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Synthesis and Properties of N,N'- and Co,N'-Vinylene Linked Bisporphyrins

Jun-ichiro SETSUNE,* Yoshihiro ISHIMARU, Yasushi SAITO, and Teijiro KITAO
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

Bis(aquo)tetra(p-tolyl)porphinatocobalt(III) perchlorate reacted immediately with acetylene, in the absence and presence of tetra(p-tolyl)porphinatocobalt(II), to give a N,N'-vinylene linked bisporphyrin biscobalt(II) complex and a Co,N'-vinylene linked bisporphyrin cobalt(III) complex (4b), respectively. 4b was oxidatively converted into N,N'-vinylene linked bisporphyrin free base. An octaethylporphyrin analogue corresponding to 4b was obtained when a mixture of bis(aquo)octaethylporphyrinatocobalt(III) perchlorate and octaethylporphyrin was allowed to react with acetylene gas.

Covalently linked bisporphyrins with layered structure have been the focus of recent studies directed to develop artificial molecular systems with functions based on their layered structure. While these bisporphyrin systems have been constructed by linking two porphyrins through peripheral substitution,[1] axial coordination,[2] and metal-metal bonding,[3] pyrrolic nitrogens have never been utilized for this purpose except one case.[4] This paper describes the first synthesis of N,N'- and Co,N'-vinylene linked bisporphyrins through novel and easy organometallic reactions of cobalt(III) porphyrins with acetylene gas.

(TPP[5])$Co^{III}(H_2O)_2ClO_4$[6] (1a) reacted immediately with acetylene gas in CH_2Cl_2 solution showing a color change from red to green. Work-up with aqueous NaSCN solution followed by chromatography on silicagel with CH_2Cl_2 gave a new complex (2a).[7] The UV-vis spectrum of 2a is virtually the same as that of N-vinyl(TPP)-$Co^{II}OAc$.[8] 2a shows a well resolved paramagnetic ^1H NMR spectrum with a C_s symmetric pattern, the assignment of which was made with reference to the spectra of a d_8-TPP (deuteriated at the pyrrole β-positions) analogue and a TTP[5] analogue (2b)[9] and with the aid of line-width analysis. The magnetic moments (μ = 3.6 μ_B for 2a and 3.4 μ_B for 2b) measured by Evans method in $CDCl_3$ at 22 °C are close to the spin only value (3.87 μ_B) for the d^7 high spin state (S = 3/2). These data are consistent with the N-substituted porphyrinatocobalt(II) structure for 2a and 2b. Demetallation of 2b with CF_3CO_2H in CH_2Cl_2 for 15 min at room temperature followed by neutralization with aqueous ammonia gave N,N'-vinylene$(TTP)_2H_2$ (3b)[10] in 87% yield from 2b (53% total yield from $(TTP)Co^{III}(H_2O)_2ClO_4$ (1b)). The unusually upfield shifted ^1H NMR signals at 0 °C associated with N,N'-vinylene protons at -5.33 ppm, pyrrole β-protons at 6.06 ppm, and meso aryl protons at 5.51 ppm and the remarkable temperature dependent line broadening of the meso aryl resonances provide the best evidence in support of the N,N'-vinylene linked layered bisporphyrin structure of 3b. Therefore, 2b is formulated as N,N'-vinylene$(TTP)_2Co^{II}_2(SCN)_2$.[7)]

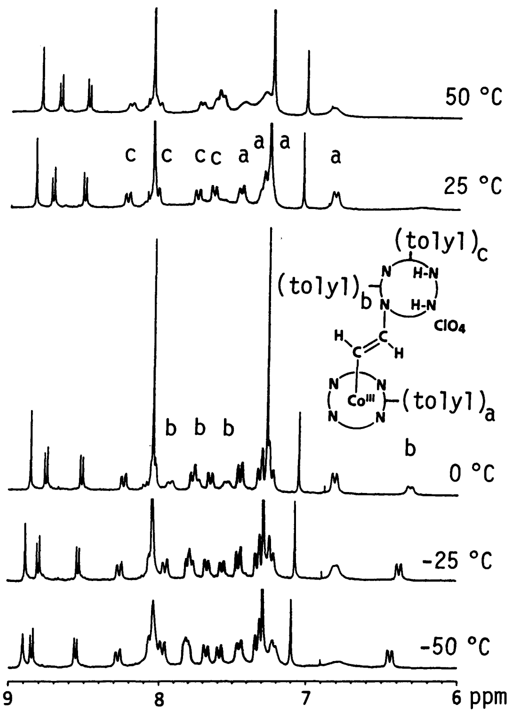


Fig. 1. Variable temperature ^1H NMR spectra of the aromatic region of 4b in $CDCl_3$. Aryl protons of meso-(p-tolyl) groups of Co(III) porphyrin [a], and of N-substituted porphyrin [b] and [c].

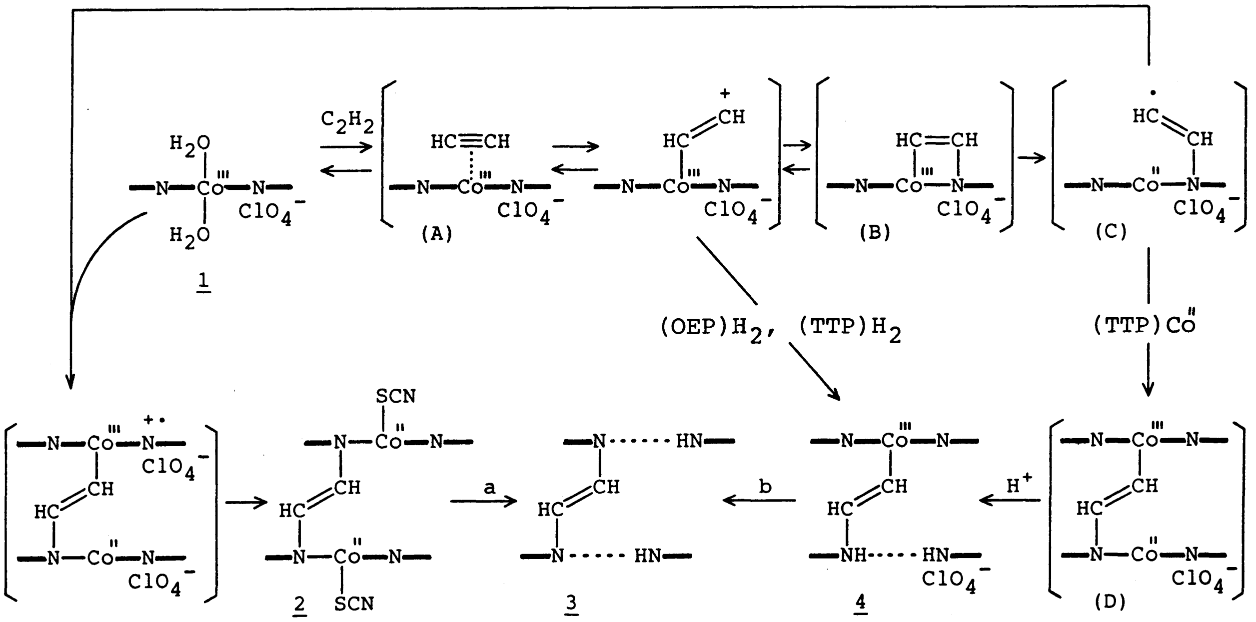
Introduction of acetylene gas into an equimolar mixture of 1b and $(TTP)Co^{II}$ in CH_2Cl_2 solution resulted in the formation of Co,N'-vinylene$(TTP)_2Co^{III}H_2ClO_4$ (4b)[11)] in 37% yield after chromatographic purification on silicagel with CH_2Cl_2 and acetone (10 : 1). The layered bisporphyrin structure with a Co,N'-vinylene linkage of 4b was evidenced by the extremely up-field shifted pair of doublets due to the vinylene protons at -2.25 and -9.11 ppm at 0 °C and the C_{4v} and C_s symmetric porphyrin resonances in 1 : 1 ratio like Co,N'-oxo linked bisporphyrin[4)] in the ^1H NMR spectrum, the meso aryl signals of which also showed remarkable temperature dependency caused by hindered rotation of meso aryl groups as shown in Fig. 1. Whereas use of alumina instead of silicagel afforded the corresponding free base, Co,N'-vinylene-$(TTP)_2Co^{III}H$ (5b),[12)] purification only by repeated recrystallizations allowed observation of the corresponding biscobalt(III,II) complex (D) as an initial product (see Scheme 1). The ^1H NMR spectrum of this crude product showed four signals due to pyrrole β-protons at 47.8, 39.2, 36.6, and -8.3 ppm characteristic of Co(II) N-substituted porphyrins like 2a and 2b.

It has been known that N-vinylporphyrinatocobalt(II) and -iron(II) complexes are interconvertible with σ-vinylcobalt(III) and -iron(III) porphyrins via one-electron redox process.[13)] While reduction of 2b with $NaBH_4$ or $Na_2S_2O_4$ resulted in the loss of the vinylene linkage to give $(TTP)Co^{II}$ quantitatively, oxidation of 4b with $Fe^{III}(ClO_4)_3\ 6H_2O$ (3 equiv.) for 1 h in CH_2Cl_2 effected migration of the vinylene linkage from cobalt to nitrogen with the bisporphyrin structure intact to give 3b in 73% yield.

We have recently found that acetylene is reversibly inserted into a Co(III)-N bond of $(OEP^{5)})Co^{III}(H_2O)_2ClO_4$ (1c) by way of Co(III) acetylene π-complex intermediate (A) which can be trapped by a bulky amine such as 2,6-lutidine to give β-(2,6-lutidinium)vinylcobalt(III)$(OEP)ClO_4$.[14)] Although bisporphyrins of OEP failed to arise through the same procedures as those for 2b and 4b, $(OEP)H_2$ and $(TTP)H_2$ cleanly reacted as bulky amines toward the π-complex intermediate (A) analogously to 2,6-lutidine, giving rise to Co,N'-vinylene$(OEP)_2Co^{III}H_2ClO_4$ (4c)[15)] and Co,N'-vinylene(OEP)$(TTP)Co^{III}H_2ClO_4$ (4d)[16)] as monoprotonated forms in 73% and 67% yield, respectively, after chromatography on silicagel with CH_2Cl_2 and acetone (5 : 1).

The difference in the reaction behaviors of 1b and 1c toward acetylene is ascribable to the nature of the Co(III)-C σ-bond of the Co,N-etheno bridged Co(III) porphyrin intermediate (B). Since the electron-donating octaethyl substituents at the porphyrin periphery stabilize a high valent state of cobalt, heterolysis of the Co(III)-C σ-bond leading to the dissociation to acetylene and 1c would be favored. On the other hand, the Co(III)-C bond homolysis becomes the major reaction pathway in case of rather electron-withdrawing meso-tetraaryl substituents, resulting in the generation of N-(TTPCo^{II})vinyl radical (C) which is immediately trapped by (TTP)Co^{II} to lead to 4b and by 1b as a form of Co(II) porphyrin π-cation radical$^{17)}$ in CH_2Cl_2 solution to lead to 2b.

The ease with which these N,N'- and Co,N'-linked layered bisporphyrins are prepared and their utility as ligands for various mono- and dinuclear metal complexes are especially noteworthy. Furthermore, the present reactions will provide a useful means of constructing layered multi-porphyrin systems. The work in this line is currently in progress in our laboratory.



Scheme 1. (reagents: a. 1. CF_3CO_2H, 2. NH_4OH; b. 1. $Fe(ClO_4)_3 \cdot 6H_2O$, 2. NH_4OH).

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5) Abbreviations. TPP : meso-tetraphenylporphin dianion; TTP : meso-tetra(p-tolyl)porphin dianion; OEP : octaethylporphyrin dianion.

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7) 2a: ^{1}H NMR (CDCl$_3$, 270 MHz) $\mathrm{H_{py(\beta)}}$ 41.8, 40.2, 33.8, -3.4; $\mathrm{H_o}$ 20.8, 16.3, 9.5, -0.6; $\mathrm{H_m}$ 15.4, 13.9, 11.8, 5.8; $\mathrm{H_p}$ 9.5, 8.7 ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 447, 573, 624, 671 nm. IR (KBr) SCN 2050 cm^{-1}.

8) H. J. Callot, R. Cromer, A. Louati, B. Metz, and B. Chevrier, J. Am. Chem. Soc., 109, 2946 (1987).

9) 2b: ^{1}H NMR (CDCl$_3$, 270 MHz) $\mathrm{H_{py(\beta)}}$ 41.5, 40.3, 34.3, -3.3; $\mathrm{H_o}$ 20.4, 15.9, 8.8, -0.6; $\mathrm{H_m}$ 15.2, 13.7, 11.6, 5.6; p-CH$_3$ 7.9, 3.6 ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 447, 573, 624, 671 nm. IR (KBr) SCN 2050 cm^{-1}.

10) 3b: ^{1}H NMR (CDCl$_3$, 0 °C, 270 MHz) $\mathrm{H_{py(\beta)}}$ 8.96 (s), 8.23 (d), 7.94 (d), 6.06 (s); $\mathrm{H_{o,m}}$ 8.37 (d), 7.84 (d), 7.79 (d), 7.52 (d), 7.29 (m)(x3), 5.51 (bs); p-CH$_3$ 2.82 (s), 2.59 (s); $\mathrm{H_{vinyl}}$ -5.33 (s) ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 426, 535, 577, 623, 683 nm.

11) 4b: ^{1}H NMR (CDCl$_3$, 0 °C, 270 MHz) $\mathrm{H_{py(\beta)}}$ 8.86 (s), 8.76 (d), 8.51 (d), 7.06 (s), 8.05 (s)(x4); $\mathrm{H_{o,m}}$ 8.24 (d), 8.04 (d), 7.77 (d), 7.65 (d), 7.93 (bd), 7.75 (bd), 7.53 (bd), 6.32 (bd), 7.45 (d)(x2), 7.32 (d)(x2), 7.24 (d)(x2), 6.82 (d)(x2); p-CH$_3$ 2.83 (s), 2.82 (s), 2.73 (s)(x2) $\mathrm{H_{vinyl}}$ -2.25 (d), -9.11 (d)(J_{vic} = 12.0 Hz) ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 410, 450, 532, 618, 666 nm.

12) 5b: ^{1}H NMR (CDCl$_3$, -25 °C, 270 MHz) $\mathrm{H_{py(\beta)}}$ 8.80 (s), 8.07 (d), 7.88 (d), 6.43 (s), 8.07 (s)(x4); $\mathrm{H_{o,m}}$ 8.31 (d), 7.89 (d), 7.71 (d), 7.57 (d), 7.71 (bd), 7.54 (bd), 7.42 (bd), 6.49 (bd), 7.39 (d)(x2), 7.28 (d)(x2), 7.24 (d)(x2), 6.81 (d)(x2); p-CH$_3$ 2.77 (s), 2.76 (s), 2.70 (s)(x2); $\mathrm{H_{vinyl}}$ -2.60 (d), -8.18 (d)(J_{vic} = 12.0 Hz) ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 408, 447, 532, 592, 625, 684 nm.

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15) 4c: ^{1}H NMR (CDCl$_3$, 270 MHz) $\mathrm{H_{meso}}$ 10.41 (s), 9.06 (s), 8.80 (s)(x2); CH$_2$ 4.64 (dq), 4.47 (dq), 4.29 (dq), 4.29 (dq), 3.96 (q)(x2), 3.22 (dq), 3.09 (dq), 3.64 (m)(x8); CH$_3$ 2.13 (t), 2.06 (t), 1.81 (t), 0.67 (t), 1.55 (t)(x4); $\mathrm{H_{vinyl}}$ -4.79 (d), -10.34 (d)(J_{vic} = 11.7 Hz); NH (bs) -7.73 ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 384, 517, 551, 583, 608 nm.

16) 4d: ^{1}H NMR (CDCl$_3$, 270 MHz) $\mathrm{H_{meso}}$ 8.89 (s); $\mathrm{H_{py(\beta)}}$ 9.08 (d), 8.85 (s), 8.50 (d), 6.79 (s); $\mathrm{H_{o,m}}$ 8.98 (d), 8.09 (d), 8.00 (d), 7.74 (d), 7.43 (d)(x2), 7.23 (d)(x2); CH$_2$ 3.49 (dq); p-CH$_3$ 2.69 (s), 2.90 (s); CH$_3$ 1.55 (t); $\mathrm{H_{vinyl}}$ -3.16 (d), -9.65 (d)(J_{vic} = 11.7 Hz) ppm. UV-vis (CH$_2$Cl$_2$) λ_{max} 389, 446, 515, 550, 618, 660 nm.

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