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New Dioxygen Complex of Molybdenum Porphyrin. Reactions of Oxomolybdenum(IV) Porphyrins with Molecular Oxygen

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New dioxygen molybdenum porphyrins were formed by the introduction of dioxygen into the toluene solutions of oxomolybdenum(IV) porphyrins, $Mo^{IV}O(tpp)$ and $Mo^{IV}O(oep)$, around -70 °C. By raising the temperature to 25 °C, or by the photoirradiation of the solutions with the wavelength of the Soret bands, the parent oxomolybdenum(IV) porphyrins were regenerated. A structure for the dioxygen complexes is proposed.

Recent reviews related to metallooxygen complexes have revealed increasing significances of the mechanistic and thermodynamical studies on the dioxygen complex formations,[1] oxygen atom transfer reactions,[2] oxo-bridging,[3] and oxygenation reactions of organic substrates.[4,5] In relation to these views, molybdenum polphyrins have been extensively studied.[6] A previous report described a reaction scheme for the systems of oxomolybdenum porphyrins and superoxide (hyperoxide) ion O_2^-.[7] The scheme suggested that a dioxygn complex was formed as an intermediate in the two reactions of $Mo^{V}O(tpp)X$ (tpp = 5,10,15,20-tetraphenylporphyrinato dianion, X = halide ion) with superoxide ion and $Mo^{IV}O(tpp)$ with dioxygen.[7] However, the corresponding dioxygen complex which was temporarily formulated as $MoO(tpp)(O_2)$ has not been detected so far.

In this communication, the first detection of the molybdenum dioxygen complexes in the reactions of oxomolybdenum(IV) porphyrins with dioxygen is reported.[8]

$Mo^{IV}O(tpp)$ was prepared by the pyrolysis of $Mo^{V}O(tpp)OCH_3$ in the solid state.[9] Octaethylporphyrin (2,3,7,8,12,13,17,18-octaethylporphyrin = H_2oep) was synthesized by the method reported by Chang.[10] $Mo^{IV}O(oep)$ was prepared by a similar method to that of $Mo^{IV}O(tpp)$. Spectral grade toluene was scrupulously purified and stored with 4 Å molecular sieves in the vessel on a vacuum line. The toluene was degassed by repeated freeze-pump-

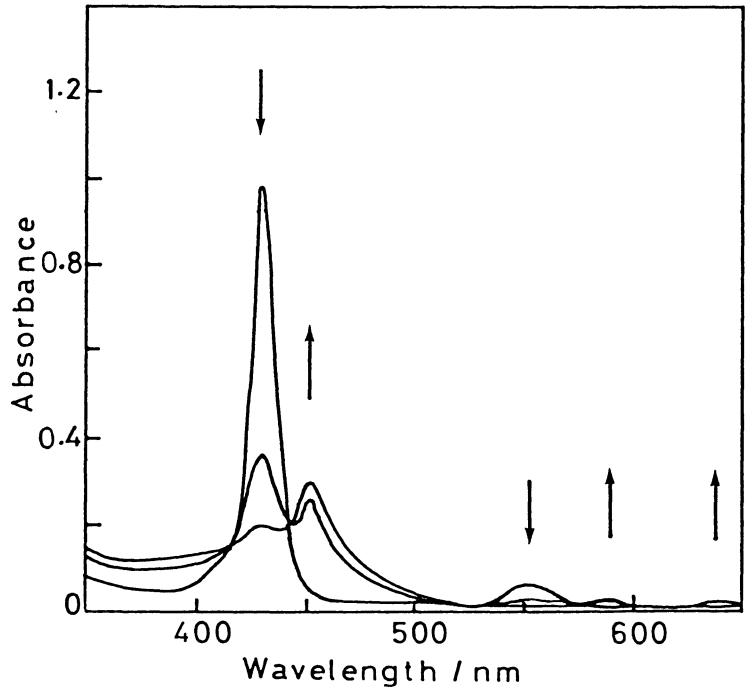


Fig. 1. Absorption spectral change by the introduction of dioxygen into the $Mo^{IV}O(tpp)$ toluene solution at -66 °C.

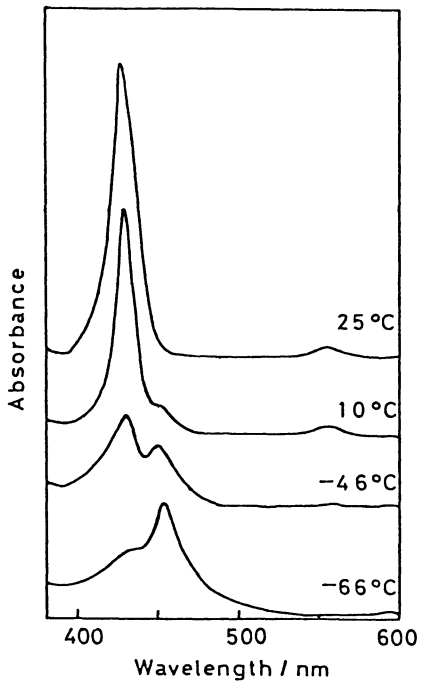


Fig. 2. Regeneration of $Mo^{IV}O(tpp)$ by raising the temperature of the dioxygen complex solution.

thaw cycles and vacuum-transferred into the opitical or ESR cells containing oxomolybdnum(IV) porphyrins prepared immediately before use from the corresponding alkoxooxomolybdenum(V) porphyrins. Then highly pure dioxygen dried by passing through the two columns containing calcium sulfate and 3 Å molecular sieves was introduced into the sample solutions. For these manipulations, break-seal techniques were used to completely eliminate contamination from air. The measurements of absorption spectra at low temperatures were performed by dipping an optical cell in a vacuum bottle with two optical windows filled with dry ice-ethanol or by using a Lauda Kryo-Star 80D thermostat.

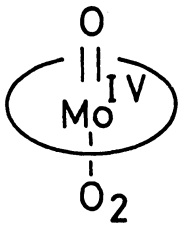
Oxomolybdenum(IV) porphyrin $Mo^{IV}O(tpp)$ in toluene at -66 °C has absorption bands at 430 and 555 nm. Introduction of dioxygen gave a new spectrum with the bands at 397, 453, 590, and 645 nm (Fig. 1).[11] By raising the temperature to 25 °C, $Mo^{IV}O(tpp)$ was regenerated (Fig. 2). The amount of formation of the new complex with the band at 453 nm depends on the solution temperature. When the solution was left to stand at room temperature in the dark, the absorbance around 450 nm increased, indicating the formation of mixture of $[Mo^{V}O(tpp)]_2O$ and $Mo^{V}O(tpp)OH$.[12] The formation of the new complex was inhibited by the presence of pyridine in the solution of $Mo^{IV}O(tpp)$. The formation of $Mo^{IV}O(tpp)(py)$ (λ = 447, 577, 619 nm in 2%(v/v) py-CH_2Cl_2) has been confirmed by the absorption spectral change in the reaction of $Mo^{IV}O(tpp)$ with pyridine at -72 °C.[7] These

results indicate that the new complex is a dioxygen complex in which dioxygen is coordinated to the central molybdenum atom from the same side of the porphyrin plane as the pyridine ligand. The coodination of dioxygen is screened by the ligated pyridine.

$$Mo^{IV}O(tpp)(py) \xleftarrow{py} Mo^{IV}O(tpp) \xrightarrow{O_2} \text{dioxygen complex} \qquad (1)$$

The photoirradiation of the dioxygen complex derived from $Mo^{IV}O(tpp)$ with the wavelength of the Soret band at 453 nm decreased the absorption of the band with simultaneous increase in the absorbances at 430 nm and 555 nm due to the regeneration of $Mo^{IV}O(tpp)$. The shading of photoirradiation caused again the formation of the dioxygen complex.

The dioxygen complex revealed no ESR signals at -70 °C, i.e., the μ-peroxo dimer of $[Mo^{V}O(tpp)]_2O_2$ is not the corresponding dioxygen complex.[13] There are three candidates for the ESR silent dioxygen complex, i.e., one candidate is $Mo^{IV}O(tpp)(O_2)$ (1) in which dioxygen is coordinated as a neutral ligand, another candidate is $Mo^{V}O(tpp)(O_2^-)$ (2) having a spin coupling between two electron spins of the central molybdenum atom (d^1) and the coordinated O_2^- that results in ESR silence, and the other one is the oxomolybdenum(VI) dioxygen complex (3) where dioxygen is coordinated as a side-on ligand with peroxide electronic configuration.



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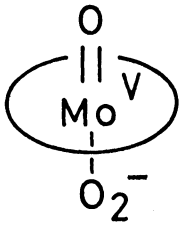
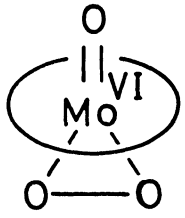


spin-coupled

2



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The dioxygen complex is formed at a relatively slow rate, $t_{1/2} \simeq 5$ min, at -70 °C by bubbling dioxygen through the $Mo^{IV}O(tpp)$ solution[14] and is stable even under low-dioxygen atmosphere once it is formed. Though degassing the solution by freeze-pump-thaw cycles at temperatures lower than -70 °C, there are no fast degradation of the dioxygen complex nor fast regeneration of the parent complex of $Mo^{IV}O(tpp)$, indicating the bond between the dioxygen and the central molybdenum atom is strong. From these results, the peroxomolybdenum(VI) porphyrin complex (3) is supposed to be the most possible structure.

$Mo^{IV}O(oep)$ also formed a dioxygen complex which has the Soret band at 441 nm at -70 °C. As the temperature was raised, $Mo^{IV}O(oep)$ was

regenerated with the formation of some amount of $[Mo^{V}O(oep)]_2O$. The formation of $[Mo^{V}O(oep)]_2O$ in the reaction of $Mo^{IV}O(oep)$ with dioxygen at room temperature has been reported.[15] In comparison with the reaction system of $Mo^{IV}O(tpp)$, the $Mo^{IV}O(oep)$ system readily gave the corresponding μ-oxo dimer even at low temperatures.

Although the low solubility of these molybdenum porphyrins in toluene at low temperatures stands in the way to ^1H NMR and IR measurements, work aimed at the detailed electronic configuration and properties of the dioxygen complexes is in progress.

References

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11) The dichloromethane solutions at -72 °C dissolving oxomolybdenum(IV) porphyrins and dioxygen gave the corresponding dioxygen complexes, though the solutions afforded simultaneously some molybdenum porphyrins which might be produced by reactive species derived from the reaction of the solvent with dioxygen.
12) H. J. Ledon, M. C. Bonnet, Y. Brigandat, and F. Veresion, Inorg. Chem., 19, 3488 (1980).
13) Although the dioxygen solution at -70 °C showed weak ESR signals, the signals still remained even after raising the temperature to 25 °C. The signals may be due to the adventitiously produced $[Mo^{V}O(tpp)]_2O$ or $Mo^{V}O(tpp)OH$ with introduction of dioxygen.
14) The initial concentration of $Mo^{IV}O(tpp)$ is ca. 1×10^{-5} mol dm^{-3}.
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