Preparation of Molybdenum Porphyrin Dioxygen Complexes without Bulky Substituents

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Molybdenum porphyrin dioxygen complexes without bulky substituents, $Mo^{VI}O(ttp)(O_2)$ **1** and $Mo^{VI}O(tpp)(O_2)$ **2** were successfully prepared by the direct dioxygenation of corresponding oxomolybdenum(IV) porphyrin complexes in the solid state.

Oxomolybdenum(IV) porphyrin having bulky substituents such as $Mo^{IV}O(tmp)$ in solution reacts with O_2 to give a corresponding dioxygen complex, $Mo^{VI}O(tmp)(O_2)$, reversibly.[1,2] On the other hand, $Mo^{IV}O(oep)$ with a planar oep porphyrin ligand affords a paramagnetic μ-oxo dimer of $[Mo^{V}O(oep)]_2O$.[3] ESR study suggests that the reaction of $Mo^{IV}O(tpp)$ with O_2 also yields a corresponding μ-oxo dimer.[4] These results inform us that steric bulkiness might be necessary conditions for the formation of molybdenum porphyrin dioxygen complexes as known for Fe(II) porphyrin systems.[5] However, a recent finding that $Mo^{IV}O(tmp)$ in the solid state reacts with O_2 to give $Mo^{VI}O(tmp)(O_2)$ suggests that a dioxygen complex can be prepared in the solid state even when the porphyrin ring of a Mo(IV) complex has no bulky substituents.[6] Actually, in the specific mesopores of FSM-16 (Folded-Sheet Mesoporus Material-16) having honeycomb structures with size-ordered cylindrical channels of 2-10 nm diameters, $Mo^{IV}O(oep)$ and $Mo^{IV}O(tpp)$ form respective dioxygen complexes.[7] In this communication, we report a preparation of discrete dioxygen complexes, $Mo^{VI}O(ttp)(O_2)$ **1** and $Mo^{VI}O(tpp)(O_2)$ **2** by the solid state reactions (Figure 1).[8] Undesirable side reactions were avoided under the reaction conditions even if bulky substituents were not introduced onto porphyrin rings.

Various attempts have been made to prepare the dioxygen complexes by treating less bulky $Mo^{IV}O(por)$ (por = ttp, tpp) with O_2-saturated solutions, but in all cases molybdenum(V) porphyrin complexes were obtained as major products. In the solid state reactions, $Mo^{IV}O(por)$ was allowed to stand in a dioxygen atmosphere at room temperature for two weeks to get new molybdenum porphyrin dioxygen complexes **1** and **2**. The elemental analysis data of each complex were consistent with their respective compositions. FAB-MS spectra showed the parent peak of MoO(por) units instead of the expected mass number of the dioxygen complexes. To certify the evolved gas in the course of the pyrolysis of **1** in the solid state, Temperature Programmed Desorption (TPD) mass was measured in the range of room temperature to 200 °C under 10^{-5} Torr (133×10^{-5} Pa) with a temperature rising speed at 2 °C per min. O_2 liberation was observed from ca. 50 to 150 °C, with a maximum liberation at 120 °C. The solid material after the measurement of TPD mass was dissolved in toluene under Ar. The solution gave a UV-vis spectrum with three absorption bands at 430, 555, and 594 nm, which were characteristic of $Mo^{IV}O(ttp)$.[9] The pyrolysis of **2** gave $Mo^{IV}O(tpp)$ also.

$$Mo^{VI}O(por)(O_2) \xrightarrow{\Delta} Mo^{IV}O(por) + O_2 \qquad (1)$$

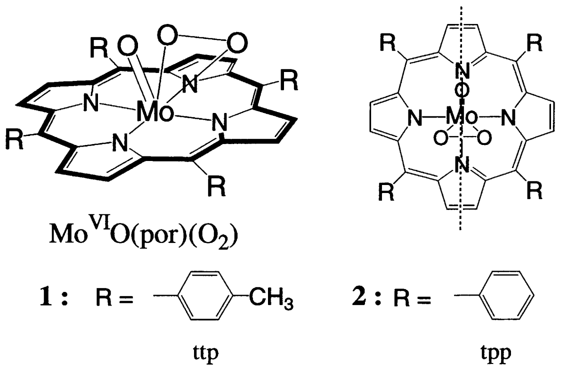

Figure 1. Predicted structure of new molybdenum porphyrin dioxygen complexes.

The dioxygen complexes showed two characteristic infrared stretches of the Mo=O and O-O bands at 910 cm^{-1} and 926 cm^{-1}, respectively. The 910 cm^{-1} band was in the range of molybdenum(VI) porphyrin complexes such as $Mo^{VI}O(tmp)(O_2)$,[1] or $Mo^{VI}(O)_2(ttp)$.[9] The O-O stretch was assigned by the isotopic shift of 926 cm^{-1} in **1** to 870 cm^{-1} in $Mo^{VI}O(ttp)(^{18}O_2)$. The value of the band was almost the same as the value of 873 cm^{-1} calculated by harmonic oscillator. The O-O stretch at 926 cm^{-1} revealed that O_2 is coordinated to the central molybdenum with a peroxide (O_2^{2-}) fashion.[1,10]

In ^1H NMR spectra of the dioxygen complexes of **1** and **2** in CD_2Cl_2, sharp signals and their observed regions indicated that the isolated complexes are diamagnetic, which are consistent with the oxidation state VI of the central molybdenum ions with no d electrons. The characteristic AB quartet signal and two singlet signals at β-pyrrole positions in each complex imply that the complexes have a C_s symmetry. All these results suggest that these dioxygen complexes have the same structure as that of $Mo^{VI}O(tmp)(O_2)$,[1] i.e., the complexes have a symmetry plane that passes though two *trans* N atoms of pyrrole rings and the single oxygen atom, and that bisects the inter-oxygen bond of the dioxygen ligand perpendicularly as shown in Figure 1.

Figure 2 showed UV-vis spectrum of the dioxygen complex **1** in toluene. Photoirradiation with visible light (Xe lamp) caused a spectral change as shown in Figure 2. The intensity of the Soret band at 432 nm increased and new absorption maxima appeared at 555 and 594 nm with the concomitant disappearance of two Q-bands at 529 and 562 nm. This spectral change had isosbestic points at 419, 441, and 541 nm. The final spectrum agreed with that of the oxomolybdenum(IV) porphyrin.[9] The results indicate that the new molybdenum porphyrin dioxygen complexes also release O_2 by photoirradiation in solution as observed for $Mo^{VI}O(tmp)(O_2)$.[1]

In the case of the $Mo^{VI}O(tmp)(O_2)$ system, the dioxygen complex is recovered quantitatively in the dark after the deoxygenation by photoirradiation.[1] However, in the **1** system

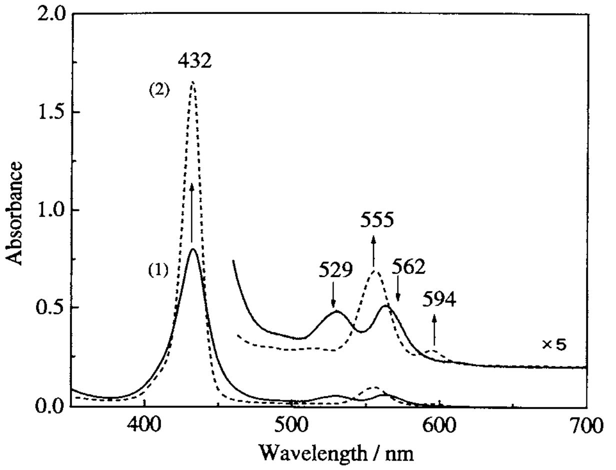

Figure 2. UV-vis spectral change of **1** by photoirradiation with visible light. Solid line (1): **1** in degassed toluene in the dark, Dashed line (2): after photoirradiation for 1 min.

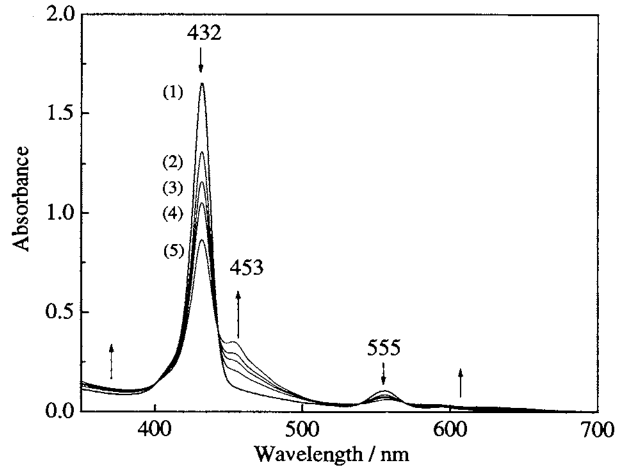

Figure 3. UV-vis spectral change by the reaction of $Mo^{IV}O(ttp)$ formed from **1** with O_2 in O_2-saturated toluene at 20 °C in the dark. Solid line (1): $Mo^{IV}O(ttp)$ formed by photoirradiation for 1 min, (2): 10 min after shading the light, (3): 20 min, (4): 30 min, (5): 60 min

in solution, the redioxygenation in the dark proceeded differently as shown in Figure 3. Besides the formation of the dioxygen complex of **1** without the recovery of the initial intensity of the Soret band, an extra absorption band appeared around 450 nm. Thus, some side reactions took place. The presence of apparent isosbestic points seems likely that the dioxygenation and the side reactions proceed in the same ratio of the reaction rates throughout the reactions. The solution after the repeated reaction cycles gave the characteristic ESR signals of paramagnetic oxomolybdenum(V) porphyrin complexes, while $Mo^{IV}O(por)$ and $Mo^{VI}O(por)(O_2)$ were ESR silent.[9] The reaction system of **2** also gave some ESR active byproducts, i.e., the reactions of O_2 with $Mo^{IV}O(por)$ formed from **1** and **2** by photoirradiation afforded the Mo(V) complexes such as $[Mo^{V}O(por)]_2O$ or $Mo^{V}O(por)OH$. The reason why the dioxygen complexes **1** and **2** cannot be obtained in solution in the syntheses is obvious from the results of photoirradiation experiments. Side reactions to go to Mo(V) complexes are preferable routes if the porphyrins have no bulky substituents. The dioxygenation of $Mo^{IV}O(por)$ in the solid state seems more favorable for the *cis*-coordination of dioxygen than that in solution. The dioxygen complexes **1** and **2** once formed are stable in the dark even in solution.

In conclusion, molybdenum porphyrin dioxygen complexes having less bulky substituents, $Mo^{VI}O(ttp)(O_2)$ **1** and $Mo^{VI}O(tpp)(O_2)$ **2**, were successfully prepared by using the direct dioxygenation of oxomolybdenum(IV) porphyrin complexes by the solid state reactions with O_2. This work clearly demonstrated that undesirable side reactions possibly can be avoided if the reactions are carried out in the solid state.

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References and Notes

1 J. Tachibana, T. Imamura, and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, **1993**, 1436; J. Tachibana, T. Imamura, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **71**, 363 (1998).

2 Abbreviations: tmp = 5,10,15,20-tetramesitylporphyrinato dianion, ttp = 5,10,15,20-tetra(*p*-tolyl)porphyrinato dianion, tpp = 5,10,15,20-tetraphenylporphyrinato dianion, oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion.

3 J. W. Buchler, "The Porphyrins", ed by D. Dolphin, Academic New York (1979), Vol. 1, p. 389.

4 M. Hoshino, Y. Iimura, and S. Konishi, *J. Phys. Chem.*, **96**, 179 (1992).

5 M. Momenteau and C. A. Reed, *Chem. Rev.*, **94**, 659 (1994), and references therein.

6 M. Osada, J. Tachibana, T. Imamura, and Y. Sasaki, *Chem. Lett.*, **1996**, 713; K. Hoshiba, N Nishimura, K. Shimazu, T. Imamura, and Y. Sasaki, *Chem. Lett.*, **1997**, 853.

7 J. Tachibana, M. Chiba, M. Ichikawa, T. Imamura, and Y. Sasaki, *Supramolecular Science*, **5**, 281 (1998).

8 $Mo^{VI}O(por)(O_2)$ (por = ttp, tpp) was prepared from $Mo^{V}O(por)(OMe)$. $Mo^{V}O(por)(OMe)$ was pylolyzed at 260 °C under reduced pressure (ca. 10^{-2} Torr) to give $Mo^{IV}O(por)$.[9,11] The resulting $Mo^{IV}O(por)$ in the solid state was left to stand in O_2 atmosphere for two weeks. The compound thus obtained was dissolved in CH_2Cl_2 and chromatographed with a silica gel column using CH_2Cl_2 as an eluent. The second red band was collected and evaporated to dryness. The product was dissolved in a small amount of CH_2Cl_2 followed by crystallization by adding *n*-pentane. For **1**; Anal. Found: C, 69.15; H, 4.77; N, 6.95 %. Calcd for $C_{48}H_{36}N_4O_3Mo$: C, 70.93; H, 4.46; N, 6.89 %. UV-vis (CH_2Cl_2, 20 °C): λ_{max} / nm (ε / 10^3 $dm^{-3}mol^{-1}cm^{-1}$), 432 (179), 529 (11.6), 560 (13.0). ^1H NMR (CD_2Cl_2, 270 MHz) δ / ppm: 9.22 (AB quartet (4.9 Hz), 4H, β-pyrrole), 8.90 (s, 2H, β-pyrrole), 8.50 (s, 2H,β-pyrrole), 7.81 ~ 8.20 (br), 7.60, 7.57 (m, 16H, *o, m*-H), 2.66, 2.65 (s each, 12H, *p*-CH_3). IR (KBr) ν / cm^{-1}: 926 ($\nu_{O\text{-}O}$), 910 ($\nu_{Mo=O}$). For **2**; Anal. Found: C, 70.61; H, 4.23; N, 7.26 %. Calcd for $C_{44}H_{28}N_4O_3Mo$: C, 69.84; H, 3.73; N, 7.40 %. UV-vis (CH_2Cl_2, 20 °C): λ_{max} / nm (ε / 10^3 $dm^{-3}mol^{-1}cm^{-1}$), 430 (158), 528 (10.5), 560 (12.2). ^1H NMR (CD_2Cl_2, 270 MHz) δ / ppm: 9.22 (AB quartet (4.9 Hz), 4H, β-pyrrole), 8.90 (s, 2H, β-pyrrole), 8.50 (s, 2H, β-pyrrole), 7.8 ~ 8.0 (br), 7.80, 7.79 (m, 20H, phenyl H). IR (KBr) ν / cm^{-1}: 928 ($\nu_{O\text{-}O}$), 910 ($\nu_{Mo=O}$).

9 Y. Matsuda and Y. Murakami, *Coord. Chem. Rev.*, **92**, 157 (1988).

10 K. Nakamoto, *Coord. Chem. Rev.*, **100**, 363 (1990).

11 T. Imamura, T. Numatatsu, M. Terui, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **54**, 170 (1981).