[9] Treatment of the Mn^{III} complex[8] (35.6 mg, 0.09 mmol) with Chloramine-T (141 mg, 0.5 mmol) in MeOH (5 mL) at room temperature for 40 h afforded complex **1** in 84 % yield.

[10] The use of trifluoromethanesulfonic anhydride or *p*-toluenesulfonyl chloride as an activator did not give good results relative to *p*-toluenesulfonic anhydride.

[11] Katsuki and his co-workers have reported that pyridine *N*-oxide is an effective additive for the asymmetric epoxidation catalyzed by salen–manganese(III) complexes, and they applied these findings to the asymmetric aziridination of alkenes with PhI=NTs: R. Irie, Y. Ito, T. Katsuki, *Synlett* **1991**, 265–266.

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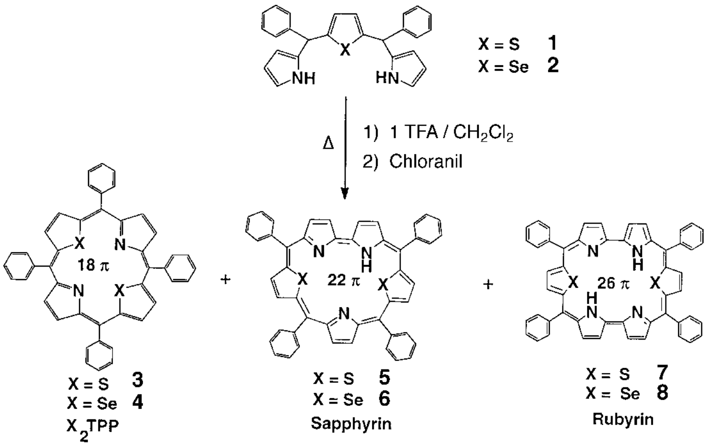
Sapphyrin Supramolecules through $C-H\cdots S$ and $C-H\cdots Se$ Hydrogen Bonds—First Structural Characterization of *meso*-Arylsapphyrins Bearing Heteroatoms**

Seenichamy Jeyaprakash Narayanan, Bashyam Sridevi, Tavarekere K. Chandrashekar,* Ashwani Vij,* and Raja Roy

Dedicated to Professors C. N. R. Rao and Jean'ne M. Shreeve on the occasion of their 65th birthdays

Controlling the assembly of macromolecules in the solid state through weak interactions such as hydrogen bonding and van der Waals forces is currently being explored for the synthesis of functional materials for molecular recognition and catalysis.[1] Many supramolecules held together by weak $C-H\cdots O$ and $C-H\cdots N$ hydrogen bonds are known.[2] In contrast, molecules held together by $C-H\cdots S$ and $C-H\cdots Se$ hydrogen bonds are very rare, and to the best of our knowledge there are only three reports to date on such interactions.[3] Here we describe the first structural characterization of two core-modified sapphyrins synthesized by an unprecedented coupling of a modified tripyrrane. Sapphyrins have been shown to self-assemble in the solid state to form a supramolecular ladder held together by weak $C-H\cdots S$ or $C-H\cdots Se$ and $C-H\cdots N$ hydrogen-bonding interactions.

Literature methods for the synthesis of sapphyrins include a traditional [3+2] acid-catalyzed MacDonald-type condensation between the appropriate precursors, reaction of diformylbipyrrole with benzaldehyde and pyrrole under Lindsey conditions,[4] and an acid-catalyzed condensation of *a,c*-biladienes with pyrrole-2-carbaldehydes.[5] Recently, a *meso*-substituted sapphyrin was isolated as a side product in 1 % yield in the Rothemund reaction of benzaldehyde and pyrrole.[6] In all these reactions at least two precursors are required for the condensation under different conditions. However, our reaction of the modified tripyrranes **1** and **2** in dichloromethane containing an appropriate acid catalyst gave 18π, 22π, and 26π macrocycles in moderate yields (Scheme 1). The product distribution and the yields of isolated products were dependent on the nature of the acid catalyst and its concentration. For S- and Se-containing tripyrranes at lower concentrations of trifluoroacetic acid (TFA), the major product was rubyrin, while at higher concentrations of TFA, sapphyrin and rubyrin were isolated in moderately good yields in addition to small amounts of X_2TPP (X = S or Se; TPP = tetraphenylporphyrin). The formation of **5** and **6** requires partial acidolysis of tripyrranes under the reaction conditions. We have observed that both **1** and **2** undergo acidolysis, and the extent of acidolysis is dependent on the TFA concentration. The higher yields of **5** and **6** at higher concentrations of TFA is consistent with this observation. For the formation of **7** and **8** we suggest an acid-catalyzed self-condensation of two tripyrrane units through an oxidative coupling,[7] forming a rubyrinogen intermediate which on dehydrogenation gives rubyrin.[8] Attempts to isolate the corresponding rubyrinogen proved futile because it oxidizes readily to the corresponding aromatic congener. The sole formation of rubyrins at the lower concentrations of TFA (0.1 equiv) at which acidolysis is minimal suggests that the self-coupling is preferred at this concentration.



Scheme 1. Synthesis of various sapphyrins and rubyrins from **1** and **2**.

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The composition of the new expanded porphyrins was established from the analytical data and FAB mass spectrometry, while their aromatic and porphyrinic nature were supported by ^{1}H NMR and UV/Vis spectral data (Table 1). The important feature of the ^{1}H NMR spectra is the revelation that the NH tautomerism of **5** is much more rapid than that of **6** at room temperature. Consequently, a broad signal appears for the inner NH protons of **6** while no corresponding signal is seen for **5.** However, when the solutions are cooled to $-90\,^\circ$C, sharp NH resonances are seen for both **5** and **6** at $\delta = -5.0$ and -5.35, respectively. Furthermore, two sets of equal-intensity resonances are seen for the pyrrole, thiophene, and selenophene rings, suggesting the existence of asymmetric tautomers in which the proton is located either on N3 or N2 of the bipyrrole unit. A similar observation was made by Latos-Grażyński and co-workers very recently for 26,28-dithiasapphyrin.[9] The rubyrins **7** and **8** did not show well-resolved resonances at room temperature. Only three broad resonances due to bipyrrole protons and *meso*-phenyl protons are observed, suggesting the rapid rotation of the selenophene rings in **8**. However, on cooling to $-50\,^\circ$C, sharp resonances were seen for the selenophene protons as well as inner-ring NH protons. Unlike **6**, no splitting of the bipyrrole protons is observed here, suggesting a symmetric tautomer in which each bipyrrole unit has one proton on either of the nitrogens. On protonation the rate of rotation slows down, and the chemical shifts and coupling constants reported in Table 1 for **8** were evaluated from the 2D COSY spectrum recorded at $-50\,^\circ$C.

Table 1. Selected physical data for the new compounds.

2: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 5.96$ (s, 2H), 6.15 (q, 2H, $J = 8$ Hz), 6.69 (d, 2H, $J = 2$ Hz), 6.79 (d, 2H, $J = 3$ Hz), 7.29 (m, 10H), 7.92 (brs, 2H); MS (70 eV): *m/z* (%): 443 (100) [M^+ with ^{80}Se]

5: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.85$ (m, 7H), 7.92 (m, 4H), 8.37 (m, 4H), 8.46 (m, 4H), 8.81 (s, 2H), 9.29 (d, 2H, $J = 3$ Hz), 9.93 (d, 2H, $J = 6$ Hz), 9.95 (d, 2H, $J = 6$ Hz), 10.06 (d, 2H, $J = 6$ Hz); ^{1}H NMR (300 MHz, CDCl$_3$/TFA, 25 °C, TMS): $\delta = -2.18$ (brs, 2H), -2.85 (s, 1H), 8.18 (m, 8H), 8.23 (m, 4H), 8.76 (m, 4H), 8.89 (m, 4H), 9.17 (s, 2H), 9.75 (d, 2H, $J = 6$ Hz), 10.12 (d, 2H, $J = 6$ Hz), 10.32 (d, 2H, $J = 6$ Hz), 10.33 (d, 2H, $J = 6$ Hz); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 470 (22.4), 584 (1.75), 623 (1.07), 730 (0.59), 820 nm (1.68); UV/Vis (CH$_2$Cl$_2$/TFA): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 499 (12.3), 660sh (1.17), 727 (2.42), 826 nm (2.74); MS (FAB): *m/z* (%): 714 (100) [M^+]

6: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = -4.4$ (brs, 1H), 7.6 (m, 8H), 7.96 (m, 4H), 8.39 (m, 4H), 8.49 (m, 4H), 8.96 (s, 2H), 9.36 (d, 2H, $J = 6$ Hz), 10.01 (d, 2H, $J = 6$ Hz), 10.35 (d, 2H, $J = 6$ Hz), 10.47 (d, 2H, $J = 6$ Hz); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 475 (30.1), 517 (6.4), 592 (2.8), 631 (1.8), 736 (0.7), 823 nm (3.2); UV/Vis (CH$_2$Cl$_2$/TFA): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 519 (19.8), 677 (0.96), 752 (1.83), 859 nm (2.9); MS (FAB): *m/z* (%): 810 (100) [M^+ with ^{80}Se]

7: ^{1}H NMR (300 MHz, CDCl$_3$/HCl, 25 °C, TMS): $\delta = -2.80$ (brs, 2H), -2.50 (brs, 2H), 8.04 (m, 12H), 7.92 (d, 4H), 8.82 (m, 8H), 9.71 (s, 4H), 10.49 (s, 4H); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 385 (0.16), 532 (14.2), 658 (1.12), 764 (0.9), 1017 nm (1.36); UV/Vis (CH$_2$Cl$_2$/TFA): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 542 (19.4), 722 (0.82), 813 (1.8), 1004 nm (5.9); MS (FAB): *m/z* (%): 779 (100) [M^+]

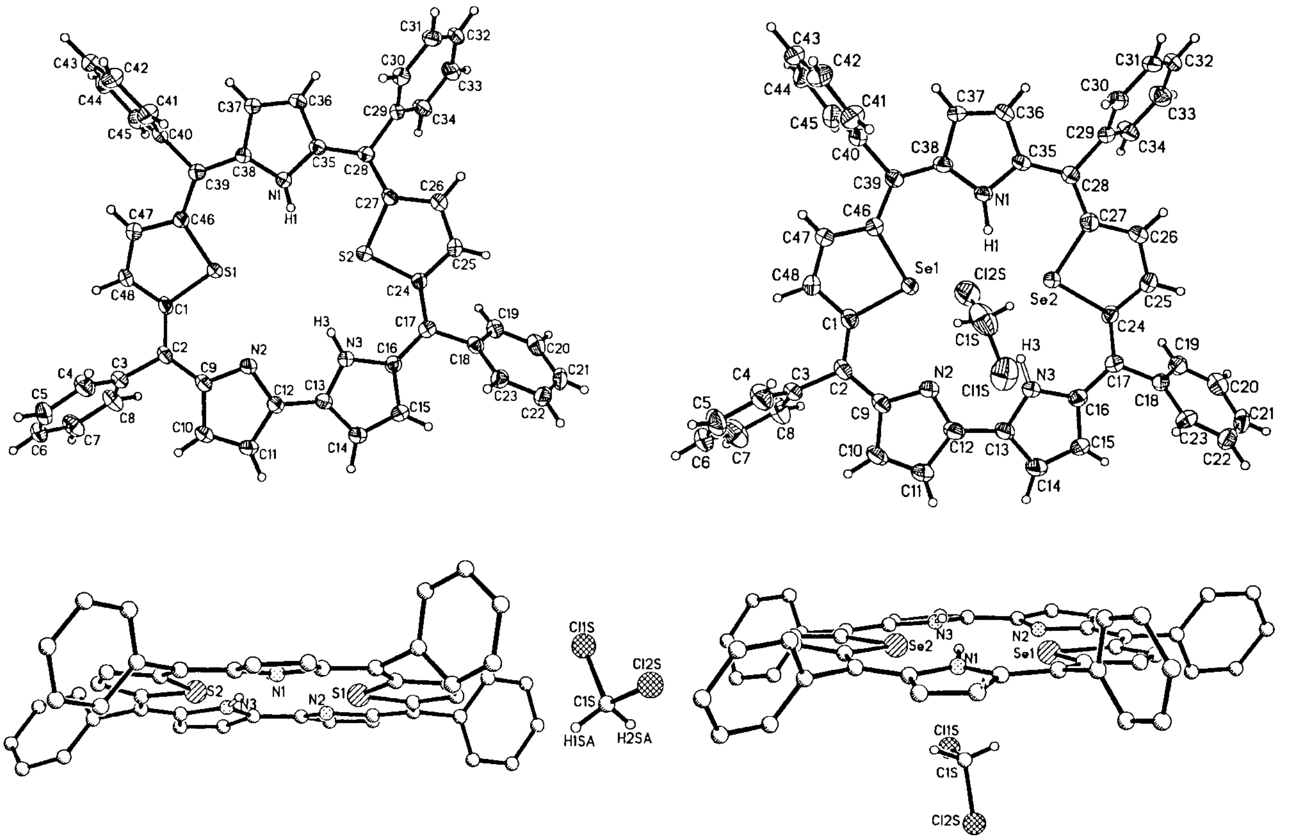
8: ^{1}H NMR (300 MHz, CDCl$_3$, -50 °C, TMS): $\delta = 9.88$ (s, 4H), 9.66 (d, 4H, $J = 4.2$ Hz), 8.91 (d, 4H, $J = 4.2$ Hz), 8.64–8.66 (m, 8H), 7.94–8.10 (m, 8H), 7.68–7.81 (m, 4H), -0.06 (brs); ^{1}H NMR (300 MHz, CDCl$_3$/HCl, 25 °C, TMS): $\delta = -1.55$ (brs, 2H), -1.00 (brs, 2H), 7.98 (m, 20H), 8.87 (d, 4H, $J = 6$ Hz), 8.77 (d, 4H, $J = 6$ Hz), 9.58 (d, 2H, $J = 6$ Hz), 10.41 (d, 2H, $J = 6$ Hz); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 530 (13.4), 666 (1.09), 766 (0.62), 849 (0.77), 970 nm (1.34); UV/Vis (CH$_2$Cl$_2$/TFA): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$) = 546 (15.4), 728 (0.98), 814 (1.11), 1016 nm (5.07); MS (FAB): *m/z* (%): 875 (100) [M^+ with ^{80}Se]

The X-ray crystal structures of **5**[10] and **6** [11] (Figure 1) reveal that the replacement of the pyrrole NH group by S or Se changes the π-electron delocalization. The bond lengths in the macrocycle are altered compared to those of free thiophene or selenophene fragments, as was observed previously for the similar systems.[12] In both the cases the macrocycle is almost planar (deviations from the mean plane in **5** are 0.054, 0.027, and 0.028 Å for S1, S2, and N2 and -0.014 and -0.102 Å for N1 and N3, respectively). In both structures the imino H atom could not be assigned unequivocally to a specific nitrogen atom. This difficulty is most likely due to a statistical distribution of NH tautomers in the crystal or rapid interconversion of tautomers during the time required for measurement.[13] Our analysis suggests 70% probability of occupation on N3 and 30% probability on N1. It is pertinent to point out here that in the N5 *meso*-tetraphenylsapphyrin reported by Latos-Grażyński and co-workers the pyrrole ring opposite to bipyrrole is inverted in its free-base form.[6] However, in **5** and **6** such a ring inversion was not observed in either solid or solution state. The important feature of the structure is the presence of hydrogen-bonding interactions in the cavity between N1–H1⋯S1 (H1–S1 2.87 (8) Å) and N1–H1⋯S2 (H1–S2 2.55 (8) Å) in **5**. The corresponding distances for **6** are 2.63 (17) (H1–Se1) and 2.28 (17) Å (H1–Se2).

The packing diagram shown in Figure 2 reveals an interesting aspect of the structure. In **5** there are two short-range C23–H23⋯S1 hydrogen-bonding interactions (2.91 (4) Å, 136.3°) to form a dimeric structure. This dimer is further extended through the formation of the longer hydrogen bond between C19–H19⋯S2 (3.16 Å, 131.2°) and C20–H20⋯N1 (2.70 (5) Å, 156.3°) thus leading to a supramolecular assembly.[14] A similar assembly was formed in **6**, and the corresponding distances and angles for **6** are C23–H23⋯Se1 (2.98 (5) Å, 146°), C20–H20⋯Se2 (3.26 (5) Å, 129°), and C20–H20⋯N1 (2.74 (5), 155°). The C–H⋯S and the C–H⋯Se distances observed here compare well with the reported data (C–H⋯Se 2.94, 107°).[3a]

The protonation of pyrrole nitrogen atoms in sapphyrin and rubyrin leads to formation of dicationic species in which the positive charge is delocalized into the ring. Thus, the dications are anticipated to bind anions depending on the cavity size of the macrocycle and the size of the anion.[15] Preliminary binding studies reveal formation of stable complexes in solution. Specifically, 22π sapphyrins bind F^- and N_3^- ions strongly relative to the larger CO_3^{2-} and PO_4^{3-} ions, while the 26π rubyrins bind CO_3^{2-} and PO_4^{3-} ions with binding constants higher than those with F^- and N_3^- ions.

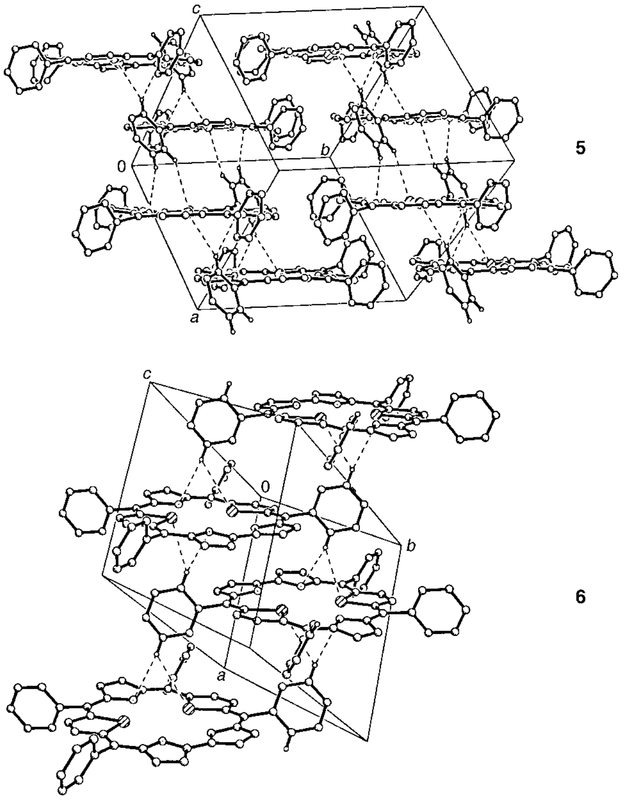
We have demonstrated the feasibility, by rational core modification of the porphyrin building blocks, of a controlled assembly of supramolecular multisapphyrin arrays through unusual C–H⋯Se and C–H⋯S and C–H⋯N hydrogen-bonding interactions. Furthermore, the synthesis presented here is not only elegant but also quite effective: 18π, 22π, and 26π macrocycles are prepared in one pot in moderately good



5

6

Figure 1. Crystal structures of **5** and **6** (in each case, top: plan view, bottom: side view). Selected distances in **5** [Å]: S1 ··· N2 2.911 (3), S1 ··· N1 3.244 (4), N2 ··· N3 2.835 (4), N3 ··· S2 3.058 (4), S2 ··· N1 3.122 (4), S1 ··· S2 4.346 (5). Selected distances in **6** [Å]: Se1 ··· N2 2.909 (4), Se1 ··· N1 3.226 (4), Se2 ··· N3 3.093 (4), Se2 ··· N1 3.035 (4), N2 ··· N3 2.820 (4), Se1 ··· Se2 3.9315 (8).



5

6

Figure 2. Molecular packing diagram of **5** and **6** showing two-dimensional ladder structures. Hydrogen-bonding interactions are represented by dotted lines.

yields. The fact that this methodology works smoothly for tripyrranes containing two different heteroatoms (S and Se) establishes the versatility of the method.

Experimental Section

Tripyrrane **1** (0.301 mmol) was dissolved in 150 mL of dichloromethane and stirred under a nitrogen atmosphere for 5 min. TFA (0.301 mmol) was added, and the stirring was continued for a further 90 min. Then chloranil (0.903 mmol) was added, and the reaction mixture heated at reflux for an additional 90 min. After removal of the solvent the residue was purified by chromatography on basic alumina (grade 3). The orange fraction, which eluted with petroleum ether/dichloromethane (4/1), was identified as **3** (2 mg, 1 %); sapphyrin **5** (30 mg, 14 %) eluted as a green band when the eluent was changed to EtOAc/CH_2Cl_2 (5/95); and the last pink band, which was eluted with EtOAc/CH_2Cl_2 (2/3), corresponded to rubyrin **7** (20 mg, 8.5 %). The same procedure was followed for other reactions with appropriate modified tripyrranes and acid concentrations.

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[10] a) Crystal structure data of **5**: $C_{48}H_{32}N_3S_2 \cdot CH_2Cl_2$, $M_r = 799.87$; crystals from CH_2Cl_2/CH_3OH (1/1); Crystal dimensions $0.50 \times 0.25 \times 0.20$ mm; triclinic, space group $P\bar{1}$, $a = 11.122$ (2), $b = 13.526$ (2), c = 15.109 (2) Å, $\alpha = 68.689$ (13), $\beta = 87.10$ (2), $\gamma = 66.785$ (11)°, $V = 1934.6$ (6) Å^3, $Z = 2$, $\rho_{calcd} = 1.373\,g\,cm^{-3}$; F (000) = 830; μ ($Mo_{K\alpha} = 3.2\,cm^{-1}$; 12202 measured reflections; 5833 observed reflections. ($F_o^2 > 2\sigma F_o^2$); $\theta_{max} = 28.3°$; $R = 0.0681$, $R_w = 0.1658$. b) The X-ray diffraction data were collected on a Siemens SMART3-circle diffractometer equipped with a CCD detector. The structure was solved by the direct method using the SHELX-904 program and refined by the least squares method on F^2 using SHELXTL Version 5.03.5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101360. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Crystal structure data of **6**: $C_{48}H_{32}N_3Se_2 \cdot CH_2Cl_2$, $M_r = 891.60$; crystals from CH_2Cl_2/CH_3OH (1/1); crystal dimensions $0.10 \times 0.20 \times 0.35$ mm; triclinic, space group $P\bar{1}$, $a = 11.2565$ (14), $b = 13.689$ (2), $c = 15.116$ (2) Å, $\alpha = 67.911$ (7), $\beta = 86.897$ (9), $\gamma = 66.592$ (2)°, $V = 1968.1$ (5) Å^3, $Z = 2$, $\rho_{calcd} = 1.505\,g\,cm^{-3}$; F (000) = 898; 11111 measure reflections; 7648 observed reflections. ($F_o^2 > 2\sigma F_o^2$); $\theta_{max} = 26.41°$; $R = 0.0510$, $R_w = 0.1099$.[10b]

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[14] The ^1H NMR spectra of **6** which was recrystallized from dichloromethane and *n*-heptane showed sharp resonances (12.15 Hz), whereas the resonances were broad (20.1 Hz) for the sample recrystallized from a dichloromethane/methanol mixture. Furthermore, a titration of different concentrations of CD_3OD to a $CDCl_3$ solution of **6** resulted in gradual broadening of the signals, suggesting the existence of aggregates due to intermolecular interactions in solution.

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A Functional Model of Cytochrome c Oxidase: Thermodynamic Implications[**]

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Zhong Wang, Miroslav Rapta, Martin Bröring,
Reinhold Schwenninger, and Bernard Boitrel

Cytochrome c oxidases (CcOs) are the terminal enzymes of the respiratory chains. These membrane bound assemblies catalyze the four-electron ($4\,e^-$), four-proton ($4\,H^+$) reduction of O_2 to H_2O, and couple this exergonic reaction to intramembrane proton translocation. The resulting energy is used to generate ATP as protons flow back through the membrane via ATP synthase.[1, 2] What makes this class of enzymes particularly well suited to the task is the fact that they do not release partially reduced intermediates, such as superoxide and peroxide, which would be devastating to the cell if released in large quantities.[3]

Recently, a plethora of research on CcO[4] has been stimulated by two X-ray crystal structures.[5–8] The fundamental question of how the enzymes convert O_2 into H_2O without releasing H_2O_2 remains unanswered, however. Attempts to prepare synthetic analogues of the O_2 binding/activating site in CcO have been reported over many years. Very few have mimicked the catalytic properties of CcO, however.[9]

Previously we reported the first functional CcO model that consisted of a Co^{II}–porphyrin with a Cu^I-coordinated distal superstructure and with a covalently attached imidazole group as the axial ligand.[10] We demonstrated that this complex catalyzes the $4\,e^-$ reduction of O_2 under physiological conditions without the release of H_2O_2. Our electrocatalytic studies also demonstrate that both the copper ion and the axial imidazole ligand are essential to achieve the reduction.

Herein we present the synthesis, characterization, and electrocatalytic chemistry of two Fe/Cu-containing synthetic analogues of the dioxygen activating site of CcO heme $a_3\,Cu_B$. The only structural difference between these compounds is the nature of the distal superstructure in which the copper ion resides (Scheme 1). Compound **A** has a 1,4,7-triazacyclononane (TACN) distal cap whereas **B** features a *N*,*N*′,*N*″-tribenzyl-tris(aminoethyl)amine (TBTren) cap.

Compounds **A** and **B** both form stable 1:1 adducts with O_2 ($\mathbf{X_A}$ and $\mathbf{X_B}$, respectively) as demonstrated by UV/Vis spectroscopy after O_2-titration. The O_2 adduct of each compound features an apparently diamagnetic NMR spectrum[11] in contrast to the paramagnetic NMR spectrum observed with their O_2-free forms, **A** and **B**. This observation

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