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INTERMEDIATE IN THE REACTION OF OXOMOLYBDENUM(V) TETRAPHENYLPORPHYRIN COMPLEX WITH SUPEROXIDE ION IN APROTIC SOLVENTS

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$Mo^VO(tpp)Br$ (tpp = meso-tetraphenylporphinato) is reduced by superoxide ion, O_2^-, to $Mo^{IV}O(tpp)$ in 1%(v/v) DMSO-CH_2Cl_2 medium at 25 °C via an intermediate. The intermediate is suggested to be a dioxygen complex and stably exists in the solution at - 72 °C. The oxidation state of the central molybdenum in the intermediate complex reversibly changes with temperature between 4+ at - 80 °C and 5+ at 0 °C.

Elucidation of the mechanisms of the formation of dioxygen complexes of metalloporphyrins provides insight into the mechanisms of transport and storage of dioxygen by hemoglobin and myoglobin and of activation of dioxygen by cytochrome-P450 and by cytochrome oxidase in vivo. The study of the mechanisms of the formation of dioxygen complexes itself is also of great interest to inorganic chemists because of its versatility in the application to complex formation and electron transfer reactions. Recently, superoxide has been given attention for its multiplicity of reactions in which superoxide acts as oxidant, reductant, or ligand depending on the conditions such as solvents and temperature.[1,2] Superoxide often behaves as a unidentate ligand in aprotic solvents to form complexes such as $[Zn^{II}(tpp)(O_2^-)]^-$,[3,4] $[Mn^{II}(tpp)(O_2^-)]^-$,[1,5] and $[Fe^{III}(ppde)(O_2^-)]$.[6] The formation of peroxo complexes, $[Fe^{III}(porph)(O_2^{2-})]^-$, by the reaction of iron(II) porphyrins with superoxide was also reported.[4,7]

In this communication, the formation of a new dioxygen complex of oxomolybdenum tetraphenylporphyrin by the reaction of $Mo^VO(tpp)Br$ with superoxide in aprotic solvent at low temperature is reported. Stability and magnetic properties of this dioxygen complex largely depend on the temperature of the solution.

Electronic spectra. The visible absorption spectrum of the dichloromethane solution of $Mo^VO(tpp)Br$ at 25 °C has the Soret band, the β band, and the α band at 508, 638, and 686 nm, respectively.[8] In dichloromethane solution containing 1%-(v/v) dimethyl sulfoxide, the absorption peaks of these bands shift to 477, 604, and 648 nm, respectively. This spectral shift is ascribed to the formation of dimethyl sulfoxide complex, $[Mo^VO(tpp)(dmso)]Br$.[9] By the addition of a large excess of O_2^- to the 1%(v/v) dimethyl sulfoxide-dichloromethane solution of $Mo^VO(tpp)Br$, the absorbances of these peaks of $[Mo^VO(tpp)(dmso)]Br$ rapidly decrease with the appearance of two new peaks at 445 and 428 nm (Fig. 1). The new peak at

445 nm reversely begins to decrease with time with increasing absorbance at 428 nm. The final spectrum agrees with the spectrum of the complex, $Mo^{IV}O(tpp)$, synthesized and isolated independently.[10)] The spectrum characterized by the absorption peak at 445 nm can be ascribed to that of the reaction intermediate (complex 1).

When a large excess of O_2^- is added to the dichloromethane solution of $Mo^{V}O(tpp)Br$ at - 72 °C, the complex 1 is formed and is stably present in the solution (Fig. 2). Namely no formation of $Mo^{IV}O(tpp)$ is observed. The molar absorption coefficients at - 72 °C of the absorption maxima of the complex 1 at 445, 565, 586, 604, and 635 nm are determined to be 35.3×10^4, 0.95×10^4, 1.29×10^4, 0.79×10^4, and 1.47×10^4 $mol^{-1}\ dm^3\ cm^{-1}$, respectively. The spectrum of the solution of the complex 1 keeps the shape with a rise in the temperature from - 72 °C to 0 °C; the molar absorption coefficients decrease by 17% over the whole visible region. By the additional rise in the temperature from 0 °C to 25 °C, the absorption peaks due to the complex 1 decrease with the appearance of the peaks of the spectrum of $Mo^{IV}O(tpp)$. This spectral change from the complex 1 to $Mo^{IV}O(tpp)$ has isosbestic points.

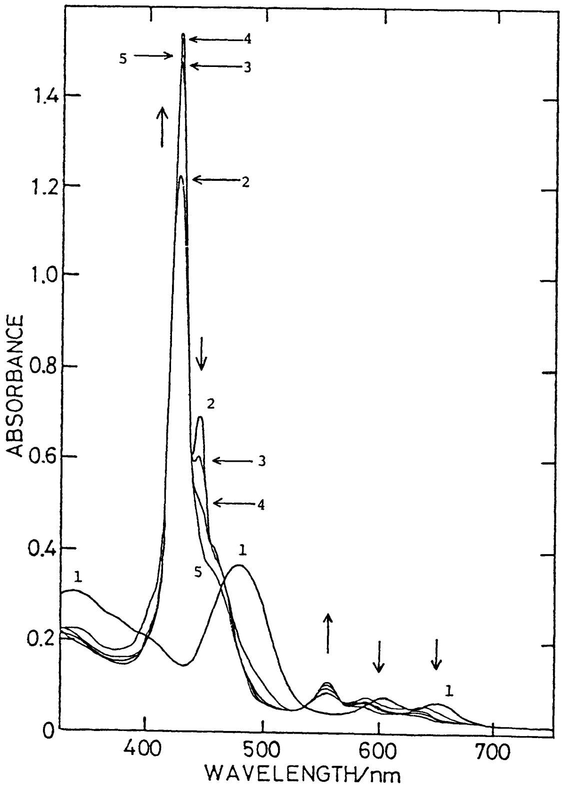


Fig. 1 The spectral change in the reaction of $Mo^{V}O(tpp)Br$ with O_2^- in 1% (v/v) $DMSO-CH_2Cl_2$ at 25 °C: (1) $[Mo^{V}O(tpp)(dmso)]Br$; (2) 40 s after the addition of O_2^-; (3) 4 min 25 s; (4) 19 min 40 s; (5) 117 min 40 s. The concentrations are $[Mo^{V}O(tpp)Br]_0 = 7.86 \times 10^{-6}$ and $[O_2^-]_0 = 2.16 \times 10^{-4}$ $mol\ dm^{-3}$.

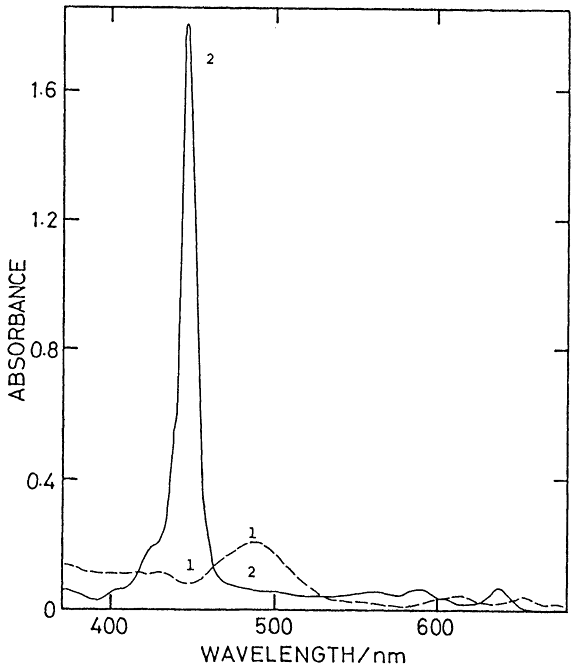
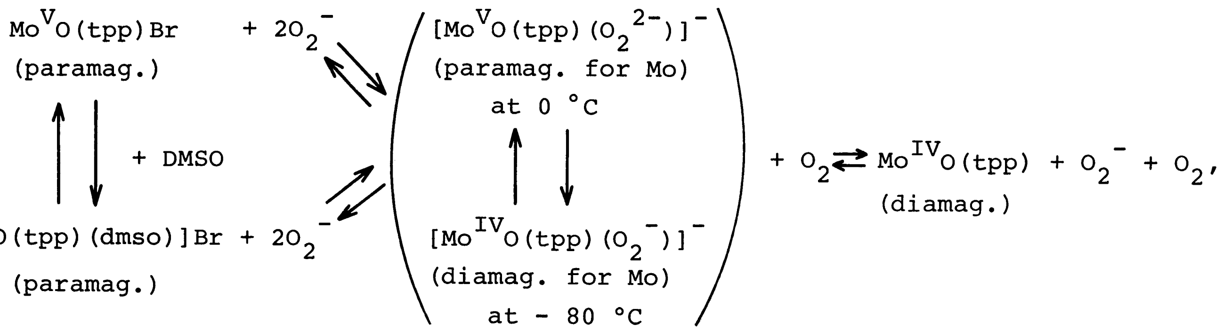


Fig. 2 Visible absorption spectra in 1% (v/v) $DMSO-CH_2Cl_2$ at - 72 °C of $[Mo^{V}O(tpp)(dmso)]Br$ (1) and of the complex 1 formed by the reaction of $Mo^{V}O(tpp)Br$ with O_2^- (2). The concentrations are $[Mo^{V}O(tpp)Br]_0 = 4.83 \times 10^{-6}$ and $[O_2^-]_0 = 9.13 \times 10^{-5}$ $mol\ dm^{-3}$.

ESR measurements. The ESR spectrum of the dichloromethane solution of $Mo^{V}O(tpp)Br$ consists of a strong central line ($\bar{g}$ = 1.967) due to $^{94,96,98,100}Mo$ nuclei (I = 0) and six weak lines due to $^{95,97}Mo$ nuclei (I = 5/2).[12] The solution prepared from $Mo^{V}O(tpp)Br$ and a large excess of O_2^- is ESR silent at - 80 °C but affords the ESR signal due to $^{94,96,98,100}Mo$ nuclei at $\bar{g}$ = 1.971 with the rise of the temperature to 0 °C. The height of the signal reversibly changes over the temperature range between - 80 and 0 °C. These results indicate that the complex 1 stably exists in the solution at low temperature in the presence of a large excess of O_2^- and that the oxidation states of the central molybdenum atom varies from 4+ (diamag.) at - 80 °C to 5+ (paramag.) at 0 °C. The rise of the temperature of the solution to 25 °C causes the decrease of the intensity of the ESR signal with time, which corresponds to the formation of $Mo^{IV}O(tpp)$ (diamag.) from the complex 1.

Mechanism of the reaction. The stoichiometry of the formation reaction of the complex 1 at - 72 °C was determined to be $Mo^{V}O(tpp)Br : O_2^- = 1 : 2$ by the molar ratio method. Gas was evolved in the course of this reaction and was confirmed to be dioxygen by mass spectrometry. These results and the magnetic properties of the complex 1 suggest that the chemical formula of the complex 1 is $[Mo^{IV}O(tpp)(O_2^-)]^-$ at - 80 °C and $[Mo^{V}O(tpp)(O_2^{2-})]^-$ at 0 °C. The overall reaction scheme is described as follows:



where the magnetism written in parentheses is that of the molybdenum atom in the complexes.

When the solution of $Mo^{V}O(tpp)Br$ contains a trace amount of alcohol, the alcoxo complex, $Mo^{V}O(tpp)OR$, is formed by the addition of O_2^-.[8]

The crude crystals of the complex 1 were obtained from $Mo^{V}O(tpp)Br$ and KO_2 powder using 18-crown-6 as a phase transfer catalyst in hexane-dichloromethane at - 72 °C. The electronic spectrum of the dichloromethane solution of the crude crystals at - 72 °C is almost the same as that of the complex 1 observed in the reaction of $Mo^{V}O(tpp)Br$ with a large excess of O_2^- shown in Fig. 2. The former spectrum is converted into the spectrum of $Mo^{IV}O(tpp)$ with a rise in the temperature to 25 °C.

Materials and procedure. $Mo^{V}O(tpp)Br$ was synthesized according to the previously described method.[8] Dichloromethane was distilled and passed through a basic alumina column to remove stabilizer.[13] The pre-purified solvent was dried over Molecular Sieves 4A and distilled under Ar immediately before use. Dimethyl sulfoxide was kept with calcium hydride for several days, distilled at 37 °C under reduced pressure, and stored under Ar atmosphere. The solution of superoxide was prepared from potassium superoxide (ICN Pharmaceuticals) solubilized by 18-crown-6 (Nippon Soda) in DMSO under Ar atmosphere.14) The concentration of superoxide in DMSO was determined by photometric titration with iodine.15) All experiments were performed under anaerobic conditions.

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10) $Mo^{IV}O(tpp)$ was prepared according to a modified method of the literature11) describing $Mo^{IV}O(ttp)$ (ttp = meso-tetra-p-tolylporphinato) and purified by sublimation in vacuo at 280 °C. λ_{max} and ε_{max} of visible absorption peaks in dichloromethane at 25 °C are 428 nm ($\varepsilon = 29.0 \times 10^4$ mol^{-1} dm^3 cm^{-1}), 554 (1.59×10^4), and 589 (0.31×10^4).
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