Synthesis and Characterization of the Dicobalt Bisporphyrin Complex Linked by 1,2-Phenylene Bridge

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The structure of a 1,2-phenylene linked dicobalt tetraarylporphyrin dimer was determined by X-ray crystallography and its dioxygen adduct was characterized by absorption and ESR spectroscopies. Since the porphyrin dimer has a long metal–metal distance and a rigid framework against inward bending, the cobalt centers were not bridged by the coordinated dioxygen.

The metal complexes of cofacial bisporphyrins have drawn considerable interest due to their unique reactivities toward small molecules.[1–10] Some cobalt complexes of bisporphyrins catalyzed the direct four-electron reduction of oxygen to water,[1–4] and dimanganese complexes, such as $[Mn^{III}_2(DTMP)]^{2+}$ (**1**) catalyzed four-electron oxidation of water to oxygen (Figure 1).[5] The intramolecular metal–metal separation in the cofacial bisporphyrin is important for the activation of small molecules.[1–10] For example, among doubly bridged amide-linked dicobalt bisporphyrins, only the four-atom bridged dimer is capable of the direct four-electron reduction of oxygen.[1,3] The O_2 reduction intermediate was reported to be a Co–O–O–Co species.[1,3,8] On the other hand, the structural information of **1** has not been reported yet.

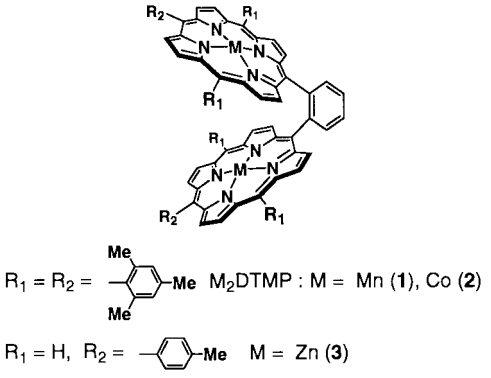

Figure 1. Dimeric porphyrin ligands and their metal complexes.

In this study, for estimating the distance and relative orientation between the metal centers of dimeric tetraarylporphyrins linked by a 1,2-phenylene bridge, we prepared the dicobalt complex $[Co^{II}_2(DTMP)]$ (**2**) and determined its structure by X-ray crystallography. Further, we characterized O_2 adduct of **2** for suggestive information of the O_2-evolving intermediate in **1**. **2** is considered to be a good probe for the elucidation of the mechanism of the O_2 evolution, because Co porphyrin can form a stable O_2 adduct.

The dicobalt(II) complex **2** was synthesized by previously described methods.[11–13] Crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of a hexane / ethyl acetate / methylene chloride solution. The ORTEP view of **2** is shown in Figure 2.[14] **2** has no exogenous axial ligands. It is notable

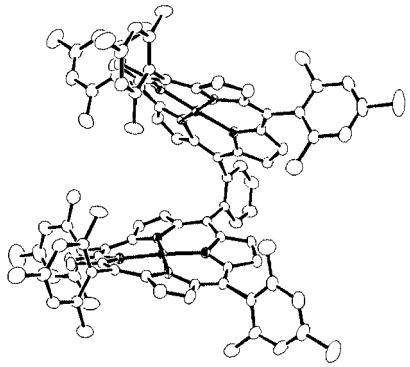

Figure 2. ORTEP view of $[Co_2(DTMP)]$ (**2**) drawn with the thermal ellipsoids at the 30 % probability level. Hydrogen atoms are omitted for clarity.

that the porphyrin rings are not stacked over each other. The relative orientation of the porphyrin rings in **2** is quite different from that of the dizinc complex of the dimeric diarylporphyrin (**3**, Figure 1) linked by the same 1,2-phenylene bridge.[9] The metal–metal distance of 6.570(2) Å in **2** is much longer than that of **3** (the average interplanar separation between the two porphyrin rings of **3** is 3.43 Å). The three *meso* aryl groups of each porphyrin in **2** sterically prevent the close stacking of the macrocycles, while there is only one aryl group other than the phenylene bridge in each porphyrin of **3**. In cofacial tetraarylporphyrin dimers, this severe steric hindrance would be more dominant than π–π stacking in cofacial tetraarylporphyrin dimers. In particular, the mesityl-substituted porphyrin dimers, **1** and **2**, provide the strongest resistance to close stacking of the porphyrins. As a further evidence, the ^{1}H NMR chemical shift difference of NH protons between the dimeric and monomeric free ligands, e.g., H_4DTMP (δ = –3.43 ppm), and H_2TMP (δ = –2.58 ppm), were found to be rather small. These results are in contrast with the finding that NH protons of the free ligand of **3** exhibit largely upfield shifts at δ = –6.31 and –5.77 ppm as a result of the stacking interaction. Thus, the metal complexes of DTMP should have the larger metal–metal distances also in solution without the substantial stacking of intramolecular porphyrin rings. Dizinc dibenzofuran-bridged diporphyrin, another example of a dimeric porphyrin having unsubstituted *meso* carbons, was reported to have a longer metal–metal separation (7.775 Å) than that of **2**.[10b] However, the diiron(III) complex of the same ligand (which has an intramolecular Fe–O–Fe moiety) has a shorter distance between each iron atom (3.504 Å, separation between porphyrin centers: 4.611 Å). The shorter iron–iron separation was due to the inward bending at the porphyrin *meso* carbons of the bridge positions and the inward displacements of the iron atoms from porphyrin mean planes.[10b] In contrast to the flexible bisporphyrin complexes that have unsubstituted *meso* carbons, DTMP has the rigid framework against inward bending.

Before the reaction with O_2, more than 10 equivalents of bulky 1-(1-adamantylmethyl)imidazole (Adim) was added to the toluene solution of **2** in order to allow O_2-binding only inside the cavity. The ESR spectrum of **2**-$(Adim)_2$ species at 77K shows a characteristic signal of a five coordinated Co^{II}-porphyrin at $g_\perp$ =2.31, $g_{//}$ =2.02 ($A_{//}^{Co}$ = 8.39 mT).[15,16] The parallel components show superhyperfine splitting due to interaction of Co^{II} with one nitrogen atom ($A_{//}^{N}$ = 1.72 mT). This result indicates that the species present in this concentration range is a 1 : 1 (Co ion : Adim) complex of **2**-$(Adim)_2$.[15] The O_2-adduct was obtained in the reaction of **2**-$(Adim)_2$ with O_2 at –80 °C. The Soret band shifted from 404 to 414 nm. The ESR spectrum of the O_2-adduct, which was different from that of **2**-$(Adim)_2$, indicated the formation of a monomeric six-coordinated cobalt-superoxo species ($g_\perp$ = 2.08, $A_\perp$= 1.65 mT, $g_{//}$ = 2.00, $A_{//}$ = 1.45 mT) instead of a dinuclear superoxo-bridged adduct.[16,17] The oxygen adducts of dicobalt anthryldiporphyrin and biphenylenyldiporphyrin were reported to have a superoxo–bridged structure,[1,8] and their metal–metal separations were found to be 4.566 and 3.807 Å, respectively.[7] The present result indicates that the distance between the metal ions in **2** seems to be too long to form M–O–O–M moiety.

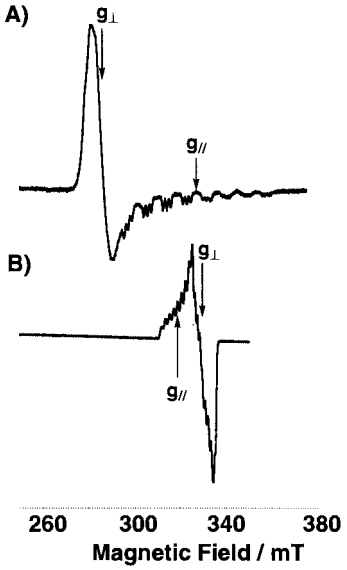

Figure 3. ESR spectra of **2** at 77 K; A) **2**-$(Adim)_2$, B) **2**-$(Adim)_2$ + O_2. These spectra were obtained in 10^{-4} M toluene solution with 1 mW microwave power and 0.5 mT modulation amplitude.

In conclusion, we have determined the structure of the dicobalt complex **2** by X-ray crystallography. **2** has a relatively large cavity due to the steric hindrance of the *meso* aryl groups. The reaction of **2** with O_2 showed the formation of a monomeric six-coordinated cobalt-superoxo species, instead of the O_2 bridged complex, indicating that the large cavity was maintained also in solution. Complex **2** has more rigid framework against inward bending than any other bisporphyrin compounds. On the basis of these results, complex **1** is predicted to have the rigid and large cavity under the catalytic oxidation of water, and the Mn–O–O–Mn structure would be less likely as an O_2-evolving intermediate. Further study on the mechanism of the water oxidation catalyzed by the Mn complexes is under way.

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References and Notes

1 J. P. Collman, P. S. Wagenknecht, and J. E. Hutchinson, *Angew. Chem., Int. Ed. Engl.*, **33**, 1537 (1994).
2 C. K. Chang, H. Y. Liu, and I. Abdalmuhdi, *J. Am. Chem. Soc.*, **106**, 2725 (1984).
3 J. P. Collman, F. C. Anson, C. E. Barnes, C. S. Bencosme, T. Geiger, E. R. Evitt, R. P. Kreh, K. Meier, and R. B. Pettman, *J. Am. Chem. Soc.*, **105**, 2694 (1983).
4 R. Karamana, S. W. Jeon, O. Almarsson, and T. C. Bruice, *J. Am. Chem. Soc.*, **114**, 4899 (1992).
5 Y. Naruta, M. Sasayama, and T. Sasaki, *Angew. Chem., Int. Ed. Engl.*, **33**, 1839 (1994).
6 a) J. P. Collman, C. M. Elliot, T. R. Halbert, and B. S. Tovrog, *Proc. Natl, Acad. Sci, U. S. A.*, **74**, 18 (1977). b) C. K. Chang, M. S. Kuo, and C. B. Wang, *J. Heterocycl. Chem.*, **14**, 943 (1977). c) J. A. Cowan, and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, **1985**, 1213. d) R. Karaman, O. Almarsson, and T. C. Bruice, *J. Org. Chem.*, **57**, 1555 (1992). e) H. Ogoshi, H. Sugimoto, and Z. Yoshida, *Tetrahedron Lett.*, **1977**, 169. f) N. E. Kagan, D. Mauzerall, and R. B. Merrifield, *J. Am. Chem. Soc.*, **99**, 5484 (1977). g) C. K. Chang, and I. Abdalalmuhdi, *J. Org. Chem.*, **48**, 5388 (1983).
7 J. P. Fillers, K. G. Ravichandran, I. Abdalmuhdi, A. Tulinsky, and C. K. Chang, *J. Am. Chem. Soc.*, **108**, 417 (1986).
8 a) L. M. Proniewicz, J. Odo, J. Góral, C. K. Chang, and K. Nakamoto, *J. Am. Chem. Soc.*, **111**, 2105 (1989). b) C. K. Chang, *J. Chem. Soc., Chem. Commn.*, **1977**, 800.
9 **3** has close overlap of the porphyrins in an almost parallel conformation (dihedral angle: 6.6°) due to the large inward bending at the *meso* carbons of the bridge positions: A. Osuka, S. Nakajima, T. Nagata, K. Maruyama, and K. Toriumi, *Angew. Chem., Int. Ed. Engl.*, **30**, 582 (1991).
10 a) C. J. Chang, Y. Deng, A. F. Heyduk, C. K. Chang, and D. G. Nocera. *Inorg. Chem.*, **39**, 959 (2000). b) Y. Deng, C. J. Chang, and D. G. Nocera, *J. Am. Chem. Soc.*, **122**, 410 (2000).
11 P. Bhyrappa, and V. Krishnan, *Inorg. Chem.*, **30**, 239 (1991).
12 a) J. S. Lindsey, and R. W. Wagner, *J. Org. Chem.*, **54**, 828 (1989). b) H. Meiyer, Y. Kobuke, and S. Kugiyama, *J. Chem. Soc., Chem. Commn.*, **1989**, 923.
13 Elemental analysis of **2**: Found C 78.95 %, H 5.564 %, N 7.309 %; Calcd. C 79.14 %, H 5.71 %, N 7.38 % ($C_{100}H_{86}N_8Co_2$), HR-MS ($C_{100}H_{87}N_8Co_2$): Found 1517.5712; calcd. 1517.5718.
14 X-Ray crystal structure determination: The X-ray diffraction data were collected at 295 K with a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data for **2**: Formula $C_{100}H_{86}N_8Co_2$, crystal size: 0.20 × 0.27 × 0.10 mm, orthorhombic, space group *P*bcn, a = 22.3370(4), b = 16.4448(2), c = 26.4570(3) Å, V = 9718.4(2) Å^3, Z = 4, μ = 3.98 cm^{-1}, $F(000)$ = 3328.00, 5908 reflections used, 566 parameters, R = 0.086, R_w = 0.148 ($I > 2.00\sigma(I)$).
15 a) J. P. Collman, C. M. Elliott, T. R. Halbert, and B. S. Tovrog, *Proc. Natl. Acad. Sci. U. S. A.*, **74**, 18 (1977). b) S. S. Eaton, G. R. Eaton, and C. K. Chang, *J. Am. Chem. Soc.*, **107**, 3177 (1985).
16 F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
17 From the absorption and ESR spectral change, the present O_2 adduct was assigned to be 1 : 1 adduct of Co : O_2. This oxygenation was reversible and the starting reduced form was recovered by bubbling of N_2 or by warming of the solution to room temperature.