Structure and Reactivity of an Unusual Tungsten(VI) Porphyrin Complex having *cis* Oxo and Peroxo Groups

Chiou-Herr Yang, Sharlene J. Dzugan, and Virgil L. Goedken*

Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006, U.S.A.

The structure of W(TPP)(O)(O_2) (TPP = tetraphenylporphyrinato) has been shown to have a *cis* arrangement of oxo and peroxo groups which are eclipsed with respect to the porphyrin nitrogen atoms.

The chemistry of tungsten porphyrin complexes has not been developed as much as that of lighter homologues and, to our knowledge, no reports of W^{VI} porphyrin or of any single crystal structural work of tungsten porphyrin complexes have appeared. A previous report described the synthesis of some W^V porphyrin complexes and their oxidative demetallation.[1] Because of the importance of oxo and peroxo metal complexes as intermediates in the oxidation of organic substrates, we report herein the synthesis and characterization of W(TPP)(O)(O_2) (TPP = tetraphenylporphyrinato) obtained by the reaction of H_2O_2 with W^V complexes. This formulation is based upon the i.r. spectrum which contained in addition to the usual porphyrin absorptions, new absorptions at 930 and 886 cm^{-1}. On the basis of the closely related oxo complexes[2] and the peroxo complexes[3] of Mo^{VI}, the 930 cm^{-1} absorption is assigned to the peroxo group and the 886 cm^{-1} to the W=O stretching modes.† The ^1H n.m.r. spectrum as well as its temperature dependence indicated a very asymmetric porphyrin environment consistent with the placement of the oxo and peroxo groups on the same side of the porphyrin plane. ^1H n.m.r. (270 MHz) δ −50 °C: 9.33 (AB quartet, 4H, pyrrole), 9.01 (s, 2H, pyrrole), 8.69 (s, 2H, pyrrole), 8.42 (m, 2H), 8.32 (m, 2H), 8.05 (d, 2H), 7.94 (d, 2H, *o*-phenyl), 7.83 (br m, 12H, *p*-phenyl); u.v.–visible spectrum in benzene (nm): 608 (2.63×10^3 dm^3 mol^{-1} cm^{-1}), 559 (14.08×10^3), 526 (12.88×10^3), 432 (239×10^3).

The crystal structure‡ of W(TPP)(O)(O_2) has a number of unusual features relevant to both metal peroxo binding and to metallo-porphyrin complexes. These are summarized as follows: (i) The W is displaced unusually far, 1.49 Å, to one side of the N_4 plane. This should be compared with the more modest value of 0.972 Å for the *cis*-dioxo Mo^{VI}(TPP) complex[2] and values of 1.174 Å for Pb(TPP)[4] and 1.35 and 1.40 Å for $Sn(Pc)_2$[5] and $U(Pc)_2$[6] respectively (Pc = phthalocyanato). (ii) Because of this large displacement, the oxo and peroxo groups are necessarily *cis*. (iii) The oxo and peroxo groups eclipse the *trans* N atoms of the porphyrin. The oxo groups of $Mo(TPP)(O)_2$ are staggered with respect to the porphyrin nitrogen atoms. Most probably as a result of (iii) two quite different W–N bond distances are observed: those where the N atoms are eclipsed by the oxo and peroxo groups are notably longer, 2.298 and 2.287 Å than the other two, 2.086 and 2.092 Å. The W=O and W–O_2 distances, 1.752(13) and 1.909(15) Å (av.) are within the ranges expected for this type of complex. The O–O distance, 1.36(1) Å is not

---

† Attempts to assign the peroxo symmetric stretching absorption using resonance Raman techniques were unsuccessful because of rapid photodecomposition of the complex.

‡ Crystals of W(TPP)(O)(O_2)·C_6H_6 are red-purple, triclinic, space group $P\bar{1}$, with $a = 12.027(7)$, $b = 13.046(5)$, $c = 14.897(5)$ Å, $\alpha = 64.16(3)$, $\beta = 71.14(5)$, $\gamma = 69.86(5)°$, $Z = 2$, $U = 1933(1)$ Å^3. $R = 4.9$, $R_w = 5.9$ for 8274 independent reflections ($2\theta < 55°$) with $|F_o| > 2\sigma(|F_o|)$ collected on a CAD-4 diffractometer with Mo-K_α radiation.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this work.

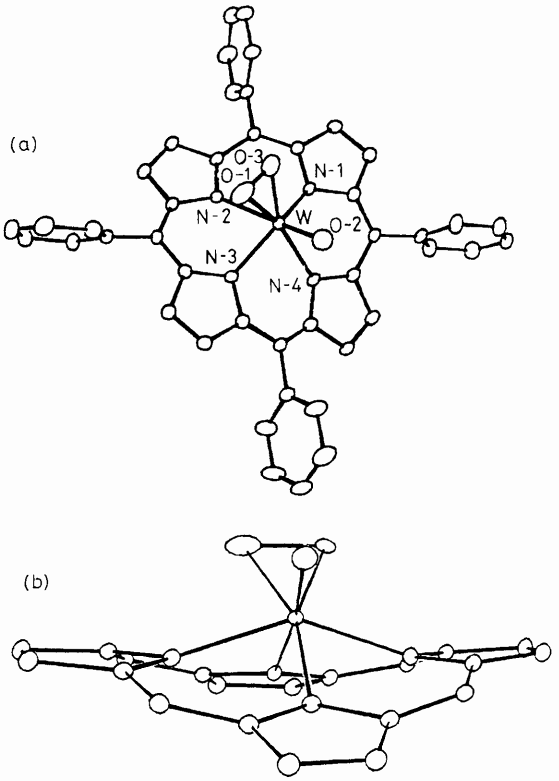

Figure 1. Two views of W(TPP)(O)(O_2) with thermal ellipsoids reduced for clarity of presentation. (a) View approximately normal to the porphyrin plane to illustrate the eclipsed nature of the O and O_2^{2-} bonding. (b) View illustrating the displacement of the W from the porphyrin plane and the double saddle shape of the ligand (the phenyl groups are omitted for clarity).

particularly reliable in view of the 0.35 : 0.65 disorder of the oxo and peroxo groups. The 'off-to-the-side' bonding of the peroxo group eliminates one of the bonding interactions, the $\pi^*(O_2^{2-}) \rightarrow d_{xy}$, which exists for complexes where the O_2^{2-} group is symmetrically placed over the porphyrin and eclipses the nitrogen atoms.[7] The non-equivalence of the two types of *trans* bonding with respect to the nitrogen atoms leads to the most warped porphyrin skeleton reported to date. Two of the pyrrole nitrogen donors are directed toward the tungsten (N-2 and N-4) with an intersection angle between pyrrole planes of 146.6° while the other two pyrrole units are tipped in the opposite sense, relative to the porphyrin, with an intersection angle of −171.9°, resulting in significant mismatch between the bonding orbitals of tungsten and the porphyrin (see Figure 1).

The large displacement of the W from the N_4 plane and the 'off-to-the-side' bonding of the peroxo group may account for the higher reactivity of the title complex compared with other metallo-porphyrin complexes and their peroxo derivatives. Long standing (days) in $CHCl_3$ leads to decomposition involving both demetallation and rupture of the porphyrin ring, as indicated by the u.v.–visible, mass, and i.r. spectra. Reaction with triphenylphosphine for several hours at room temperature (or 10 min at 80 °C) produces a new W^{VI} complex, the *cis*-dioxo species, W(TPP)$(O)_2$. I.r.: symmetric and antisymmetric M=O stretch 918 and 867 cm^{-1} [compare with 900 and 866 cm^{-1} for Mo(TPP)$(O)_2$],[2] ^1H n.m.r. (270 MHz) δ (room temp.): 9.04 (8H, pyrrole), 8.35—7.8 (br, 8H, *o*-phenyl), 7.78 (br m, 12H, *p*-phenyl). The *cis*-dioxo W^{VI} is even more unstable than its oxo-peroxo precursor, undergoing demetallation within hours in solution as indicated by the gradual appearance of the characteristic absorptions of H_2TPP in the visible spectrum and in the ^1H n.m.r. spectrum. This demetallation is consistent with the previously reported oxidative demetallation of the W^V complexes.[1]

Received, 5th July 1985; Com. 956

References

1 E. B. Fleischer, R. D. Chapman, and M. Krishamurthy, *Inorg. Chem.*, 1979, **18**, 2156.
2 E. B. Mentzen, M. C. Bonnet, and H. J. Ledon, *Inorg. Chem.*, 1980, **19**, 2061.
3 B. Chevrier, Th. Diebold, and R. Weiss, *Inorg. Chim. Acta*, 1976, **19**, L57.
4 K. M. Barkigia, J. Fajer, A. D. Adler, and G. J. B. Williams, *Inorg. Chem.*, 1980, **19**, 2057.
5 W. E. Bennett, D. E. Broberg, and N. C. Baenziger, *Inorg. Chem.*, 1973, **12**, 930.
6 A. Gieren and W. Hoppe, *Chem. Commun.*, 1971, 413.
7 J. Ellinger, J. M. Latour, J. C. Marchon, and R. Subra, *Inorg. Chem.*, 1978, **17**, 2024.