Synthesis and Characterization of a Novel Dioxygen Complex of Molybdenum Porphyrin

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A new molybdenum porphyrin dioxygen complex [Mo^{VI}O(tmp)(O$_2$)],† formed by the reversible reaction of [Mo^{IV}O(tmp)] with dioxygen in aprotic solvents at room temperature, is isolated and characterized by temperature-programmed desorption mass, IR, ^{1}H NMR, and UV–VIS spectroscopy.

Dioxygen complexes are key substances in the oxygen activation cycles such as those of cytochrome P-450 enzyme[1] and catalytic oxygenation reactions of organic substrates;[2-4] molybdenum complexes often acting as coenzymes.[5] It is thus important to clarify their structure, electronic configuration and properties; the reactions of molybdenum porphyrins with dioxygen species have been studied from these viewpoints.[6] [Mo^{V}O(ttp)OMe] undergoes reaction with H$_2$O$_2$ to give [Mo^{VI}(ttp)(O$_2$)$_2$][7,8] and [Mo^{V}O(ttp)X] (X = monoanionic ligand) gives [Mo^{V}O(ttp)(O$_2$)]$^{-9}$ on treatment with O$_2^-$. Formation of a molybdenum porphyrin dioxygen complex in solution by the reaction of [Mo^{IV}O(tpp)] with dioxygen at low temperature has also been described.[10] However, the isolation and synthesis of the dioxygen complexes formed by the reactions of molybdenum porphyrins with dioxygen have not been reported.

Here we describe the first detection, isolation and characterization of a new molybdenum porphyrin dioxygen complex formed by the reversible reaction of [Mo^{IV}O(tmp)],‡ having a bulky porphyrin ligand, with dioxygen in aprotic solvents at room temp. (Fig. 1).§

The electronic spectrum of a toluene solution of [Mo^{IV}O(tmp)] has absorption bands at 430 and 554 nm. By the introduction of dioxygen to the solution at room temp., the peak at 430 nm decreased in intensity, with a concurrent small
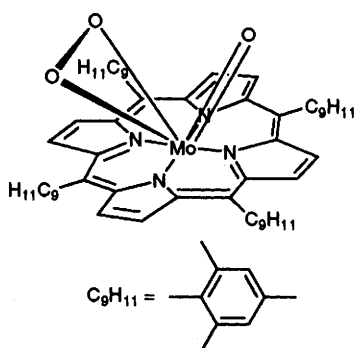
shift of its position to 432 nm, while new peaks at 531 and 563 nm appeared at the expense of the peak at 554 nm. The isosbestic points were observed at 415, 438, 540 and 565 nm (Fig. 2). The final spectrum is similar to that of the tungsten *cis*-oxoperoxo complex, [W^{VI}O(tmp)(O$_2$)] (λ_{max}: 434, 527, 563 nm in toluene) synthesized by the treatment of tungsten(v) tetramesitylporphyrin with H$_2$O$_2$.[13] The photoirradiation of the solution with visible light increased the absorbances at 430 and 554 nm owing to the quantitative regeneration of [Mo^{IV}O(tmp)]. The shading of photoirradiation caused again the formation of the new complex in the presence of dioxygen. These results suggest the reversible formation of a new molybdenum porphyrin dioxygen complex as shown in eqn. (1).

$$[Mo^{IV}O(tmp)] + O_2 \underset{h\nu, \text{ room temp.}}{\rightleftharpoons} [Mo^{VI}O(tmp)(O_2)] \quad (1)$$
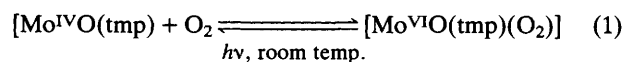
The dioxygen evolution from the solid sample of the dioxygen complex¶ was measured by temperature-
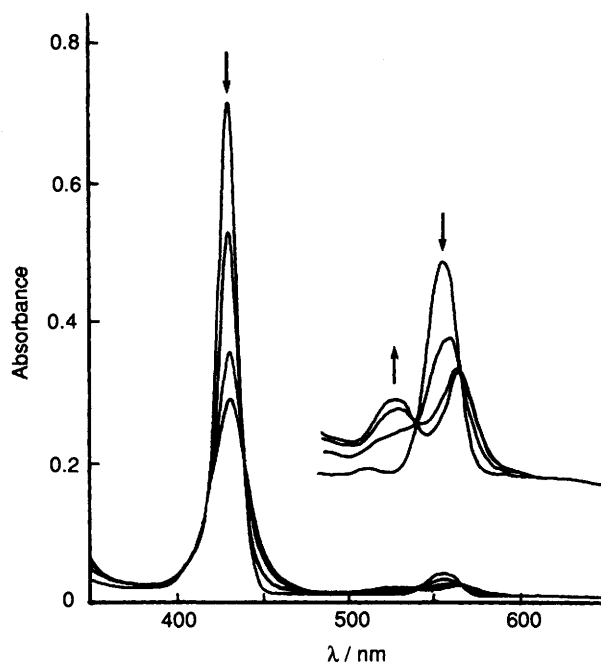

Fig. 1 Predicted structure of the new dioxygen complex [Mo^{VI}O(tmp)(O$_2$)]

Fig. 2 UV–VIS spectral change over 30 min, by the slow introduction of dioxygen into the [Mo^{IV}O(tmp)] toluene solution at 25 °C

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† H$_2$tmp = 5,10,15,20-tetramesitylporphyrin, H$_2$tpp = 5,10,15,20-tetraphenylporphyrin and H$_2$ttp = 5,10,15,20-tetra-*p*-tolylporphyrin.

‡ [Mo^{IV}O(tmp)] was prepared by the pyrolysis[11] of [Mo^{V}O(tmp)-OMe] or of the new complex [Mo^{VI}O(tmp)(O$_2$)] in the solid state. [Mo^{V}O(tmp)OMe] was synthesized by a similar method from [Mo^{V}O(tpp)OMe].[12] UV–VIS spectrum of [Mo^{IV}O(tmp)] in toluene (nm) at 25 °C: 430 (453 × 10^3 dm^3 mol^{-1} cm^{-1}), 554 (36.4 × 10^3); ^{1}H NMR δ ([^{2}H$_8$]toluene, 20 °C): 8.99 (8 H, pyrrole H), 7.16 (4 H, *m*-H), 7.12 (4 H, *m*-H), 2.47 (12 H, *p*-Me), 1.94 (12 H, *o*-Me), 1.75 (12 H, *o*-Me). Since the complex in the solid state absorbs dioxygen from air to form the dioxygen complex, elemental analysis by a general method was of no practical use in gauging its purity.

§ The present complex is different from the complex formed at low temperature by the reaction of [Mo^{IV}O(tmp)] with dioxygen. The UV–VIS spectrum of the complex formed in toluene at low temperature has absorption bands at 398, 455, 468 (shoulder), 590, and 650 nm at −70 °C.

¶ A solid sample of the new complex was obtained in the dark as follows: H$_2$tmp (1 g) and an excess (2 g) of [Mo(CO)$_6$] were refluxed gently for 2 h in the mixed solvents of decaline (72 ml) and octane (18 ml). The solution was evaporated to dryness *in vacuo*. The residue was dissolved in toluene and loaded on a silica gel column followed by elution using toluene as an eluant. The red second band was collected and evaporated to afford a mixture of [Mo^{IV}O(tmp)] and the target complex. The products were dissolved in dioxygen-saturated toluene to complete the dioxygenation of [Mo^{IV}O(tmp)]. The complex was crystallized by the addition of *n*-pentane to the solution and dried under a dry dioxygen atmosphere (yield, 32%). Elemental analyses were satisfactory. UV–VIS spectrum in toluene (nm) at 20 °C: 432 (169 × 10^3 dm^3 mol^{-1} cm^{-1}), 531 (12.2 × 10^3), 563 (14.0 × 10^3).
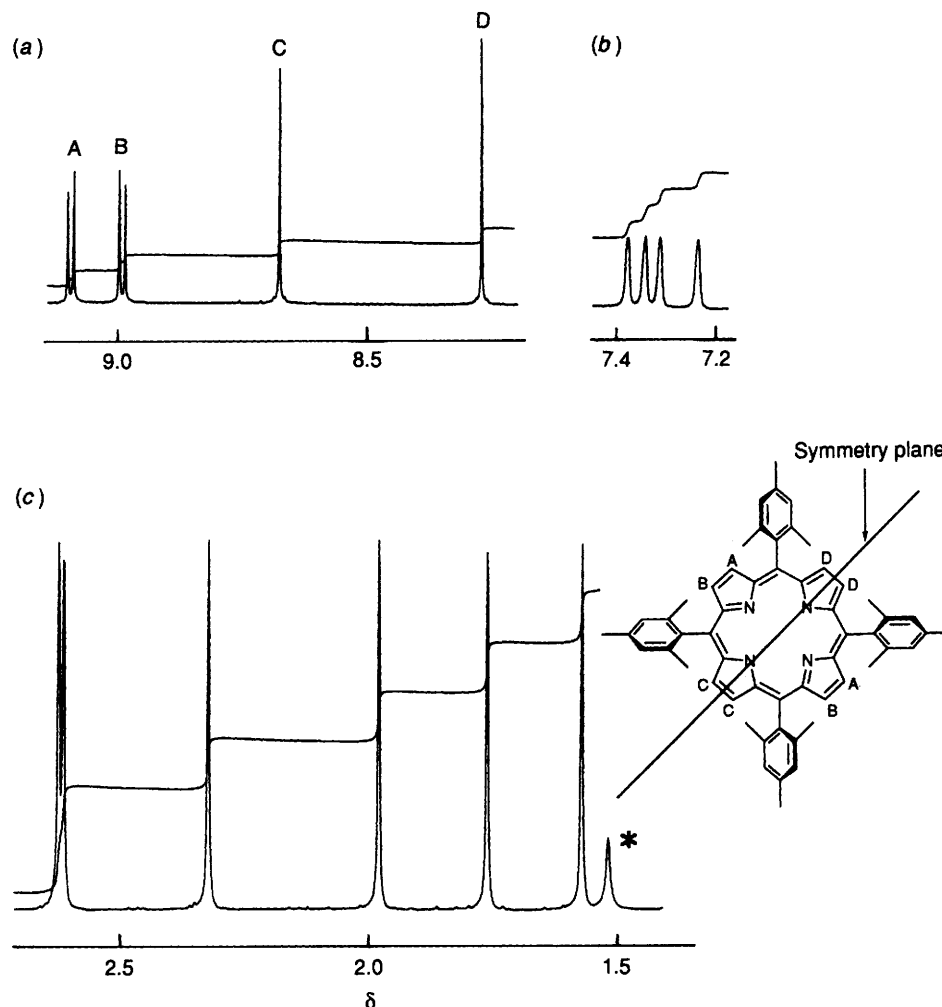
Fig. 3 ^{1}H NMR spectra of [Mo^{VI}O(tmp)(O$_2$)] in CD$_2$Cl$_2$ at 25 °C. Signals indicated: (a) β-protons of the pyrrole moieties, (b) m-protons of mesityl groups and (c) o- and p-methyl protons of mesityl groups (* H$_2$O impurity)

programmed desorption (TDP) mass spectrometry under 10^{-4}–10^{-5} Pa between 30 and 300 °C. Liberation of the dioxygen was detected at ca. 40 °C, and occurred maximally at 80 °C leaving [Mo^{IV}O(tmp)]. The difference in mass before and after the pyrolysis, evaluated after compensation for buoyancy, indicated that the dioxygen complex is composed of 1:1 molar ratio of [MoO(tmp)] to O$_2$. [Mo^{IV}O(tmp)] also absorbed dioxygen in the solid state to regenerate the dioxygen complex.

The IR spectrum of the dioxygen complex (KBr pellets) showed bond stretches at 928 and 503 cm^{-1}, attributable to ν(^{16}O–^{16}O) and ν(Mo–^{16}O), respectively. For the dioxygen complex synthesized using ^{18}O$_2$ instead of ^{16}O$_2$, the bond stretches shifted to 875 and 476 cm^{-1}, respectively. The extent of the isotopic shifts are in good agreement with the assignments to diatomic O–O and Mo–O vibrations, respectively. The IR measurements clarified that O$_2$ is coordinated to the central molybdenum with an electronic configuration of a peroxide, i.e. the oxidation state of the central molybdenum is +6. The other band observed at 911 cm^{-1} was assigned to ν(Mo=O), by comparison with the cis-dioxo complex [Mo^{VI}(ttp)(O)$_2$].[7]

Structural data were deduced from the ^{1}H NMR study. The ^{1}H NMR signals of the dioxygen complex in CD$_2$Cl$_2$ at room temp. were characteristic of diamagnetic porphyrins as shown

in Fig. 3, in accord with the +6 oxidation state of the central molybdenum. The β-protons of the pyrrole moieties gave two doublet signals at δ 9.09 and 8.99, and two singlets at δ 8.68 and 8.27. This spectral feature and the integral intensities of the protons indicate that the complex molecule has three kinds of pyrrole rings. Namely, (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. This result shows that the structure of the dioxygen complex has a symmetry plane passing through two trans N atoms. The mesityl proton resonances (o-Me: δ 2.31, 1.97, 1.75, 1.56; p-Me: δ 2.61, 2.60; m-H: δ 7.37, 7.33, 7.31, 7.23) support the symmetry of the complex derived from the pyrrole protons. The ^{1}H NMR data for β-protons and mesityl groups are the result that the oxo and peroxo ligands of the dioxygen complex are coordinated to the central molybdenum from the same side of the porphyrin plane and eclipse the trans N atoms of the porphyrin ring.

These results of mass, IR, ^{1}H NMR, UV–VIS spectroscopy and elemental analysis, confirm that the new molybdenum porphyrin dioxygen complex, formed by the reversible reaction of [Mo^{VI}O(tmp)] with molecular oxygen, has a structure as shown in Fig. 1. The complex is very attractive to the study of catalytic oxygenation reactions of organic substrates.

Further studies of the detailed molecular structure and potential functions of this novel dioxygen complex are now in progress.

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