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85081-42-1; 4, 85028-57-5; 5, 85048-11-9; 6, 85028-58-6; 8, 85048-12-0; I2, 7553-56-2; Cl2, 7782-50-5; PhICl2, 932-72-9; HI, 10034-85-2; HCl, 7647-01-0; Mo, 7439-98-7; ethylene, 74-85-1.

Supplementary Material Available: Tables of observed and calculated structure factors for compounds 2 and 8 (18 pages). Ordering information is given on any current masthead page.

Further Studies of the Dimeric β -Linked "Face-to-Face Four" Porphyrin: FTF4

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Abstract: High-pressure liquid chromatographic analysis of the previously reported cofacial porphyrin dimer (FTF4), which is linked by two four-atom amide bridges in transverse β -pyrrolic positions, revealed that it contained two minor impurities. ¹H NMR, UV-visible, and mass spectroscopic analyses showed these to be two related meso monochlorinated face-to-face porphyrin dimers. Rotating ring-disk voltammetric measurements of the dicobalt derivatives revealed that the chlorinated dimers were better catalysts for the four-electron reduction of O2 to H2O than the corresponding nonfunctionalized parent molecule. Reinvestigation of the origin of the contaminants led to a new synthetic route to pure FTF4.

When adsorbed on edge-plane pyrolytic graphite, the dicobalt derivative of the β -linked porphyrin dimer with two four-atom amide bridges $(Co_2(FTF4))^{2,3}$ (Figure 1) catalyzes the fourelectron reduction of oxygen to water at ca. 0.68 V vs. NHE at pH less than 3.5,5 with a turnover rate of ca. 400 dioxygen molecules per second per catalyst site.⁶ At present, Co₂(FTF4) is the only synthetic compound that displays such remarkable activity. Platinum, the most effective metal catalyst, operates at 0.63 V vs. NHE in acid, with a turnover rate of 0.3-5 dioxygen molecules per second per platinum site.7

As shown in Figure 1, the β -linked dimer can exist in two possible isomeric forms, syn and anti, depending on the relative orientation of the two rings. In turn, each of these two diastereomers can exist as an enantiomorphic pair. Attempts to resolve these two possible diastereomers using high-pressure liquid chromatography (HPLC) led to the surprising result that the

(3) A series of face-to-face porphyrins has been synthesized by Collman and co-workers as an approach to the design of catalysts for the rapid fourelectron reduction of O_2 to H_2O . For an account, see ref 4, 5, and 6, and references cited therein

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original FTF4 dimer⁶ (prepared as shown in Figure 2) was actually contaminated with two minor impurities. These experiments (vide infra) showed that only one of the two possible diastereomers was present. Apparently, the kinetically controlled binary cyclophane formation affords only the less hindered anti isomer. In dealing with a multicomponent mixture, it is always possible that the observed catalysis is derived from the activity of a minor component while the major component—the assumed catalyst— is inactive. It was, therefore, essential for each of the components of the mixture to be isolated, characterized, and studied for catalytic activity in the reduction of O_2 . This work presents the results of such a study and also describes two independent synthetic pathways to pure FTF4.

Results and Discussion

High-Pressure Liquid Chromatography. The HPLC analysis of the original FTF4,⁴ prepared as shown in Figure 2, revealed that it had two minor impurities (ca. 8%) which exhibited optical spectra characteristic of these cofacial porphyrin dimers. The pure FTF4 and the two minor contaminants were separated on an analytical Whatman partisil 10 column with 85:10:5 CH₂Cl₂-C- H_3CN-CH_3OH as eluent. The resulting chromatogram is shown in Figure 3. Through repeated injections, a few hundred micrograms of fractions a, b, and c were isolated and characterized by mass spectrometry and ¹H NMR and UV-visible spectroscopy.

In order to determine the source of these impurities, we analyzed the two starting reagents for the FTF4 coupling (Figure 2), the C2 di-p-nitrophenyl ester 3 and the C1 diamine 5 by using HPLC. The chromatogram of compound 3 showed a single component. Analysis of the C1 diamine 5 as its ditrityl derivative, however, revealed the presence of two impurities (Figure 4). It therefore seemed likely that these were the origin of the FTF4 impurities.

Mass Spectra. Both field-desorption (FD) and electron-impact (EI) mass spectra of the HPLC fractions a, b, and c were obtained. Perfluorokerosene was used as a mass marker, with an upper limit at m/e 1023. Each fraction was checked from m/e 400 to well beyond m/e 1023.

Fraction c gave a very strong molecular ion at m/e 982, which is consistent with the molecular weight calculated for FTF4 $(C_{62}H_{66}N_{10}O_2)$. Both the FD and EI spectra of fraction c fit the

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⁽²⁾ Abbreviations used in this paper: FTF4, free-base face-to-face por-phyrin depicted in Figure 1; NHE, normal hydrogen electrode; SCE, standard calomel electrode; HPLC, high-pressure liquid chromatography; C2 diethyl ester, C1 diamine, and C2 di-p-nitrophenyl ester are the porphyrin monomers i, 5, and 3 in Figure 2; C2 hydrazide is the porphyrin monomer 4 depicted in Figure 9; FD, field-desorption mass spectrometry; EI, electron-impact mass spectrometry; OEP, octaethylporphyrin; THF, tetrahydrofuran; TLC, thinlayer chromatography.



Figure 1. Syn and anti diastereoisomers of the β -linked porphyrin dimer FTF4 containing four-atom bridges.



Figure 2. Original synthesis of β -linked face-to-face porphyrin dimers.

computer-generated isotope pattern for FTF4. The major peak observed for both of the fractions a and b appeared at m/e 1016, which corresponds to FTF4 with a chlorine replacing a hydrogen atom.

Fractions a and b also had a significant peak at m/e 982. At the high emitter temperature used, it is possible that this peak was a thermal degradation product of the compound with m/e1016. The isotope pattern from the EI spectrum of fraction a closely matched that expected for C₆₂H₆₅ClN₁₀O₂, but the pattern from fraction b did not.

The above results strongly suggested that fraction c, the major component, was pure FTF4, whereas the smaller fractions, a and b, were two monochloro-substituted FTF4 isomers. The HPLC results suggested that the chlorine atoms were located in the amine side of the cofacial porphyrin dimer.

Electronic Spectra. Fractions a, b, and c all exhibited electronic spectra characteristic of metal-free cofacial porphyrins, i.e., the Soret bands ($\lambda = 376$ nm) were blue-shifted compared with the monomeric porphyrins (Soret: λ ca. 400 nm) and the bands in the visible region were red-shifted. All these bands were broader

HPLC PURIFICATION OF FTF 4 DIMERS











Figure 5. Comparison of UV-vis spectra of FTF4 dimer and C2 diethyl ester monomer.

than those observed for monomeric porphyrins. These differences can be seen in Figure 5, which presents a comparison of the electronic spectra of the C2 ethyl ester monomer and FTF4.

NMR Spectroscopy. As described above, FTF4 can exist in two diastereomeric forms, each as a racemic mixture. From the structures depicted in Figure 1, it can be seen that for each diastereomer both of the porphyrin rings have two pairs of equivalent meso protons. Each diastereoisomer, thus, should have four chemically different pairs of protons in the meso region. Therefore, in the ¹H NMR no more than four signals in the meso region would be expected for each cofacial diastereoisomer, or eight for an isomeric mixture. This analysis also applies to the protons of the β -methyl groups.

The ¹H NMR spectrum of fraction c is presented in Figure 6. This spectrum exhibits four peaks in the meso region (δ 8.70, 8.75, 8.77, 8.91). The ring methyl protons also appear as four signals



Figure 6. 360-MHz ¹H NMR spectrum of fraction C (X = Y = H).

(δ 3.55, 3.74, 3.60, 3.10), which suggests that only one of the enantiomorphic pairs is present, either the *d*,*l*-syn or the *d*,*l*-anti. If this is the case, we expect it is the anti diastereomer that is formed because kinetic control during the slow cofacial coupling should lead to the less sterically hindered isomer. This is still subject to confirmation by X-ray crystallographic studies.

It can also be seen in Figure 1 that there are four methylene groups in the two amide bridges of each isomer. Two of them are adjacent to the carbonyl groups and are chemcially equivalent. However, the two protons of each of these methylene groups are diastereotopic and should, therefore, give rise to two ¹H NMR signals. The other two equivalent methylene groups are next to the NH amide groups and are also magnetically nonequivalent. Each of these two diastereotopic protons should be coupled to the amide proton, giving a doublet of doublets. The syn isomer should display a basically similar pattern, but the chemical shifts and coupling constants should be different.

Only peaks attributable to one diastereomer were observed in Figure 6. Decoupling experiments on the resonances associated with the bridge protons identified the signals at δ 5.39 and 5.91 as arising from protons adjacent to the amide nitrogens. The diastereotopic methylene protons adjacent to the carbonyl groups are found as a doublet centered at δ 4.67. In both cases, a ~15-Hz splitting is observed, which is typical for geminal coupling between protons.

The chemical shift of the internal pyrrolic NH protons is found at higher fields (δ -8.1) than that for the corresponding porphyrin monomer (δ ca. -3.8). This is a result of the large anisotropic shielding effects that the two porphyrin rings exert on each other when they are held in a close, mutually coplanar arrangement. Such an enhanced chemical shift of the internal pyrrolic NH protons is also observed in the ¹H NMR spectra of fractions a and b, further supporting their cofacial nature.

The introduction of a chlorine atom into the FTF4 reduces the symmetry of the molecule. This should be reflected in the ¹H NMR spectra of the two contaminants. Assuming meso chlorination, as many as seven distinct singlets are expected in the meso region of each chlorinated cofacial porphyrin.

Figure 7 shows the meso region of fraction a as having five peaks, with one three times more intense than the others. In fraction b, seven meso signals are observed. This implies that substitution has occurred at the meso position, which is not surprising, given that these are the most reactive sites in the porphyrin ring.^{8,9}

Such a disruption of the symmetry in the two contaminants is also manifested in the protons of the β -methyl groups. The ring methyl protons of fraction a appear as seven signals, with one





Figure 7. Resonances of the meso and β -pyrrolic methyl protons of fractions a, b, and c.





Figure 8. Chemical shifts (360-MHz NMR) associated with the amide bridge protons of fractions a, b, and c.

signal having double the intensity of the others. In Figure 7, the eight methyl groups in fraction b are clearly shown as singlets.

Figure 8 represents the chemical shifts associated with the bridge protons of the three fractions. The diastereotopic me-

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Figure 9. Curtius rearrangement of C2 diethyl ester porphyrin.

thylenes adjacent to the amide nitrogen in fraction a are clearly split into four resonances, showing that the two bridges of the dimer are now located in very different environments. By comparison, the ¹H NMR spectrum of fraction b shows only a small difference in the resonances of the bridge methylene groups. It appears, therefore, that fraction a is the isomer in which the meso-chloro substituent is adjacent to one of the amide bridges, as indicated in Figure 8 for 6a. The chlorine in fraction b, thus, is on the meso carbon between the methyl and ethyl β -pyrrolic substituents.

Synthesis. Since both the C2 di-p-nitrophenyl ester 3 and the C1 diamine 5 were derived from the C2 diethyl ester 1 (Figure 2), it seems likely that the chlorine impurities in the diamine arose during the Curtius rearrangement and hydrolysis sequence. A reexamination of the conditions used in the Curtius rearrangement of the C2 diethyl ester 1 to the C1 diamine 5 (Figure 9) suggested that replacement of hydrochloric acid with another acid would produce the desired pure C1 diamine.

Hence, the C2 dihydrazide 4 was converted into the azide 7, by using sodium nitrite and phosphoric acid in acetic acid. The azide was then converted to the isocyanate 8 by heating at reflux in toluene and further hydrolyzed to the diamine with phosphoric acid. Protection of the diamine, using trityl bromide and triethylamine in dry methylene chloride, afforded the ditrityl derivative. Analytical HPLC showed the protected diamine to possess two small impurities (ca. 8%). Coinjection, however, with a ditrityl diamine derived from use of hydrochloric acid in the above protocol, showed that these impurities possess different R_f values.

Similar Curtius degradation experiments utilizing sulfuric and trifluoroacetic acids gave more complicated product mixtures. Thus no modification of the Curtius rearrangement conditions could be found that produced the diamine free of impurities.

Our observations that treatment of meso-chlorinated diethyl ester porphyrins with hydrazine removed the meso-chloro substituents suggested a means by which samples of crude FTF4 could be purified. It was found, however, that synthesis of FTF4 using diamine porphyrin samples that had been purified by treatment with NH2NH2 always led to lower yields and contamination of the porphyrin dimer with a monomeric porphyrin. It seems that NH_2NH_2 reacted with the diamine, giving an undesired byproduct. This contaminant was not detected by the HPLC analysis, perhaps because the diamine was studied as its ditrityl derivative. Reaction of the diamine with trityl bromide may have resulted in the separation of contaminants from the diamine.



Figure 10. New synthetic route to pure C1 diamine porphyrin.

Successful preparation of pure FTF4 was accomplished by removal of the meso-chlorine atoms from chloro-contaminated FTF4 by treatment with hydrazine in pyridine.

Synthesis of "mixed-metal" face-to-face porphyrin dimers¹⁰ required clean samples of the diamine monomeric precursors. Therefore, we had to devise a new synthetic approach to pure diamine. The fact that changing the nature of the hydrolyzing acids in the Curtius rearrangement resulted in different mesosubstituted porphyrins led us to suspect that it was the oxidizing nature of HNO₂, and not the acids themselves, that was responsible for the meso contamination in the diaminoporphyrin.

Generation of a π cation radical by HNO₂, followed by the nucleophilic attack of a Cl⁻ anion could have generated the meso-chlorinated porphyrin contaminants. A similar reaction has been reported11 in which octaethylporphyrin (OEP) reacts with $NaNO_2$ in $HOAc/H_2SO_4/H_2O$ to yield meso-mononitrated OEP.

An alternative route was found to involve the synthesis of pure diamine 5 by treatment of diacid 2 with NaN_3 in H_2SO_4 (Figure 10). This synthetic pathway avoids the oxidative conditions and is a more direct route than the Curtius degradation. Cobalt derivatives of the dimeric face-to-face porphyrins obtained from the above alternative procedures behaved identically as catalysts for oxygen reduction when analyzed by rotating-disk voltammetry.

Electrochemistry. It had been anticipated that electronegative substituents in $Co_2(FTF4)$ would shift the reduction potential of the cobalt(III) centers toward more positive values, thus enhancing the efficiencies of these electrocatalysts.⁶ With these fortuitous meso-chlorinated porphyrin dimers in hand, it was decided to test this idea. Cobalt was introduced into fractions a, b, and c, and their behavior as electrocatalysts was examined. Unfortunately, it was not possible to obtain voltammetric responses from the adsorbed chlorine-containing catalysts in the absence of dioxygen that were well-defined enough to permit their formal potentials to be estimated. Our examination of the catalysts was therefore restricted to the current-potential responses they produced for the reduction of dioxygen.

As previously reported,⁴⁻⁶ we employed a rotating ring-disk electrode (RRDE)^{12,13} to examine the effect of our dimeric face-to-face porphyrins on the reduction of dioxygen. This electrode consists of a pyrolytic graphite disk embedded in Teflon and a concentric platinum ring that is separated from the disk by an insulating Teflon gap. The porphyrin to be studied was carefully applied to the disk from a CH₂Cl₂ solution. After the solvent had evaporated, the electrode was introduced into dioxygen-saturated aqueous acid electrolyte ($0.5 \text{ M CF}_3\text{COOH}$).

The disk current-potential curve was recorded to determine the potential where the dioxygen was reduced at the catalyst-coated electrode. The potential of the ring electrode was held at +1.4V vs. NHE so that any H₂O₂ formed at the disk could be detected by means of anodic ring current resulting from the oxidation of H_2O_2 to O_2 .

A comparison of the disk and ring currents as a function of disk potential for the cobalt derivatives of fractions b and c is presented in Figure 11. There are two important differences to be noted

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Figure 11. Disk and ring currents vs. potential of fractions b and c.

in the behavior of the two compounds. First, the half-wave potential for the reduction of dioxygen catalyzed by the cobalt meso-chlorinated fraction, b, is more positive than that for the pure face-to-face dimer, c. No H_2O_2 was detected at the ring electrode with either catalyst in the vicinity of $E_{1/2}$, but some H_2O_2 does appear at potentials on the limiting-current plateaus. The plateau current obtained with the cobalt derivative of fraction b is higher than that for pure $Co_2(FTF4)$, and there is a correspondingly smaller ring current. Similar enhancement of the catalytic activity of $Co_2(FTF4)$ by the presence of an electronegative meso chlorine atom was also found for the cobalt derivative of fraction a.

The more positive potentials at which the chloro-substituted cobalt porphyrins catalyze the reduction of dioxygen could result either from more positive formal potentials of the catalysts or from a higher rate of their reaction with dioxygen or both. The data we were able to obtain do not allow these two possibilities to be distinguished. However, a shift in the formal potential of the catalyst seems the more likely possibility because it would be surprising if the rate of reaction between a Co(II) porphyrin and dioxygen increased as the cobalt(II) center was rendered less potent as a reductant.

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 heated at reflux for over 6 h with, and then distilled from, CaH₂ (hexanes, methylene chloride, THF), magnesium methoxide (methanol), and P₂O₅ (toluene) under N₂. 2,6-Lutidine (Aldrich) 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.

HPLC analysis was conducted on a Du Pont Model 830 liquid chromatograph, using an analytical Whatman partisil 10 column. Column elution was monitorted with a variable-wavelength UV-vis detector (Schoeffel Instruments Model SF770 Spectraflow Monitor) connected to a strip chart recorder (Houston Instruments, Omni Scribe Model A5211-2).

Physical and Spectroscopic Methods. Electronic spectra were recorded on a Cary 219 spectrometer. A 360-MHz NMR instrument (Bruker HXS-360 MHz, Stanford Magnetic Resonance Laboratory) was employed for the characterization of the FTF4 HPLC fractions. Pulsed Fourier transform NMR spectra were obtained on the Varian XL-100, using a Nicolet Technology Corp. Model 1180FT disk data system. Mass spectra of the FTF4 porphyrins were obtained on a Varian MAT 731 (Kodak). The emitter heating current for the FD spectra was 22–23 mA. For the EI studies, the temperature of the probe was 240 °C, with an accelerating potential of 8 kV in both cases. Elemental analyses were performed by the Stanford Microanalytical Laboratory.

The ring-disk electrode, the electrode rotator, and the dual potentiostat were obtained from Pine Instruments Co., Grove City, PA. The calculated collection efficiency of the electrode was 0.18, and the experimental value obtained by reducing ferricyanide at the disk was 0.17. The disk potential was scanned at the rate of 5 mV/s in order to record current-potential curves. All potentials were measured vs. a SCE reference electrode but are reported vs. the NHE.

Techniques for Handling Unstable Compounds. Some of the free-base porphyrins (diamine and face-to-face porphyrins in particular) are highly sensitive to light and/or oxygen. Techniques for their manipulation have been reported elsewhere.⁶

C2 Diacid 2. The C2 diester porphyrin 1 (500 mg) was dissolved in CF₃COOH (30 mL) under N₂, and concentrated HCl (10 mL) was added. The solution was heated at a gentle reflux (ca. 90 °C) for 6.5 h. After being cooled to room temperature, the solvents were removed completely by rotary evaporation. The residue was dissolved in methanol (25 mL) and the solution slowly neutralized with pyridine (wet universal indicator paper turned green). After several hours of cooling at 4 °C, the crystalline product was collected by filtration, washed with CH₃OH, and dried under vacuum; yield 95%. ¹H NMR (pyridine-d₅) revealed the absence of any esters: δ -3.01 (br s, 2 H, internal pyrtole NH), 1.81 (t, J = 7.5 Hz, 6 H, methyl of β -pyrrole ethyl), 3.55 (s, 6 H, β -pyrrole methyl), 3.76 (s, 6 H, β -pyrrole methyl), 4.06 (q, J = 7.3 Hz, 4 H, methylene of β -pyrrole ethyl), 5.44 (s, 4 H, C2 side-chain methylene), 10.39 (s, 2 H, meso H), 10.76 (s, 2 H, meso H).

C2 Di-p-nitrophenyl Ester 3. A solution of diacid 2 (270 mg, 0.5 mmol) in pyridine (135 mL) was prepared in a flame-dried flask under argon at 50 °C for ca. 30 min. p-Nitrophenyl trifluoroacetate (840 mg, 3.57 mmol) was added to the solution against a countercurrent of argon. After heating for 2 h at 50-55 °C, a microcrystalline precipitate was visible. The reaction mixture was heated an additional 15 min and cooled (10 °C) for over 6 h, taking care to seal the flask with Parafilm in order to prevent contamination with water. The resulting product was collected, washed $(1 \times 8 \text{ mL pyridine}, 3 \times 15 \text{ mL hexanes})$, and dried under vacuum to give compound 3 (341 mg, 87.4%): IR ν_{CO} 1760, ν_{NO_2} 1520, 1350 cm⁻¹; ¹H NMR (pyridine- d_5) δ -3.08 (br, s, 2 H, internal pyrrole NH), 1.83 (t, J = 4.5 Hz, 6 H, methyl of β -pyrrole ethyl), 3.60 (s, 6 H, β -pyrrole methyl), 3.77 (s, 6 H, β -pyrrole methyl), 4.13 (q, J = 7.6 Hz, 4 H, methylene of β -pyrrole ethyl), 5.67 (s, 4 H, C2 side-chain methylene), 7.47 and 8.18 (m, 8 H, AA'BB' pattern of p-nitrophenyl substituents), 10.48 (s, 2 H, meso H), 10.69 (s, 2 H, meso H).

C1 Diamine Porphyrin 5c. The C2 diacid porphyrin (2) (800 mg) was dissolved in concentrated H_2SO_4 (150 mL) under N_2 . Sodium azide (8 g) was added in six portions over 30 min. The mixture was then stirred at room temperature for 45 min, followed by heating at 135 °C in an oil bath for 60 min. One neck of the reaction flask was left open during the first 15 min of heating to allow the large amount of gas (HN₃ and N₂, use hood) produced to escape. After cooling the reaction flask to ca. 10 °C in an ice bath, the sulfuric acid solution was poured onto 1 L of packed ice. The solution was stirred and cooled with an ice bath while 27% NH₃(ag) (ca. 300 mL) was added dropwise to make the solution basic. The solid was dissolved in CHCl₃ (400 mL), and the solution was washed with H₂O until neutral. The organic layer was extracted and dried over K_2CO_3 . The C1 diamine was crystallized by adding ethanol and then slowly removing the CHCl₃ by rotary evaporation. The crystalline product was filtered, washed with ethanol, and dried under vacuum for several hours; yield 75-80%. Further purification, when necessary, was accomplished by means of chromatography on a 5×27 cm silica column, eluting with 10:90 CH₃OH-CHCl₃ until the first band began to come off the column. Then the eluent was changed to 30:70 CH₃OH-CHCl₃ to speed up the elution of the diamine: yield 314 mg (60%) chlorine free Cl diamine porphyrin; ¹H NMR (pyridine- d_5) δ -3.03 (br s, 2 H, internal pyrrole NH), 1.84 (t, J = 7.5 Hz, 6 H, methyl of β -pyrrole ethyl), 3.54 (s, 6 H, β -pyrrole methyl), 3.66 (s, 6 H, β -pyrrole methyl), 4.0.9 (q, J = 7.4 Hz, 4 H, methylene of β -pyrrole ethyl), 5.47 (s, 4 H, side-chain methylene), 10.39 (s, 2 H, meso H), 10.69 (s, 2 H, meso H). Anal. Calcd for C₃₀H₃₆N₆: C, 74.8; H, 7.6; N, 17.5. Found: C, 74.24; H, 7.45; N, 17.33.

Face-to-Face Four Dimer 6c. The reactions were conducted in reagent-grade pyridine (stored over 4-Å molecular sieves) in a flame-dried, 1-L, three-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, and a reflux condenser with an argon inlet. To 800 mL of degassed pyridine (maintained at 65-70 °C) were added six equimolar portions of the *p*-nitrophenyl ester porphyrin (3) (65 mmol) and the diamine porphyrin 5 (65 mmol) under argon at 2-h intervals. These partial additions made it possible to synthesize large amounts of FTF4 under very dilute conditions, thereby minimizing competitive polymeri-

2699

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 CH2Cl2 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 \times 3.5 cm silica column. First, pure CH₂Cl₂ was used to elute a narrow pink band of unreacted p-nitrophenyl ester (3), followed by a bright yellow band of p-nitrophenol. CH₃CN-CH₂Cl₂ (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 CH2Cl2-CH3OH; yield 60-65%. FTF dimers are highly light-sensitive and must be handled in the dark.

Treatment of Chloro-Contaminated FTF4 with NH2NH2 To Obtain Pure FTF4. Pure FTF4 may be obtained from the synthetic pathway depicted in Figure 2. Treatment of the FTF4 mixture 6 with NH₂NH₂ 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 \times 100 mL), dried (Na₂SO₄), 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 CH₂Cl₂, followed by 10:90 CH₃CN-CH₂Cl₂ 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 CoCl₂ 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 CoCl₂ 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.

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Registry No. 1, 85097-07-0; **2**, 85084-68-0; **3** (Ar = p-NO₂C₆H₄), 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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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 N₄ 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 ($E^{\circ} = 0.68 \text{ V}$).^{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 ($E^\circ = +1.23$ 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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