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A Reversible Metalloporphyrin Oxygen Carrier Both in the Solid State and in Solution: Preparation, Characterization, and Kinetics of Formation of a Molybdenum(VI) 5,10,15,20-Tetramesitylporphyrin Dioxygen Complex

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The molybdenum(VI) porphyrin dioxygen complex, $[Mo^{VI}O(O_2)(tmp)]$ (tmp=5, 10, 15, 20-tetramesitylporphyrinato), prepared from the reaction of $[Mo^{IV}O(tmp)]$ with dioxygen at room temperature is characterized in detail. Bulky mesityl substituents on the porphyrin rings enable the isolation of the dioxygen complex. Photoirradiation of the toluene solution of the dioxygen complex with visible light regenerated $[Mo^{IV}O(tmp)]$ immediately. Upon heating the solid sample of the dioxygen complex, dioxygen gas was liberated around 40—90 °C, leaving $[Mo^{IV}O(tmp)]$. The solid and a toluene solution of $[Mo^{IV}O(tmp)]$ thus formed, again absorbed O_2 from air to make $[Mo^{VI}O(O_2)(tmp)]$. The IR and ^1H NMR data confirmed that O_2 was coordinated as a peroxide mode to the central molybdenum(VI) ion from the same side of the porphyrin plane with the oxo ligand and that both the axial ligands (peroxo and oxo) eclipsed the *trans*-N atoms of the porphyrin rings. The second-order rate constant for the formation of the dioxygen complex in toluene was evaluated to be $(3.9\pm0.1)\times10^{-1}\ dm^3\ mol^{-1}\ s^{-1}$ at 20 °C. The rate constant is extremely small as compared with those of the oxygenation of iron(II) porphyrins, by at least a factor of 10^{-5}.

With the intention of clarifying the oxygen activation or transport mechanisms of cytochrome P-450[1)] and hemoglobin,[2)] and the catalytic oxygenation mechanisms of organic substrates,[3)] the reactions of metalloporphyrins with O_2 and the properties of corresponding dioxygen complexes have been extensively studied for the systems containing the metal centers of Fe,[4)] Ru,[5)] Cr,[6)] Mn,[7)] Co,[8)] Rh,[9)] Nb,[10)] and Mo.[11—13)] Some of the dioxygen adducts with structurally encumbered porphyrin ligands such as picket fence,[4c)] picnic basket,[5c,8l)] capped,[4d)] and cofacial porphyrin[8h—8k)] ligands are somewhat stable at room temperature. However, the dioxygen complexes with simple porphyrin ligands such as oep (oep = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrinato), tpp (tpp = 5, 10, 15, 20-tetraphenylporphyrinato), and ttp (ttp = 5, 10, 15, 20-tetratolylporphyrinato) are generally unstable at room temperature, and detectable in solution only at low temperatures of about −80 °C,[4g,7a,8c,9a,11)] or by the matrix isolation methods,[4a,4b,7c,7d,8e)] and as the reaction products in the solid state.[6a)] The only instance of a moderately stable dioxygen complex with a simple porphyrin ring is the complex reported here.[13)]

Among the above metal ions, molybdenum, one of the essential elements for life, is of great interest since it plays significant roles at the active sites in the metalloproteins such as xanthine oxidase, aldehyde oxidase, sulfite oxidase, and nitrogenase.[14)] In some artificial substances, molybdenum ions also show high catalytic abilities in the oxygenation reactions of organic compounds.[15)] From these viewpoints, several reactions of molybdenum porphyrin complexes with dioxygen species (O_2^- or O_2^{2-}) have been studied. The reactions produced some complexes having dioxygen ligands. For example, a *trans*-diperoxo complex, $[Mo^{VI}O(O_2)_2(ttp)]$, was formed by the reaction of $[Mo^VO(OMe)(ttp)]$ with H_2O_2 and characterized by X-ray crystallography.[16)] The *trans* diperoxo complex, $[Mo^{VI}O(O_2)_2(ttp)]$, was transformed to the corresponding *cis*-dioxo complex of $[Mo^{VI}(O)_2(ttp)]$ by photoirradiation,[17)] or by pyrolysis in the solid state.[18)] The molybdenum(V) superoxo species of $[Mo^VO(O_2)(ttp)]^-$ was also formed by the reaction of $[Mo^VO(tpp)(X)]$ ($X^- = Cl^-$, Br^-, or NCS^-) with O_2^- at −72 °C.[19)] Compared to the reaction systems with O_2^- or H_2O_2, only a small number of studies on the reactions of molybdenum porphyrins with gaseous O_2 have been reported. Rohbock and Buchler reported that the paramagnetic μ-oxo dimer of $[\{Mo^VO(oep)\}_2(\mu\text{-}O)]$ was eventually formed by the reaction of $[Mo^{IV}O(oep)]$ with O_2.[20)] Hoshino et al. reported that a paramagnetic dioxygen complex was formed in the reaction of $[Mo^{IV}O(tpp)]$ with O_2 at room temperature.[12)] On the other hand, a certain diamagnetic dioxygen complex was recently detected by studying the reaction of $[Mo^{IV}O(tpp)]$with O_2 at temperatures around −70 °C.[11)] Thus, the chemistry of the reactions of molybdenum porphyrin complexes with gaseous O_2 has not yet been settled. Isolation and characterization of dioxygen complexes are necessary in order to understand the details of the chemistry of molybdenum porphyrin dioxygen complexes.

In a preliminary communication, we reported the synthesis of a new dioxygen complex of molybdenum with a bulky porphyrin tmp (Fig. 1).[13] The dioxygen complex is formed by the reversible reaction of [$Mo^{IV}O$(tmp)] with gaseous O_2 at room temperature without the formation of any μ-oxo dimers. The complex is remarkable in the sense that the dioxygen uptake is reversible and the dioxygen release takes place both thermally and photochemically in both solution and the solid state. The present paper reports the detailed studies on the preparation and characterization of the dioxygen complex and the kinetics of the reversible dioxygen uptake of [$Mo^{IV}O$(tmp)]. The [$Mo^{VI}O(O_2)$(tmp)] is the first stable dioxygen complex of molybdenum porphyrin.

Experimental

Materials. H_2tmp was synthesized as per the literature method.[21] [$Mo^{IV}O$(tmp)] was prepared by the pyrolysis[22] of [$Mo^{V}O$(OMe)(tmp)] (vide infra) for 2 h under 10^{-5} Torr (1 Torr = 133.332 Pa) at 260 °C or of the new complex [$Mo^{VI}O(O_2)$(tmp)] (vide infra) at 120 °C in the solid state. For elemental analysis, [$Mo^{IV}O$(tmp)] was handled under ultra pure argon (Anal. Calcd for $C_{56}H_{52}ON_4Mo$: C, 75.32; H, 5.87; N, 6.27 %. Found: C, 75.28; H, 6.02; N, 6.31%). ^{1}H NMR ($C_6D_5CD_3$, 20 °C) $\delta = 8.99$ (8H, pyrrole H), 7.16 (4H, *m*-H), 7.12 (4H, *m*-H), 2.47 (12H, *p*-Me), 1.94 (12H, *o*-Me), and 1.75 (12H, *o*-Me). IR (KBr disc) 978 cm^{-1} (ν(Mo=O)). UV-vis λ_{max} ($C_6H_5CH_3$, 25 °C) 430 (log $\varepsilon = 5.66$) and 554 nm (4.56). [$Mo^{V}O$(OMe)(tmp)] was synthesized by a similar method to [$Mo^{V}O$(OMe)(tpp)].[23] UV-vis λ_{max} ($C_6H_5CH_3$, 25 °C) 455, 582, and 622 nm. ESR ($C_6H_5CH_3$, 25 °C) $\bar{g} = 1.97$. Toluene (spectral grade) was dried over 3 Å Molecular sieves and distilled under argon. Dioxygen gas (Nippon Sanso, pure oxygen B, > 99.9%) was dried by passing through the two columns containing Drierite and 3 Å Molecular sieves. All preparation of the sample solution was performed in the dark unless otherwise specified.

Isolation of the Dioxygen Complex. H_2tmp (1 g, 1.3 mmol) and an excess of $Mo(CO)_6$ (2 g, 7.6 mmol) were dissolved in the mixed solvent of decaline (72 cm^3) and octane (18 cm^3). The solution was refluxed gently for 2 h, followed by the removal of extra solvent and volatile $Mo(CO)_6$ by heating the reaction mixture at 80 °C in vacuo (1×10^{-3} Torr). The residual solid thus obtained was dissolved in toluene, followed by bubbling dioxygen gas for 1 h. The solution was chromatographed on a silica gel column (2.6 × 15 cm) using toluene as an eluent. The brown band containing H_2tmp was eluted first, followed by two red bands. The first red band eluted after the brown band was collected and evaporated to dryness. The solid was recrystallized from *n*-pentane–toluene and dried in a dry dioxygen atmosphere for 10 d at room temperature. The UV-visible spectrum of the isolated complex in dioxygen-saturated toluene was identical with that of the dioxygen complex observed in the reaction system of [$Mo^{IV}O$(tmp)] with O_2. UV-vis λ_{max} ($C_6H_5CH_3$, 20 °C) 432 (log $\varepsilon = 5.23$), 531 (4.09), and 563 nm (4.15). Elemental analysis of the isolated complex agreed well with the formula of [$MoO(O_2)$(tmp)] (Anal. Calcd for $C_{56}H_{52}O_3N_4Mo$: C, 72.72; H, 5.67; N, 6.06%. Found: C, 72.86; H, 5.61; N, 6.09%). The spectrum of the second red band was similar to that of *cis*-dioxo complexes such as [$Mo^{VI}(O)_2$(ttp)][17] and [$Mo^{VI}(O)_2$(tpp)].[24]

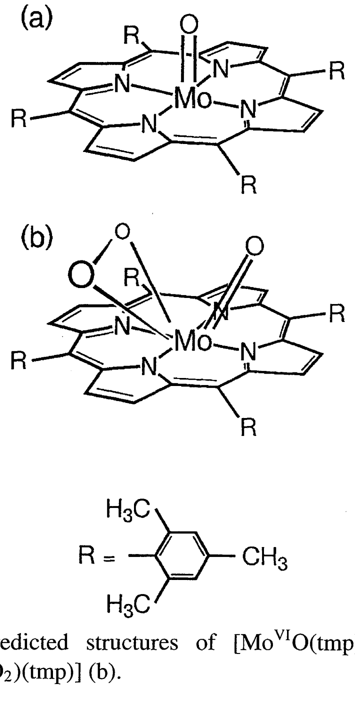


Fig. 1. Predicted structures of [$Mo^{VI}O$(tmp)] (a) and [$Mo^{VI}O(O_2)$(tmp)] (b).

Measurements. Electronic spectra were measured with a Hitachi spectrophotometer Model 808. Infrared spectra were recorded on a Hitachi 270-50 spectrophotometer. ^{1}H NMR spectra were measured with a JEOL JNM 2X-400 FT-NMR (400 MHz) spectrometer. FAB mass spectra were obtained with a JEOL JMS-HX110 spectrometer. TPD (temperature-programmed desorption) mass spectrometry was run from room temperature to 300 °C under 10^{-7} Torr at the heating rate of 2 °C min^{-1}. The desorbed gases were analyzed by a quadrupole mass spectrometer, NEVA NAG-515. To normalize the sensitivity of the mass spectra, a small amount of argon was continuously fed into the system. ESR spectra were recorded at 25 °C on a JEOL JES-FE3X spectrometer operating at 100-kHz modulation.

Composition of the Dioxygen Complex. The composition of the complex [$MoO(O_2)$(tmp)] was determined to be 1 : 1 for [MoO-(tmp)] and O_2 moieties by gravimetric analysis, i.e., by measuring the weight of the solid before and after the reaction of [$Mo^{IV}O$-(tmp)] with O_2. Appropriate correction for the weights was made by measuring buoyancy. Dioxygen absorbed into [$Mo^{IV}O$(tmp)] was figured out to be 9.38×10^{-5} mol (0.0030 g); the mole of [$Mo^{IV}O$-(tmp)] was 9.07×10^{-5} mol (0.0810 g). Thus, it was concluded that 1 mol of [$Mo^{IV}O$(tmp)] reacted with 1 mol of O_2 to form 1 mol of the dioxygen complex.

Kinetic study Kinetic experiments of the reversible dioxygenation of [$Mo^{IV}O$(tmp)] in toluene were carried out using a Hitachi 808 spectrophotometer with thermostated cells. The changes in absorbance around 430 nm, where both the dioxygen complex and [$Mo^{IV}O$(tmp)] have Soret bands, were monitored. The visible spectral changes were analyzed by plotting $\ln((Abs_t - Abs_\infty)/(Abs_0 - Abs_\infty))$ vs. time, where Abs_0 is the initial absorbance at 430 nm, Abs_∞ the final absorbance, and Abs_t the intermediate absorbance at an appropriate time. The concentration of O_2 was determined by the partial pressure of O_2 in the optical cell and the Ostwald's solubility coefficient (12.8×10^{-8} m^3) of O_2 in toluene at 20 °C.[25]

Results and Discussion

Reaction of [$Mo^{IV}O$(tmp)] with O_2 in Solution. The electronic spectrum of [$Mo^{IV}O$(tmp)] in toluene has absorption bands at 430 and 554 nm at 25 °C. Introduction of O_2 (1 atm) to the solution decreased the intensity at 430 nm with a concurrent small shift of its position to 432 nm. The absorbance change was also accompanied by the appearance of new peaks at 531 and 563 nm and the disappearance of the peak at 554 nm. The spectral change exhibited isosbestic points at 415, 438, 540, and 565 nm. The reaction completed in 10 min. The final spectrum had the bands at 432, 531, and 563 nm.

Photoirradiation of the reacted solution with light at 432 nm of the Soret band recovered immediately the absorption of the bands at 430 and 554 nm, indicating the regeneration of [Mo^{IV}O(tmp)] (Fig. 2). The shading of photoirradiation caused the formation of the new complex again. When the final solution was photoirradiated after the solution was degassed by freeze-pump-thaw cycles, [Mo^{IV}O(tmp)] formed, remaining unaffected even in the dark.

These results indicate that a dioxygen complex was formed reversibly by the reaction of [Mo^{IV}O(tmp)] with O$_2$.

$$[\mathrm{Mo^{IV}O(tmp)}] + \mathrm{O_2} \underset{h\nu}{\rightleftharpoons} \text{dioxygen complex} \tag{3}$$

Isolation of the dioxygen complex from the reaction mixture was not possible because a very dilute solution was used. Instead, the procedure given in the experimental section was found to be an efficient way to obtain a solid sample of the dioxygen complex. The solid sample is the same compound as the species observed in solution. This is confirmed by the quantitatively identical absorption spectra of the two samples in toluene.

Characterization of the Dioxygen Complex. TPD mass spectroscopy of the dioxygen complex shows the peaks of mass numbers of 32 and 16 at temperatures of 50 to 100 °C. Thus the evolution of O$_2$ from the solid sample was verified, which illustrated that dioxygen was contained in the complex. Figure 3 shows the changes in intensity for mass numbers of 32 (^{16}O$_2$) and 16 (^{16}O) during the temperature rise from 30 to 300 °C under 10^{-7} Torr. Gradual heating (2 °C min^{-1}) caused liberation of O$_2$ at ca. 40 °C, maximum intensity at 76.2 °C. The species of ^{16}O was derived from the liberated O$_2$. The toluene solution of the solid after the O$_2$ liberation showed the UV-visible spectrum of [Mo^{IV}O(tmp)] with absorption bands at 430 and 554 nm. These results indicate that each dioxygen complex involves an O$_2$ group and becomes [Mo^{IV}O(tmp)] with liberation of O$_2$ by heating.

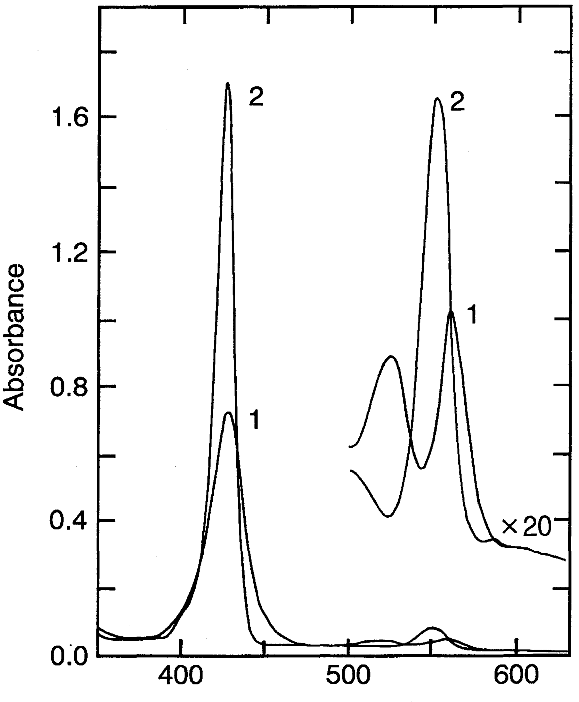


Fig. 2. UV-visible spectral change (1) before and (2) immediately after the photoirradiation with light at 432 nm of the toluene solution of the dioxygen complex at 25 °C.

$$\underset{\text{(the solid state)}}{\text{Dioxygen complex}} \xrightarrow{\Delta} [\mathrm{Mo^{IV}O(tmp)}] + \mathrm{O_2} \tag{4}$$

No liberation of other gases or solvents was observed by heating the dioxygen complex in the range of about 110—300 °C.

To clarify in more detail the composition of the dioxygen complex, FAB mass spectra were measured (Fig. 4). Although no peaks corresponding to the predicted formula of the dioxygen complex, [MoO(O$_2$)(tmp)], were observed, the peaks for [MoO(tmp)]$^+$ were observed around 894 (m/z^+), as shown in Fig. 4(a). Gravimetric analysis (see experimental section) indicated that the dioxygen complex is composed of a 1 : 1 molar ratio of [MoO(tmp)] to O$_2$. The results clearly show that the dioxygen complex can be represented as [MoO(O$_2$)(tmp)].

The IR spectra of the dioxygen complexes synthesized from ^{16}O$_2$ and ^{18}O$_2$ are shown in Figs. 5(a) and 5(b), respectively. The stretches at 928 and 503 cm^{-1} in (a) respectively shifted to 875 and 476 cm^{-1} in (b). The extents of the isotopic shifts are consistent with their respective assignments to the diatomic O–O and Mo–O stretches. Supposing that the stretch at 546 cm^{-1} observed in (b) is ν(Mo–^{18}O), the

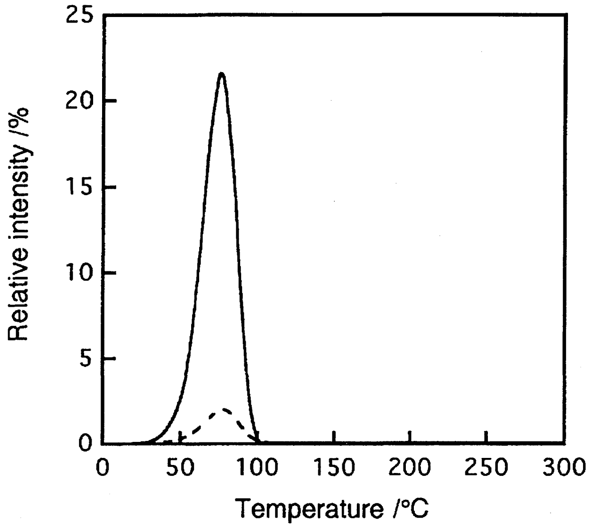


Fig. 3. TPD mass spectra of the solid sample of the dioxygen complex under 1.0×10^{-7} Torr. Temperature was raised with the rate of 2 °C min^{-1}. (—) mass number 32 (^{16}O$_2$) and (····) 16 (^{16}O).

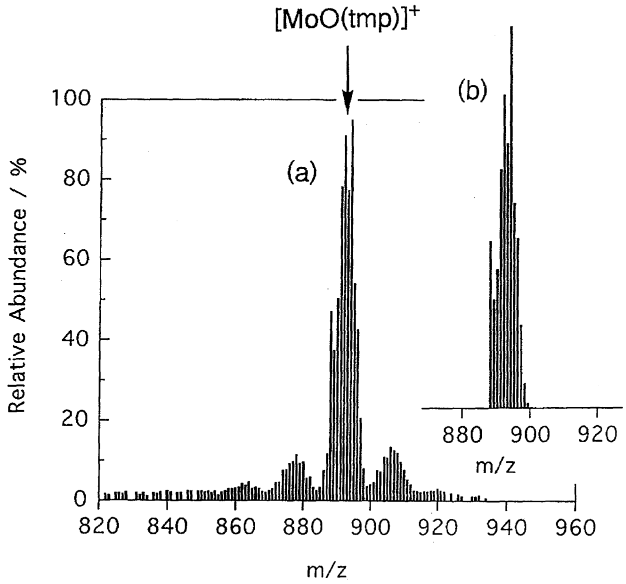


Fig. 4. (a) FAB mass spectrum of the dioxygen complex. (b) Simulation spectrum of [MoO(tmp)].

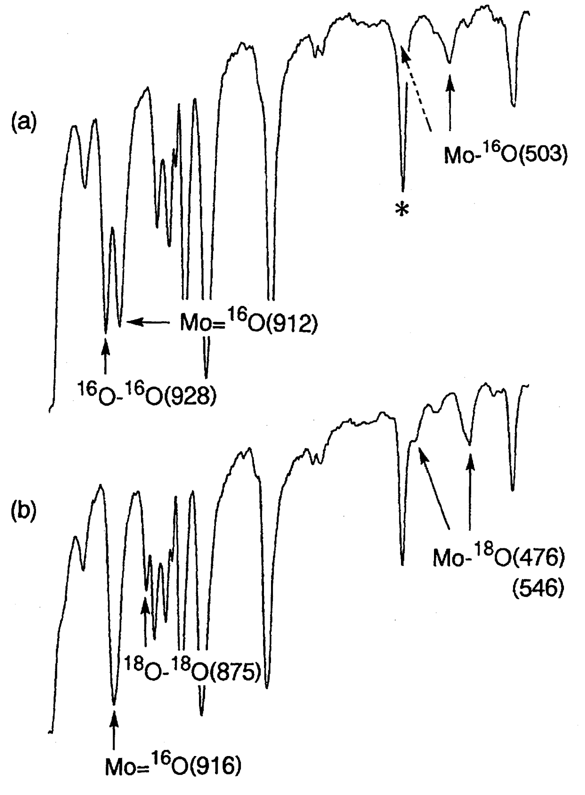
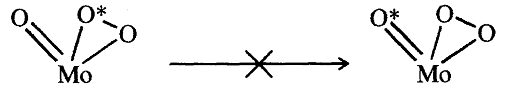


Fig. 5. Infrared spectra of the dioxygen complex (KBr disc). (a) [Mo(^{16}O)(^{16}O$_2$)(tmp)] (b) [Mo(^{16}O)(^{18}O$_2$)(tmp)].

frequency of ν(Mo–^{16}O) should be 574 cm^{-1} in (a) approximated by a harmonic oscillator. However, the expected stretch at 574 cm^{-1} of ν(Mo–^{16}O) in (a) seems to be concealed behind a large peak ($*$ marked in Fig. 5(a)) around 561 cm^{-1}. Two Mo–O streches should be attributed to symmetric and antisymmetric vibrations.26) The ^{16}O–^{16}O16) stretches at 928 cm^{-1} indicates that O$_2$ is coordinated to the central molybdenum with an electronic configuration of a peroxide.26) These facts reveal that Mo and two O atoms of O$_2$ have isosceles triangular geometry, i.e., O$_2$ ligates to Mo with side-on coordination.

The stretch at 912 cm^{-1} in (a) attributable to ν(Mo=^{16}O) was also observed at 916 cm^{-1} in (b). If the dioxygen complex derived from ^{18}O$_2$ has a Mo=^{18}O band, the corresponding stretches should be observed around 868 cm^{-1} in (b). However, Fig. 5 had no Mo=^{18}O stretches around that frequency. These results indicate that the oxo ligand (Mo=^{16}O) in the parent complex of [Mo$^{\mathrm{IV}}$(^{16}O)(tmp)] is still retained during the oxygenation reaction with ^{18}O$_2$. Thus the oxo ligand is not exchanged with oxygen atoms of the peroxide ligand, at least during dioxygenation process.



(5)

Generally, Mo=O stretches of Mo(IV), Mo(V), and Mo(VI) porphyrins are observed in the ranges 952—980, 896—953, and 866—900 cm^{-1}, respectively.27) The Mo=O stretch (912 cm^{-1}) of the dioxygen complex was observed at lower wave number than those of Mo(IV) porphyrin complexes. This evidence refutes the idea that the oxidation state of Mo atom of the dioxygen complex is +4. Considering that the O$_2$ group of dioxygen complex has an electronic configuration of peroxide, one sees that the formal oxidation state of molybdenum is changed from +4 to +6 by two-electron transfers from the central molybdenum atom to O$_2$ during the formation reaction of the dioxygen complex, i.e., the oxidation state of the central molybdenum of dioxygen complex is +6. All other IR peaks of the dioxygen complex can be attributed to Mo-tmp moieties. The solution of the dioxygen complex showed no ESR signal. This is consistent with the molybdenum oxidation state of +6 in the dioxygen complex.

Structure Predicted by ^{1}H NMR Spectral Measurements. Figure 6 shows the ^{1}H NMR spectra of the dioxygen complex in toluene-d_8 at 20, 60, and 80 °C.28) Sharp signals are consistent with a diamagnetic Mo(VI) (d^0) complex. The chemical shifts of the NMR spectra of the complex in CD$_2$Cl$_2$ are summarized in Table 1. The structure is presented on the basis of the spectrum at 20 °C. The β-protons of the pyrrole moieties in the complex gave an AB pattern signal with two doublets at 9.09 and 8.99 ppm, and two singlet signals at 8.68 and 8.27 ppm. This spectral feature and the integral intensities of the protons indicate that the complex has three kinds of pyrrole rings: i.e., (i) two of the four pyrroles are in the same environment and each pyrrole has two nonequivalent protons, (ii) the other two pyrroles are different from each other but each has equivalent protons. The results are indicative of a structure with a symmetry plane passing through two *trans*-N atoms in the porphyrin ring as shown in Fig. 7.

The mesityl proton resonances are consistent with the structure predicted above. A tmp ligand has four mesityl

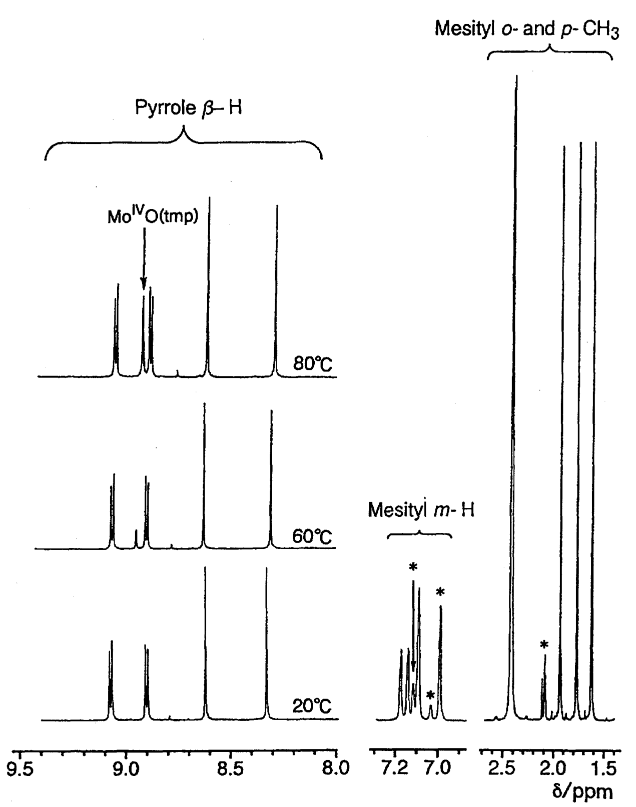


Fig. 6. ^{1}H NMR spectra of [Mo^{VI}O(O$_2$)(tmp)] in toluene-d_8 at 20, 60, and 80 °C under O$_2$ atmosphere (*Solvent).

groups, and each mesityl group has three methyl groups at *o*-, *o*-, and *p*-positions of a phenyl ring, and two protons at *m*-positions. The methyl protons of the mesityl groups gave six singlet signals between 2.61—1.56 ppm, and the *m*-protons gave four singlets between 7.37—7.23 ppm in CD$_2$Cl$_2$. The numbers and the integral intensities of the signals elucidate the C_S symmetry shown in Fig. 7 and the nonequivalence of two sides of the porphyrin plane. Thus the ^{1}H NMR data for β-protons and mesityl groups are adequately explained by the prediction that the oxo and peroxo ligands are coordinated to the central molybdenum from the same side of the porphyrin plane, and eclipse the *trans*-N atoms of the porphyrin ring (Fig. 1). The proposed structure was analogous to the *cis*-oxo peroxo complex [W^{VI}O(O$_2$)(tpp)] which was obtained by the reaction of tungsten(V) tetraphenylporphyrin with H$_2$O$_2$ and characterized by the X-ray structural analysis.[29] The ^{1}H NMR pattern of [Mo^{VI}O(O)$_2$(tmp)] is similar to that of the W^{VI}-tmp analog [W^{VI}O(O$_2$)(tmp)] prepared by the treatment of tungsten(V) tetramesitylporphyrin with H$_2$O$_2$.[30]

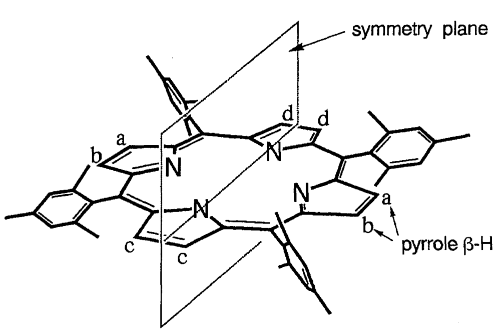


Fig. 7. Symmetric profile deduced from ^{1}H NMR spectra for the dioxygen complex.

On increasing the temperature, signals attributed to [Mo^{IV}O(tmp)] appeared at the expense of those of the dioxygen complex (Fig. 6). This change is reversible. The essential features of the NMR signals of the dioxygen complex remain unchanged over the temperature range between −70 and 80 °C, although some signals slightly shift with temperature.

Kinetics of the Dioxygen Complex Formation. The reaction kinetics between [Mo^{IV}O(tmp)] and O$_2$ in toluene at 20 °C was followed by visible-spectrophotometry. The toluene solution of [Mo^{VI}O(O$_2$)(tmp)] (1.86×10^{-6}—3.69×10^{-6} mol dm^{-3}) under 10^{-3} Torr was photoirradiated for 30 s with 420—700 nm visible light to give free [Mo^{IV}O(tmp)] before introduction of dioxygen. The solution was shaken vigorously for a short time and left standing until no change in pressure was observed. It took less than 1 min after the introduction of dioxygen before measurements of the dioxygenation in the dark were started. The change in absorbance at 432 nm vs. time obeyed the pseudo-first-order rate law in the presence of a large excess of O$_2$ (Fig. 8). The plot of pseudo-first-order rate constants vs. concentration of O$_2$ gave a straight line passing through the vicinity of the origin, as shown in Fig. 9, indicating the dissociation rate was negligibly small compared to the association rate. Thus the second-order association rate was described to be $k_1\{[\mathrm{Mo^{IV}O(tmp)}]\}[\mathrm{O_2}]$ for the reaction (6), where k_1, $\{[\mathrm{Mo^{IV}O(tmp)}]\}$, and [O$_2$] are the association rate constant, the concentration of [Mo^{IV}O(tmp)], and the concentration of O$_2$, respectively.

$$[\mathrm{Mo^{IV}O(tmp)}] + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{MoO(O_2)(tmp)}] \qquad (6)$$

The association rate constant, k_1, was evaluated to be $(3.9\pm0.1)\times10^{-1}$ dm^3 mol^{-1} s^{-1} from the slope of the line in Fig. 9. The k_{-1} should be less than 7×10^{-5}

Table 1. ^{1}H NMR Spectroscopic Data of the [MoO(O$_2$)(tmp)] in CD$_2$Cl$_2$ at 20 °C

Pyrrole β-H	Mesityl m-H	Mesityl p-CH$_3$	Mesityl o-CH$_3$
9.09[a] (2H[b], d[c], 4.9[d])	7.37 (2H, s)	2.61 (6H, s)	2.31 (6H, s)
8.99 (2H, d, 4.9)	7.33 (2H, s)	2.60 (6H, s)	1.97 (6H, s)
8.68 (2H, s)	7.31 (2H, s)		1.75 (6H, s)
8.27 (2H, s)	7.23 (2H, s)		1.56 (6H, s)

a) δ/ppm. b) Intensity. c) s: singlet and d: doublet. d) J/Hz.

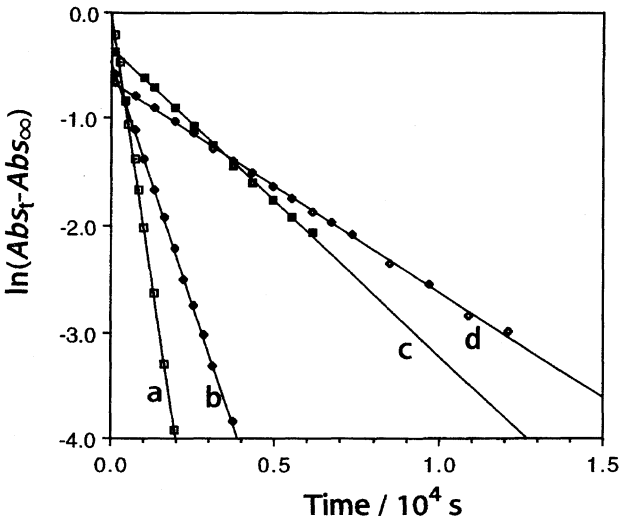


Fig. 8. Typical pseudo-first-order plots of $\ln(Abs_t - Abs_\infty)$ vs. time. (a) 742, (b) 300, (c) 104, and (d) 59 Torr of dioxygen pressure (20 °C, in toluene, $\{[\mathrm{Mo^{IV}O(tmp)}]\} = 1.86 \times 10^{-6}$—$3.69 \times 10^{-6}$ mol dm^{-3}).

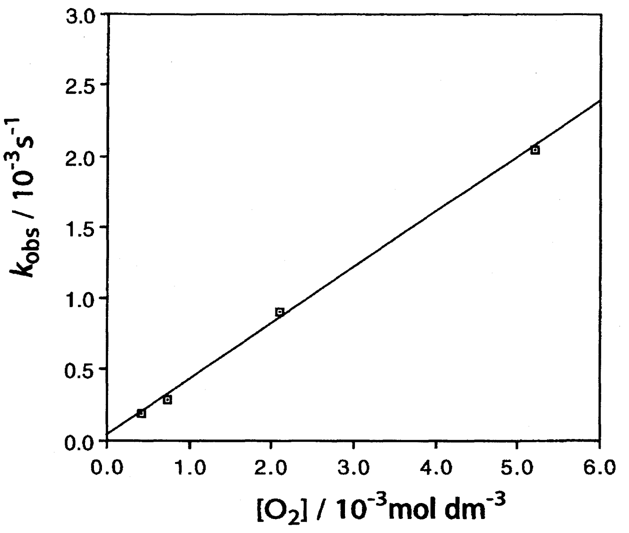


Fig. 9. Plot of the pseudo-first-order rate constant vs. $[O_2]$.

s^{-1}. The value of k_1 is extraordinarily smaller than the rate constants for the oxygenation reaction of Fe(II) porphyrines to form $\mathrm{Fe^{III}}$–(O_2^-) dioxygen complexes (10^5—10^8 dm^3 mol^{-1} s^{-1}).[2a)] Two electron transfers from Mo to O_2 would be the reason for the slow dioxygenation.

Formation of the Dioxygen Complex in the Solid State Process. As observed in the TPD mass spectral measurements, the pyrolysis of the dioxygen complex in the solid state gave [MoO(tmp)] at temperatures higher than 40 °C. The powder of [MoO(tmp)] obtained by heating the dioxygen complex at 120 °C under 10^{-3} Torr underwent reaction with dioxygen to regenerate $[\mathrm{MoO(O_2)(tmp)}]$ which showed characteristic IR bands. Even when the KBr disc of [MoO(tmp)] was left standing in a dioxygen atmosphere or in dry air for a few days, the product gave the characteristic IR spectrum of the dioxygen complex, indicating that the formation of the dioxygen complex also takes place in the solid state. The reversible reaction between [MoO(tmp)] in the solid state and dry dioxygen was confirmed by the in situ UV-vis spectral method, i.e., [MoO(tmp)] formed by photoirradiation of the casted $[\mathrm{MoO(O_2)(tmp)}]$ on the optical cell as a solid film took dioxygen to give the parent complex of $[\mathrm{MoO(O_2)(tmp)}]$ in the dark.[31)]

In the reaction system of [MoO(por)] (por=general porphyrinato) having no bulky substituents, such as [MoO(oep)] and [MoO(tpp)], paramagnetic μ-oxo complexes are formed in solution in the presence of O_2.[20)] The formation mechanisms of the μ-oxo molybdenum(V) porphyrin complexes are presumed to be the same as those of iron(II) systems: via the final stage of the dimerization reaction of $[\mathrm{Fe^{IV}O(por)}]$ with $[\mathrm{Fe^{II}(por)}]$, or the dehydration reaction between two $[\mathrm{Fe^{III}(OH)(por)}]$ molecules.[32)] In the present reaction system, two bulky methyl groups of the tmp ligand positioned perpendicularly to the porphyrin plane would hinder the formation of the corresponding μ-oxo complex. In turn, the results described above suggest that even the metalloporphyrins such as [MoO(tpp)], having no large substituents, can afford a corresponding dioxygen complex in the solid state process. This is because, in the solid state, large porphyrin molecules cannot move freely. Such research is now underway.

Conclusion

The diamagnetic dioxygen complex, $[\mathrm{Mo^{VI}O(O_2)(tmp)}]$, prepared by the reaction of $[\mathrm{Mo^{IV}O(tmp)}]$ with O_2 at room temperature was characterized in detail. The O_2 ligand of the dioxygen complex coordinates side-on to the central molybdenum atom and has the electronic configuration of peroxide. The oxo and the O_2 ligands of the dioxygen complex are coordinated from the same side of the porphyrin plane and eclipse the *trans*-N atoms of the porphyrin ring. The dioxygen complex retains its structure of C_S symmetry between −70 and 80 °C in solution.

By photoirradiation or heating of the dioxygen complex both in solution and in the solid state, $[\mathrm{Mo^{IV}O(tmp)}]$ is formed with the liberation of O_2. $[\mathrm{Mo^{IV}O(tmp)}]$ undergoes reaction with O_2 to give again the dioxygen complex reversibly at room temperature in the dark. The formation rate constant of the dioxygen complex in toluene is smaller than those of the dioxygen adducts of iron porphyrin complexes, probably because of the two-electron transfers from Mo to O_2 ligand.

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