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Facile Pyrolytic Preparation of *cis*-Dioxoporphyrinatomolybdenum(VI) from *trans*-Diperoxoporphyrinatomolybdenum(VI)

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Synopsis. *cis*-Dioxo (tetraphenylporphyrinato)molybdenum(VI) [$Mo^{VI}(O)_2$(tpp)] (tpp=5,10,15,20-tetraphenylporphyrinato) is easily prepared by the pyrolysis of the corresponding diperoxoporphyrinato complex [$Mo^{VI}(O_2)_2$(tpp)] releasing dioxygen gas at 200 °C under 10^{-3}—10^{-4} Torr (1 Torr ≈ 133.3 Pa).

The chemistry of oxo-metal complexes is intense interests in relation to the mechanism of oxygen-atom- and electron-transfer reactions and ability as catalysts for oxygenation reactions.[1] *cis*-Dioxoporphyrinatomolybdenum(VI) is only one stable isolated metalloporphyrin[2] whose two oxo ligands are coordinated to the central metal atom from the same side of the porphyrin plane.[3] The *cis*-dioxo complex is supposed to act as an oxygenation catalyst for other compounds; in practice, it reacts with triphenylphosphine to give triphenylphosphine oxide[4,5] and also catalizes the formation of acetone from 2-propanol in the presence of air.[6]

The *cis*-dioxo complex was first prepared by Ledon et al. from *trans*-diperoxoporphyrinatomolybdenum(VI) photochemically.[4] Our preliminary study of the photochemistry of *trans*-diperoxo(tetraphenylporphyrinato)molybdenum(VI) [$Mo^{VI}(O_2)_2$(tpp)] (tpp=5,10,15,20-tetraphenylporphyrinato) confirmed that the corresponding *cis*-dioxo complex [$Mo^{VI}(O)_2$(tpp)] was surely formed by the photoirradiation of the dichloromethane solution of [$Mo^{VI}(O_2)_2$(tpp)] with visible light as reported.[6] However, successive photoirradiation causes reduction of the *cis*-dioxo complex to form [$Mo^{IV}(O)$(tpp)].[7] This result and high molar absorption coefficients of these metalloporphyrins have stood in the way of the large scale photochemical preparation of the *cis*-dioxo complex.

In this communication, facile new preparation of *cis*-dioxoporphyrinatomolybdenum(VI) by the pyrolysis of *trans*-diperoxoporphyrinatomolybdenum(VI) in the solid state is reported.

The [$Mo^{VI}(O_2)_2$(tpp)] complex has electronic spectral bands at 445, 573, and 612 nm in toluene at room temperature. The powder of [$Mo^{VI}(O_2)_2$(tpp)] was heated at 200 °C for 4 h under 10^{-3}—10^{-4} Torr (1 Torr ≈ 133.3 Pa). A small amount of [$Mo^{VI}(O_2)_2$(tpp)] was sublimed during the pyrolysis. The toluene solution of the pyrolyzed product thus obtained has electronic spectral bands at 424, 533, and 563 nm (Fig. 1). These bands agreed with those of the corresponding *cis*-dioxo comlex [$Mo^{VI}(O)_2$(tpp)] which was separately prepared photochemically (Table 1). The solution shows no ESR signals, indicating the formation of ESR-silent species such as d^0 [$Mo^{VI}(O)_2$(tpp)]. The ^{1}H NMR spectra of the product in CD_2Cl_2 at 270 MHz revealed that only one porphyrin species was formed by the pyrolysis. The ortho protons, meta and para protons of phenyl groups, and β-pyrrole protons were observed around δ 8.21, 7.84, and 9.02 at 21 °C respectively. The sharpness of the resonance lines indicated that the porphyrin is diamagnetic. The coalescent spectrum of ortho protons at 21 °C was split into doublet at −10 °C and quartet at −70 °C reflecting the non-equivalent behavior of the ortho-ortho′ protons due to asymmetric axial ligation.

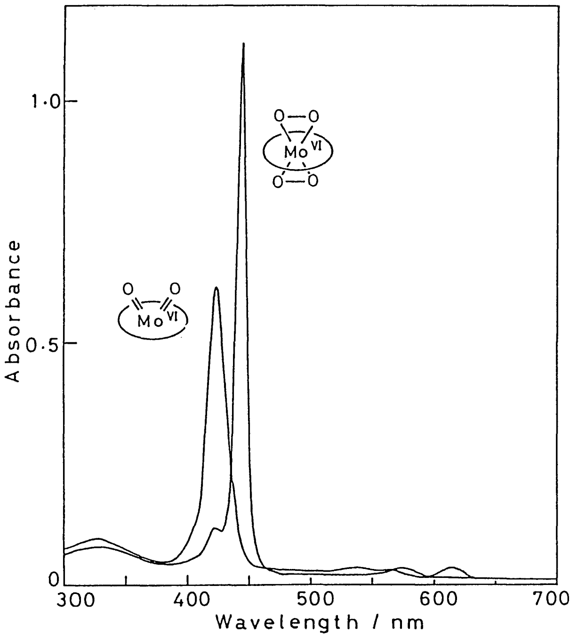


Fig. 1. Visible absorption spectra in toluene at 25 °C of [$Mo^{VI}(O_2)_2$(tpp)] and [$Mo^{VI}(O)_2$(tpp)] of the pyrolyzed product.

Table 1. Absorption Bands in UV-Visible Region

Complex	Solvent	λ_{max}/nm (ε/10^4 $mol^{-1} dm^3 cm^{-1}$) at 25 °C				
[$Mo^{VI}(O_2)_2$ (tpp)]	CH_2Cl_2	321(6.19)	443(62.3)	530(1.19)	573(3.74)	612(4.17)
	Toluene	322	445		573	612
[$Mo^{VI}(O)_2$ (tpp)]	CH_2Cl_2	321(8.83)	422(37.3)	485(1.59)	532(3.00)	563(2.44)
	Toluene	322	424		533	563

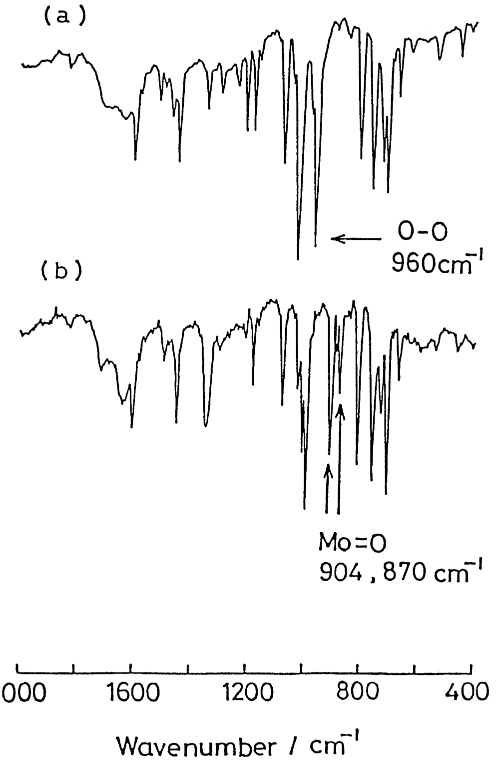
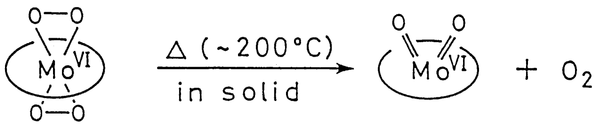


Fig. 2. Infrared spectra (KBr pellet) of $[Mo^{VI}(O_2)_2(tpp)]$ (a) and $[Mo^{VI}(O)_2(tpp)]$ of the pyrolyzed product (b).

This ^1H NMR spectral feature of the ortho protons is essentially the same with that of the $[Mo^{VI}(O)_2(ttp)]$ (ttp=5,10,15,20-tetra-*p*-tolylporphyrinato) system.[4] The evolution of dioxygen gas in the pyrolysis was confirmed by EI-mass spectral measurements that showed characteristic bands due to dioxygen and oxygen atom at m/z=32 and 16 respectively. The IR spectrum of $[Mo^{VI}(O_2)_2(tpp)]$ (KBr pellet) has a characteristic band at 960 cm^{-1} of O–O stretchings (Fig. 2a). By the pyrolysis, the band disappeared with appearance of new bands at 904 and 870 cm^{-1} which are ascribed to the stretchings of Mo=O bonds (Fig. 2b). Usually further purification is unnecessary.[8] The result of elemental analysis of the red-purple complex obtained agreeds with the empirical formura $C_{44}H_{28}N_4O_2Mo$ of the *cis*-dioxo complex (~100% yield). Anal. Calcd for $[Mo^{VI}(O)_2(tpp)]$: C, 71.34; H, 3.82; N, 7.57%. Found: C, 71.23; H, 3.72; N, 7.45%. Namely, the pyrolysis of $[Mo^{VI}(O_2)_2(tpp)]$ at 200 °C affords $[Mo^{VI}(O)_2(tpp)]$ releasing dioxygen gas (Scheme 1). This method is very facile and suitable for large scale preparations of the *cis*-dioxo complex.



Scheme 1.

The *cis*-dioxo complex does not form seven coordinate complexes such as $[Mo^{VI}(O)_2(tpp)L]$ (L=dimethyl sulfoxide, pyridine) in toluene even at low temperatures although $[Mo^{IV}O(tpp)]$ forms $[Mo^{IV}O(tpp)L]$.[9] X-Ray structural analysis for $[Mo^{VI}(O)_2(ttp)]$ shows that the molybdenum atom lies at 0.972 Å from the 4N plane formed by pyrrole nitrogens.[3] The displacement of the molybdenum atom for the *cis*-dioxo complex having horse-saddle-type structure is much larger than that of the $[Mo^{IV}O(tpp)]$ pyramidal complex: 0.6389 Å.[10] This may make difficult the coordination of such ligands to the central molybdenum from the reverse side of the dioxo ligands.

Experimental

Absorption spectra were recorded on a Hitachi 808 spectrophotometer. Infrared spectra were measured with a Hitachi 270-50 spectrophotometer. A Hitachi RMU-6 EI-mass spectrometer was used to detect the gas evolved in the pyrolysis of *trans*-diperoxoporphyrinatomolybdenum(VI) $[Mo^{VI}(O_2)_2(tpp)]$. The complex was prepared by the reported method.[11] Toluene was purified and stored in the vessel on a vacuum line.

References

1) For example, see: R. H. Holm, *Chem. Rev.*, **87**, 1401 (1987); K. A. Jøgensen, *Chem. Rev.*, **89**, 431 (1989).

2) The formation of unstable $W^{VI}(O)_2(tpp)$ has been reported in *J. Chem. Soc., Chem. Commun.*, **1985**, 1425, by C.-H. Yang, S. J. Dzugan, and V. L. Goedken.

3) B. F. Mentzen, M. C. Bonnet, and H. J. Ledon, *Inorg. Chem.*, **19**, 2061 (1980).

4) H. Ledon, M. Bonnet, and J.-Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, **1979**, 702.

5) H. Ledon and M. Bonnet, *J. Mol. Catal.*, **7**, 309 (1980).

6) H. Ledon, F. Varescon, T. Malinski, and K. M. Kadish, *Inorg. Chem.*, **23**, 261 (1984).

7) P. Bergamini, S. Sostero, and O. Traverso, *J. Chem. Soc., Dalton Trans.*, **1986**, 2311.

8) When occasion demands, the product is chromatographed on a silica-gel column using dichloromethane and recrystallized from benzene-hexane solution followed by drying at 150 °C in vacuo.

9) K. Hasegawa, T. Imamura, and M. Fujimoto, *Inorg. Chem.*, **25**, 2154 (1986).

10) Th. Diebold, B. Chevrier, and R. Weiss, *Inorg. Chem.*, **18**, 1193 (1979).

11) B. Chevrier, Th. Diebold, and R. Weiss, *Inorg. Chim. Acta*, **19**, L57 (1976).