reaction mixture was heated at reflux until metalation was complete (ca. 1 h). The visible spectrum shows no free-base bands at ca. 505 and 626 nm.

CoAg(FTF4) (20). This compound was obtained from Co insertion into H_2Ag(FTF4). The crude reaction mixture was chromatographed on neutral alumina (activity III), and the product was eluted with THF. $CoCl_2$ remains at the origin. The eluate was evaporated in vacuo to give nearly quantitative amounts of the cobalt silver porphyrin dimer: visible spectrum, λ_{max} 385, 516 (sh), 55 nm; MS *m/e* 1144 (calcd 1144.34).

CoH_2(FTF4) (3). This compound was obtained by removing the silver from CoAg(FTF4). A 50-fold excess of $NaBH_4$ was added to the CoAg(FTF4) (15 mg) in THF (25 mL) in an inert atmosphere box. After the solution was stirred at room temperature for 10 min, water (0.5 mL) was added and stirring was continued for 10 min. The color of the reaction mixture changes from red to brownish-orange. Sufficient acetic acid was added dropwise to hydrolyze the remaining $NaBH_4$ and to neutralize the reaction mixture. (Metallic silver precipitated out from the solution at this point.) The flask was then removed from the drybox, and the reaction product isolated under dimmed light. The reaction mixture was filtered through Celite and the solvent removed by rotary evaporation. The solid was redissolved in CH_2Cl_2 and washed with water several times until neutral. The organic layer was extracted, dried over K_2CO_3, and filtered, and the solvent was removed by rotary evaporation. The product was recrystallized from 90:10 CH_2Cl_2–CH_3OH: visible spectrum λ_{max} 378, 508 (sh), 538, 566, 620, 638 nm; MS, *m/e* 1040 (calcd 1040).

CoFe(FTF4) (4). In the inert atmosphere box, CoH_2(FTF4) was dissolved in 1:3 THF–toluene and heated to reflux. When the solution reached this temperature, an excess of $FeBr_2$ was added, and the solution stirred while heating under reflux for ca. 45 min. The metal insertion was monitored by observing the disappearance of the 620- and 638-nm bands and the shoulder at 508 nm. Upon metalation, the solvent was partially removed under reduced pressure and the solution loaded onto a neutral alumina column (activity III). The product was eluted with 1:5:0.1 THF–toluene–MeOH, leaving the $FeBr_2$ at the origin. The eluate was evaporated under reduced pressure, leaving the CoFe(FTF4) in ~90%: visible spectrum λ_{max} 380, 524 (sh), 552 nm, MS, *m/e* 1093 (calcd 1094).

CoMn(FTF4) (5). CoH_2(FTF4) was dissolved in DMF under an argon atmosphere. A 10-fold excess of anhydrous $MnCl_2$ was added and the reaction mixture heated to 125 °C. Progress of the metalation reaction was monitored by UV–vis spectroscopy. When the reaction was complete, the DMF was removed on a rotary evaporator. The solid was redissolved in a minimum amount of CH_2Cl_2, chromatographed through a neutral alumina (activity III) column, and eluted with 10:1 CH_2Cl_2–CH_3OH. The solvent was removed and the compound crystallized from THF–hexane; visible spectrum λ_{max} 352, 382, 473, 534, 560 nm; MS, *m/e* 1092 (calcd 1092).

Acknowledgment. This work derives from a collaborative effort that also includes the groups of Professors M. Boudart and H. Taube (Standord University) and Dr. H. Tennent, formerly of Hercules Inc. Research Center. Mass spectral analyses were carried out at the Middle Atlantic Mass Spectrometry Laboratory, a National Science Foundation Shared Instrumentation Facility. We thank Dr. E. R. Evitt for helpful discussions. This work was supported by National Science Foundation Grants CHE77-22722 and CHE81-10545. Use of the Stanford Magnetic Resonance Laboratory (NSF Grant GP23633 and NIH Grant RR00711) is also acknowledged. C.S.B. thanks the Venezuelan Council for Scientific and Technological Research (CONICIT) for her doctoral scholarship.

Registry No. 1, 74427-75-1; **2**, 71253-24-2; **3**, 84928-51-8; **4**, 84928-55-2; **5**, 84928-50-7; **7**, 84928-52-9; **8**, 84929-17-9; **9**, 74427-71-7; **10**, 74427-69-3; **18**, 84929-18-0; **19**, 84929-15-7; **20**, 84929-16-8.

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