Rearrangement of the CH=C-$N,N^{21'},N^{22'}$-Linkage in the Mixed Bis(porphyrin) of Octaethylporphyrin and *meso*-Tetraphenylporphyrin *via* the CH-CH-$N^{21},N^{22},N^{21'},N^{22'}$-Linkage

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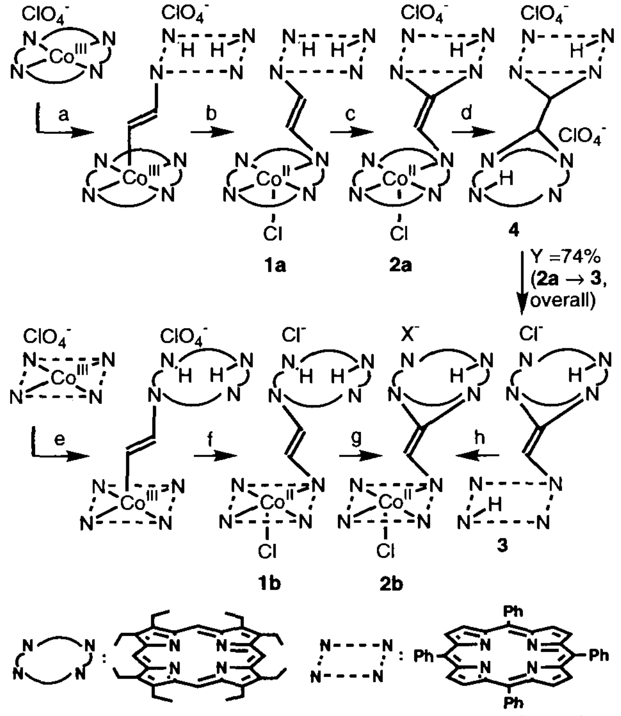
The CH=C-$N,N^{21'},N^{22'}$-linked bis(porphyrin) consisting of an N-(vinyl)octaethylporphyrin moiety and a monoprotonated N^{21},N^{22}-vinylidene-bridged *meso*-tetraphenylporphyrin moiety was rearranged to the CH=C-$N,N^{21'},N^{22'}$-linked bis(porphyrin) consisting of an N-(vinyl)-*meso*-tetraphenylporphyrin moiety and a monoprotonated N^{21},N^{22}-vinylidene-bridged octaethylporphyrin moiety. The CH-CH-$N^{21},N^{22},N^{21'},N^{22'}$-linked bis(porphyrin) which is a key intermediate of this rearrangement was identified by X-ray crystallography.

Interests in the multi-electron redox system have led to the development of a number of face-to-face porphyrins.[1] We have found a convenient method using acetylene for connecting porphyrins by making a vinylene-linkage between the pyrrole nitrogens.[2] These CH=CH-N,N'-linked bis(porphyrin)s give stable binuclear metal complexes[2] and the electronic interaction between two Cu^{II} ions is observed.[3] This CH=CH-N,N'-linkage can be transformed to provide new face-to-face porphyrins with a different inter-ring separation and orientation. This is demonstrated by the oxidative N-C bond formation in the bis(porphyrin) Co^{II} complex, (CH=CH-N,N')($OEPCo^{II}Cl$)(TPPH) (**1a**),[4] leading to (CH=C-$N,N^{21'},N^{22'}$)($OEPCo^{II}Cl$)(TPPH)ClO_4 (**2a**) (Scheme).[5] Here, we describe the transformation of the CH=C-$N,N^{21'},N^{22'}$-linkage to the CH-CH-$N^{21},N^{22},N^{21'},N^{22'}$-linkage in the course of demetallation of **2a**.

The CH=C-$N,N^{21'},N^{22'}$-linked bis(porphyrin) Co^{II} complex **2a** consisting of an N-(vinyl)$OEPCo^{II}Cl$ moiety and a monoprotonated N^{21},N^{22}-vinylidene-bridged TPP moiety was dissolved in trifluoroacetic acid and the solution was stirred for 0.5 h at room temperature. After work-up with aqueous ammonia and saturated aqueous NaCl solution, the products mixture was allowed to stand in CH_2Cl_2 solution for 72 h and then chromatographed on silica gel to give a metal-free bis(porphyrin) **3**[6] in a 74% yield. The ^1H NMR spectrum of **3** shows two signals at -3.46 and -5.4 ppm due to the N-H protons and a singlet at -9.53 ppm assignable to the vinyl proton of the CH=C-$N,N^{21'},N^{22'}$-linkage. Unexpectedly, the Co^{II} complex **2b**[7] prepared by the insertion of a Co^{II} ion into **3** was different from the original Co^{II} complex **2a**. The ^1H NMR spectrum of **2b** indicates that the chemical shifts due to the TPP peripheral protons are greatly influenced by the high-spin (S = 3/2) Co^{II} ion[2] in contrast to the remarkable paramagnetic shift for the protons due to the OEP periphery in the case of **2a**.[8] This is indicative of the presence of a Co^{II} ion in the TPP core of **2b**.

The complex **2b** was identical with the CH=C-$N,N^{21'},N^{22'}$-linked bis(porphyrin) Co^{II} complex which was synthesized by the reaction of $TPPCo^{III}(H_2O)_2ClO_4$ with $OEPH_2$ and C_2H_2 followed by the two stage oxidation reactions with $FeCl_3$ and then with $Cu(ClO_4)_2{\bullet}6H_2O$ as shown in the Scheme.[2,5] Thus, the complex **2b** consists of an N-(vinyl)$TPPCo^{II}Cl$ moiety and a monoprotonated N^{21},N^{22}-vinylidene-bridged OEP moiety. This means that the CH=C-$N,N^{21'},N^{22'}$-linkage rearranged in the course of demetallation of **2a**. The ^1H NMR analysis of the crude product precipitated by evaporating CH_3CN after **2a** was treated with 5% $HClO_4$ aqueous solution in CH_3CN for 24 h at room temperature showed signals at -3.38 and -11.08 ppm.[9] Since the singlet at -11.08 ppm is assigned to the vinyl proton, the original CH=C-$N,N^{21'},N^{22'}$-linkage of **2a** seems to be retained under strongly acidic conditions where the OEP pyrrole nitrogens are protonated. When a CH_2Cl_2 solution of this crude product was washed with 5% aqueous ammonia and then with saturated aqueous NaCl solution, it changed to a 3 : 1 mixture of two bis(porphyrin)s, **4**[10] and **3**. It was not possible to separate **4** from **3**, because **4** changed spontaneously to **3** and this process was promoted by chromatography on silica gel. The signal splitting pattern in the ^1H NMR spectrum is consistent with the



Octaethylporphyrin dianion *meso*-Tetraphenylporphyrin dianion

reagents: a) C_2H_2, $TPPH_2$; b) $Fe(ClO_4)_3{\bullet}6H_2O$, then aq. $NaHCO_3$; c, g) $Cu(ClO_4)_2{\bullet}6H_2O$; d) aq. $HClO_4$, then aq. NH_3 and aq. NaCl; e) C_2H_2, $OEPH_2$; f) $FeCl_3$; h) $Co(OAc)_2{\bullet}4H_2O$, then aq. NaCl.

Scheme.

C_s-symmetric molecular structure of **4**. There is a mirror plane passing through the C5 (and C43) and C15 (and C53) *meso*-carbons and bisecting both OEP and TPP rings. The AB doublets at -6.44 and -11.00 ppm with J_{vic} = 6.6 Hz is not consistent with the CH=C-$N,N^{21'},N^{22'}$-linkage.

The CH-CH-$N^{21},N^{22},N^{21'},N^{22'}$-linkage of **4** was determined by the X-ray crystallographic analysis of a crystal obtained from a product mixture of the reaction of **2a** with $HClO_4$ as shown in Figure 1.[11] The two porphyrin planes of **4** are almost parallel with the dihedral angle of 6.7°. The separation between the two porphyrin planes of **4** (3.37 Å) is at the limit of van der Waals contact and it is greatly shortened from the corresponding distance (4.39 Å) in the CH=CH-N,N'-linked bis(porphyrin) $Co^{II}Zn^{II}$ complex derived from **1a**.[2] As is expected from the very short distance (3.21(2) Å) between C9 of the OEP ring and C47 of the TPP ring, the stereochemical interaction between two porphyrin rings may be responsible for the labile nature of **4** in solution.

The demetallated bis(porphyrin) **3** is of great interest in view of the unique redox properties of the N,N'-bridged porphyrins[12] and the ability to incorporate various metal ions into N-substituted porphyrins.[13]

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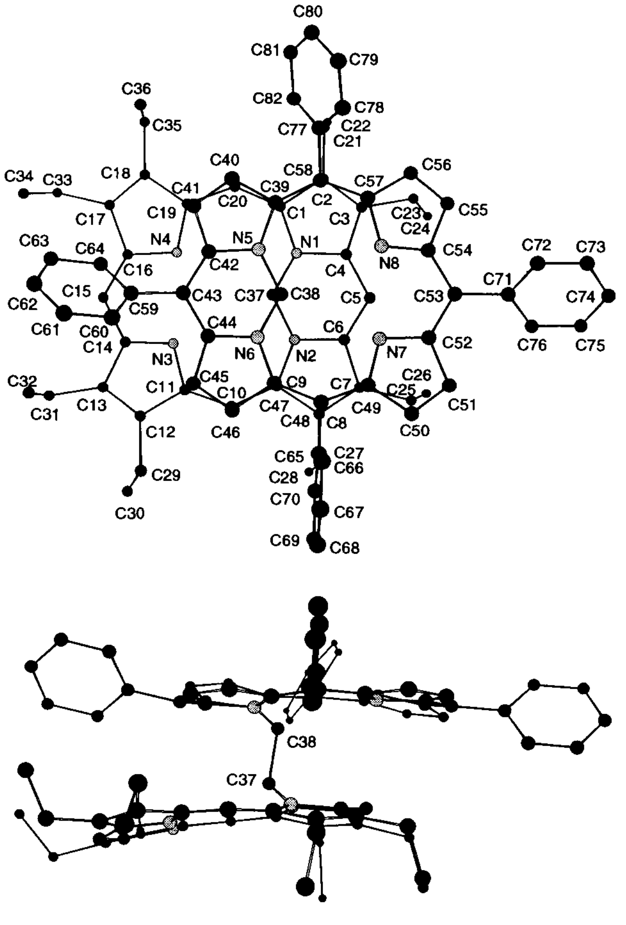

Figure 1. Molecular structure and atom-numbering scheme for (CH-CH-$N^{21},N^{22},N^{21'},N^{22'}$)(OEPH)(TPPH)$(ClO_4)_2$ (**4**); a top view (top) and a side view (bottom). Two ClO_4 ions are not shown for clarity.

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4 abbreviations: OEP (2,3,7,8,12,13,17,18-octaethylporphyrin dianion); TPP (5,10,15,20-*meso*-tetraphenylporphyrin dianion).

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6 **3**: ^{1}H NMR (δ, $CDCl_3$) 10.81, 9.65, 9.18, 7.79 (sx4, 1Hx4, OEP-*meso*-H); 4.8 ~ 2.6 (m, 16H, OEP-CH_2); 2.41, 1.84, 1.76, 1.68, 1.56, 1.50, 1.13, 0.99 (tx8, 3Hx8, OEP-CH_3); 8.94, 8.84, 8.68, 8.34, 8.32, 7.44, 6.65, 6.26 (dx8, 1Hx8, TPP-pyrrole-β-H); 9.35 ~ 7.48 (m, 20H, TPP-phenyl-H); -3.46, -5.4 (sx2, 1Hx2, NH); -9.53 (s, 1H, N-CH=). UV-vis (λ_{max}(log ε) in CH_2Cl_2) 389 (5.26), 530 (4.10), 572 (3.97), 623 (3.57), 711 (3.51) nm. Anal. Calcd for $C_{82}H_{75}N_8Cl \cdot 4H_2O$: C, 76.94; H, 6.54; N, 8.75. Found: C, 77.03; H, 6.14; N, 8.40.

7 **2b**: ^{1}H NMR (δ, $CDCl_3$) 18.3, 8.3, 2.2, -2.4 (1Hx4, OEP-*meso*-H); 14.5, 12.8, 12.2, 12.0, 11.1, 8.8, 4.6, 4.2, 4.2, 3.5, 1.2, 0.0, 0.0, -0.7, -1.6, -1.8 (1Hx16, OEP-CH_2); 9.5, 4.6, 4.4, 2.5, 2.3, -1.7, -2.9, -3.0 (3Hx8, OEP-CH_3); 55.6, 54.5, 50.3, 49.1, 35.6, 33.1, -4.1, -5.2 (1Hx8, TPP-pyrrole-β-H); 23.3, 22.2, 22.0, 20.6, 8.3, 6.0, -1.7, -6.5 (1Hx8, TPP-phenyl-o-H); 15.8, 15.4, 11.7, 11.3, 8.6, 7.7, 7.4, 7.2 (1Hx8, TPP-phenyl-m-H); 9.9, 9.7, 7.1, 6.5 (1Hx4, TPP-phenyl-p-H); -36.4 (1H, NH); -120 (1H, Co-N-CH=). UV-vis (λ_{max}(log ε) in CH_2Cl_2) 392 (5.22), 534 (4.04), 572 (4.07), 610 (3.88), 699 (3.56) nm. Anal. Calcd for $C_{82}H_{74}N_8O_4Cl_2Co \cdot H_2O$: C, 71.19; H, 5.54; N, 8.10. Found: C, 71.45; H, 5.70; N, 8.02.

8 ^{1}H NMR of **2a** (δ, $CDCl_3$): -0.9, -13.1, -17.8 (1Hx3, OEP-*meso*-H; 1H is not assigned); 33.0, 28.7, 26.6, 24.0, 23.0, 22.8, 20.8, 19.3, 19.0, 17.6, 12.4, 12.4, 12.0, 10.7, 9.4, 7.9 (1Hx16, OEP-CH_2); 10.7, 10.4, 9.3, 9.3, 8.8, 8.7 -0.4, -4.1 (3Hx8, OEP-CH_3); 11.8, 9.0, 10.6, 10.3, 6.0, 3.6, 4.8, 2.5 (1Hx8, TPP-pyrrole-β-H); 20.0, 16.7, 0.2 (1Hx3, TPP-phenyl-o-H; 5H are not assigned); 14.2, 13.6, 11.6, 5.8 (1Hx4, TPP-phenyl-m-H; 4H are not assigned); 9.5, 8.5 (1Hx2, TPP-phenyl-p-H; 2H are not assigned); -32.7 (1H, NH); -113 (1H, Co-N-CH=).

9 ^{1}H NMR (δ, $CDCl_3$) 10.10, 9.70, 8.81, 8.03 (sx4, 1Hx4, OEP-*meso*-H); 1.92, 1.86, 1.82, 1.69, 1.65, 1.58, 0.58, -0.11 (tx8, 3Hx8, OEP-CH_3); 10.27, 9.88, 9.63, 9.01, 8.52, 7.76, 7.40, 7.33 (dx8, 1Hx8, TPP-pyrrole-β-H); -3.38 (br, 1H, NH); -11.08 (s, 1H, N-CH=).

10 ^{1}H NMR of **4** (δ, $CDCl_3$) 10.08, 7.09 (sx2, 1Hx2, OEP-*meso*-H); 10.05 (s, 2H, OEP-*meso*-H); 4.6 ~ 3.1 (m, 16H, OEP-CH_2); 2.12, 1.95, 1.01, 0.61 (tx4, 6Hx4, OEP-CH_3); 8.93, 8.38, 8.20, 7.10 (dx4, 2Hx4, TPP-pyrrole-β-H); 9.60 ~ 5.58 (m, 20H, TPP-phenyl-H); -3.18 (br, 1H, NH); -6.44, -11.00 (dx2, 1Hx2, N-CH-CH-N, J = 6.6 Hz).

11 Crystal data for **4**: $C_{82}H_{76}N_8O_8Cl_2$, M = 1372.46, monoclinic, space group $P2_1/n$(#14), a = 14.807(3), b = 27.519(4), c = 18.109(3) Å, β = 107.39(1)°, V = 7042(2) Å^3, Z = 4, D_{calc} = 1.29 g/cm^3, μ(Mo-Kα) = 1.57 cm^{-1}, T = 293 K, crystal size 0.20 x 0.20 x 0.25 mm. A total of 11754 unique reflections were collected using graphite-monochromated Mo-Kα radiation (0.71069 Å). 3406 reflections with I > 2.00σ(I) were observed. All C and N atoms except those of phenyl groups were refined anisotropically. Four phenyl groups and two ClO_4 ions were refined as rigid groups. Each ClO_4 ion was disordered and treated as having eight oxygens with occupancies of 0.5 each around the chlorine atom. All hydrogen atoms were included at standard positions (C-H = 0.95Å), but not refined. The refinement converged at R = 0.100, R_w = 0.058. GOF = 1.95.

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