Photoejection of a Dioxygen Ligand during the Photolysis of Bisperoxo-molybdenum(VI) Porphyrin. Synthesis and Characterisation of *cis*-Dioxo-molybdenum(VI) Tetra-*p*-tolylporphyrin

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Summary Photolysis of bisperoxo-molybdenum(VI) porphyrins with a tungsten lamp produces the related *cis*-dioxo-molybdenum(VI) complex.

THE synthesis of bisperoxo-molybdenum(VI) tetra-*p*-tolylporphyrin (TTP)$Mo^{VI}(O_2)_2$ (**1**) (TTP = tetra-*p*-tolylporphyrin) has recently been reported.[1] As peroxo-molybdenum complexes are well known oxidizing reagents,[2,3] we studied the reactivity of (**1**). It seemed that in such a complex the co-ordination of a substrate such as an olefin to the metal atom would be unlikely owing to the steric hindrance of the porphyrin ligand, thereby making it possible to distinguish between the previously proposed mechanisms of intramolecular reaction of the co-ordinated substrates and attack of free olefins on a dioxygen complex.[4]

The peroxo-complex (**1**) was prepared from (TTP)$Mo^{V}O$(OMe)[5] following the published procedure,[1] but extreme care was taken to conduct the reaction in the dark as (**1**) is light-sensitive in solution. The reaction was monitored by u.v.–visible spectroscopy. Compound (**1**) was found to be unexpectedly thermally stable and no traces of oxidation products from reaction with cyclohexene or triphenyl phosphine were detected.

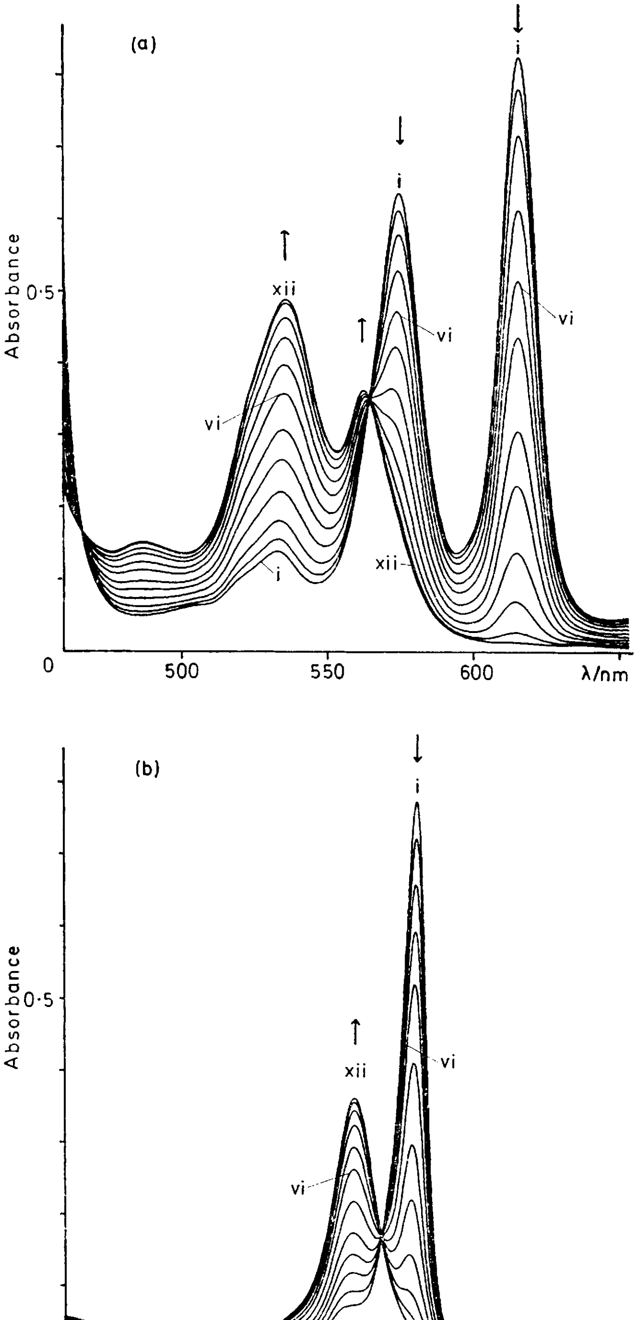

FIGURE 1. U.v.-visible spectra of a C_6H_6 solution of (**1**) irradiated with a 100 W tungsten lamp. (a): $c = 1{\cdot}6 \times 10^{-5}$ mol l^{-1}; $l = 2$ cm; time (i) 0, (ii) 1, (iii) 2, (iv) 5, (v) 8, (vi) 12, (vii) 17, (viii) 22, (ix) 28, (x) 35, (xi) 44, and (xii) 55 min. (b): $c = 8{\cdot}5 \times 10^{-7}$ mol l^{-1}; $l = 2$ cm; time (i) 0, (ii) 15, (iii) 35, (iv) 60, (v) 90, (vi) 125, (vii) 180, (viii) 245, (ix) 320, (x) 410, (xi) 520, and (xii) 660 s.

Upon irradiation under argon (100 W tungsten lamp with Pyrex filter), a deep green benzene solution of (**1**) [λ_{max} ($\epsilon \times 10^{-3}$ l mol^{-1} cm^{-1}) 615 (23·8), 574 (19·4), 533 (4·2), and 445 nm (465)] slowly turned cherry-red [562 (11·0), 535 (15·2), 487 (4·6), 425 (216), and 323 nm (40·4)].† As shown in Figure 1, five well-defined isosbestic points were obtained at 564, 468, 435, 364, and 345 nm, indicating that only two absorbing species were present in the solution. The same reaction was observed in toluene dichloromethane, and tetrahydrofuran. Concentration of the solution, followed by chromatography over silica gel to remove the unchanged bisperoxo complex (**1**), and crystallisation from benzene afforded dark red crystals of a compound which was shown, by elemental analysis, to have the formula (TTP)$MoO_2{\cdot}1{\cdot}0\ C_6H_6$ (**2**). Mass spectra were obtained in the field-desorption mode; at 30 °C the expected molecular ion $M^{+\cdot}$ (m/e 792, ^{92}Mo) was observed. At higher temperatures and in the electron impact mode, only m/e 776 was observed, which is consistent with $(M - O)^{+\cdot}$; a good fit was obtained between the calculated and observed isotopic distributions.[6] Careful examination of the fragmentations observed in the electron impact mode revealed that they were the same as those obtained for (TTP)$Mo^{V}O$(X) (X = Cl or OMe), indicating that there was no modification of the porphyrin ring during the reaction.

The high resolution ^{1}H n.m.r. spectra of (**2**) were recorded at 250 MHz in $ClCD_2CD_2Cl$ from +110 °C to room temperature and in CD_2Cl_2 down to −100 °C. The sharpness of the resonance lines indicated that this complex is diamagnetic. The β-pyrrole protons and the methyl protons of the tolyl groups appear, respectively, as singlets at δ 8·88 and 2·59 relative to Me_4Si. Figure 2 shows the temperature dependence of the resonance lines of the aromatic tolyl protons. At +110 °C only one AB system is observed, then coalescence occurs near room temperature and at −70 °C the spectrum exhibits two AB systems. This behaviour is typical of an asymmetric axial ligation of the metalloporphyrin.[7] At high temperatures the rotation of the tolyl groups with respect to the plane of the porphyrin is fast relative to the n.m.r. time scale but is frozen at low temperatures causing non-equivalence of the *ortho–ortho′* and *meta–meta′* protons so that two AB patterns appear.

The i.r. spectrum of (**2**) (KBr pellets) exhibits new absorptions at 990s, 900s, 882w, 866s, 680m, and 441w cm^{-1}, whereas the ν_{O-O} vibration at 970 cm^{-1} in (**1**) disappears, and the intensity of the absorption at 1025 cm^{-1} is largely reduced.‡ ^{18}O-Labelling experiments were carried out as Sharpless[4] has shown that, in the case of oxo-peroxomolybdenum complexes, only the oxo-oxygen atoms are exchanged with $H_2{}^{18}O$. A benzene solution of (**2**) was treated with 100 equiv. of 99% ^{18}O-enriched water for 10 h. Only the vibrations at 900 and 866 cm^{-1} were affected in the i.r. spectrum thus identifying these bands as oxo-molybdenum vibrations. The band at 900 cm^{-1} was split into a doublet of approximately equal intensity at 900 and 892 cm^{-1}, and that at 866 cm^{-1} was found to be shifted to 832 cm^{-1}. These results rule out the peroxo-molybdenum(IV) structure (**2a**) which should suffer no oxygen

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† This reaction was found to be quantitative when carried out in very dilute solution (10^{-5}—10^{-6} mol l^{-1} for u.v.-visible spectra) but on a preparative scale it was found to be more convenient to stop the irradiation after *ca.* 95% conversion, as a very slow decomposition of (**2**) was observed under prolonged photolysis.

‡ At variance with Chevrier (ref. 1), we never observed a vibration at 685 cm^{-1} in the i.r. spectra of (**1**) or of the related tetraphenylporphyrin complex.

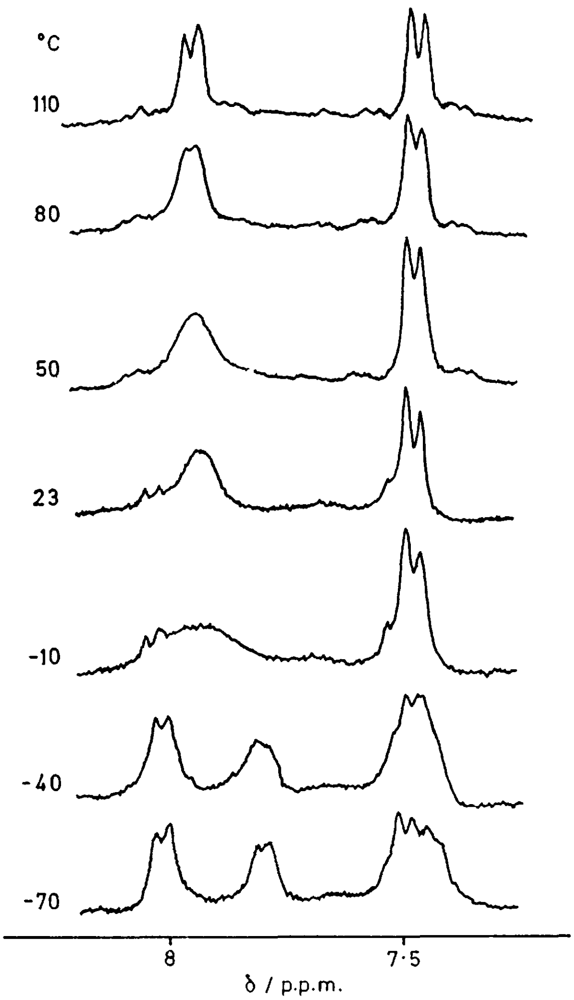
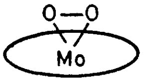
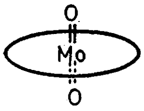


FIGURE 2. Temperature dependence of the 250 MHz ^{1}H n.m.r. spectrum of (**2**) in the aromatic tolyl protons region. Shifts are given in p.p.m. from Me$_4$Si.

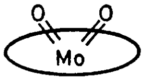
isotopic exchange with H$_2$^{18}O. The only possible structure is then a dioxo-molybdenyl porphyrin, (**2b**) or (**2c**). The *trans*-dioxo structure (**2b**) is inconsistent with the n.m.r. results which indicate an asymmetric axial ligation of the metalloporphyrin. Two strong absorptions have been found near 900 cm^{-1} in the i.r. spectrum, which are also observed in dichloromethane solution, suggesting a *cis*-dioxo arrangement of the oxygen atoms as in (**2c**),[8] a structure which is invariably found in molybdenum complexes.[9] The two bands may be attributed to the symmetric and asymmetric stretch of the *cis*-dioxo group, respectively.



(2a)



(2b)



(2c)

The proposed *cis*-dioxo-molybdenum(VI) tetra-*p*-tolylporphyrin structure for (**2**) was confirmed by its reactivity towards phosphines. Preliminary results show that triphenylphosphine reacts with (**2**) in benzene solution at room temperature, affording a mixture of triphenylphosphine oxide (ν 721 and 542 cm^{-1}, characteristic of the phosphine oxide) and oxo-molybdenum(IV) porphyrin [λ_{max} ($\epsilon \times 10^{-3}$ l mol^{-1} cm^{-1}) 555 (15) and 432 nm (200)] as expected.[10]

In conclusion, irradiation of bisperoxo-molybdenum(VI) porphyrins affords the related *cis*-dioxo complexes. This is the first example of a metalloporphyrin having a *cis*-bis-(monodentate) axial ligation[11] and, to the best of our knowledge, *cis*-dioxo-molybdenum complexes with a planar quadridentate ligand have not been reported previously.[12] We attribute the high reactivity of (**2**) towards triphenylphosphine oxidation to the steric strain release during the oxygen atom transfer stage.

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