The Autoxidation of a Chromium(II) Porphyrin: Synthesis and Structural Characterisation by X-Ray Crystallography of αβγδ-Tetraphenylporphinato-oxochromium(IV)

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Summary The reaction of dioxygen with αβγδ-tetraphenyl-porphinatochromium(II) in toluene proceeds in two stages; a μ-oxo-chromium(III) intermediate is formed initially and this then further reacts with dioxygen to give the title complex, the structure of which has been determined by X-ray crystallography.

STUDIES on the autoxidation of iron(II) porphyrin compounds in toluene have implicated the iron(IV) ferryl species, PFeO (P = porphyrin dianion), as a reactive intermediate leading to the formation of the stable μ-oxo dimer product, {PFe}$_2$O.[1] Ferryl porphyrin complexes have also been postulated as key intermediates in enzymatic oxidations involving haem-containing oxygenases and peroxidases and recent research on Cr^V,[2] Mn^{IV},[3] Mn^V,[4] 'Fe^{IV},'[5] and 'Fe$^{V'2}$,[6] oxometalloporphyrin complexes supports this contention. In this communication we describe the formation of the chromyl porphyrin, TPPCrO (TPP = dianion of αβγδ-tetraphenylporphyrin), by O$_2$ oxidation of TPPCr in toluene solution, and its characterisation by single-crystal X-ray analysis. This analysis was undertaken to resolve an initial uncertainty as to the nature of the axial ligands.

TPPCr was prepared by zinc amalgam reduction of TPPCrCl[7] in tetrahydrofuran. The tetrahydrofuran was removed *in vacuo* and the residue extracted with hot deoxygenated toluene. The dark red solution of TPPCr (λ$_{max}$ 422, 542, 575sh, and 600sh nm) was then filtered and exposed to the air. The solution immediately turned burgundy-red (λ$_{max}$ 431, 544, and 577sh nm) with TPPCrO being formed in 80% yield, based on TPPCrCl. Similar results were obtained using a sample of TPPCr prepared by tetrakisacetylacetonatodichromium reduction[8] of TPPCrCl. Satisfactory elemental analyses were obtained for TPPCrO; i.r. (KBr disc): ν(Cr=O), 1020 cm^{-1};[2] n.m.r. (CD$_2$Cl$_2$): δ 7·83 (m, 12H, m- and p-Ph), 8·22 (s, 8H, o-Ph), and 9·11 (s, 8H, pyrrole); μ$_{eff}$. *ca.* 0 B.M.

A crystal of TPPCrO, suitable for X-ray analysis, was grown from toluene–hexane by solvent diffusion. *Crystal data:* C$_{44}$H$_{28}$CrN$_4$O, $M = 680\cdot24$, tetragonal, space group $I4/m$, $a = 13\cdot351(6)$, $c = 9\cdot749(5)$ Å, $U = 1737\cdot75$ Å^3, $D_m = 1\cdot30(1)$, $D_c = 1\cdot30$ g cm^{-3}, $Z = 2$, $F(000) = 703\cdot94$. Single-crystal data were measured with a Philips automatic four-circle diffractometer using graphite-monochromated Cu-K_α radiation ($\lambda = 1\cdot5418$ Å); 346 unique reflections [$I > 3\sigma(I)$] were measured by the θ–2θ scan technique ($3° \leqslant \theta \leqslant 60°$). The small irregular crystal (*ca.* $0\cdot12 \times 0\cdot12 \times 0\cdot10$ mm) dictated the use of Cu-K_α radiation and precluded the application of an absorption correction.

In the closely related six-co-ordinate zinc and iron TPP complexes[9] the metal atoms, that are out of the TPP plane, and associated axial ligands are disordered, as the result of being inverted with respect to the TPP ligand in 50% of the

molecules. Even though it was clear from the space group and unit-cell dimensions that this compound was isomorphous with the zinc and iron TPP compounds,[9] the displacement of the chromium atom from the origin was not known. The chromium and oxygen atoms were located in a difference Fourier synthesis computed with coefficients derived from a structure-factor calculation based on the atomic co-ordinates of the TPP moiety of the iron complex. The complete model with hydrogen atoms in calculated positions was refined by full-matrix least-squares techniques to a final R of $0\cdot0772$ (R_2 $0\cdot0709$). All non-hydrogen atoms were assigned anisotropic thermal parameters and each reflection was weighted by a factor σ^{-2} (F) (σ is the standard deviation for a reflection). The atomic scattering factors used[10] were for Cr°, N°, O°, C°, and H° and were corrected for anomalous dispersion.[11]†
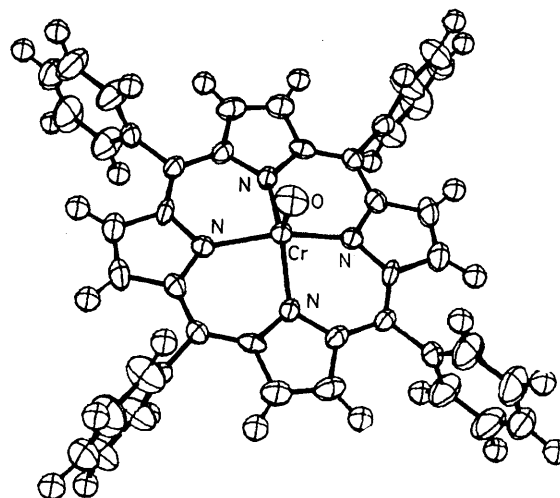

FIGURE 1. Molecular structure of TPPCrO (60% ellipsoids, except H which has 30% ellipsoids) showing the molecular symmetry: a 4-fold axis. The statistically averaged molecule has 4/m symmetry.

The structure of TPPCrO (Figure 1) is similar to that of TPPMoO[12] and also other five-co-ordinate oxometallo-porphyrin complexes.[13] The chromium atom is $0\cdot489(6)$ Å out of the porphyrin plane towards the oxygen atom and the Cr–O and Cr–N bond lengths are, respectively, $1\cdot62(2)$ and $2\cdot036(9)$ Å. The structures of TPPCrO and TPPMoO differ in that the latter porphyrin is slightly domed. The four pyrrole nitrogen atoms are in the plane of the porphyrin for TPPCrO, but are $0\cdot09$ Å from the plane in TPPMoO.[12]
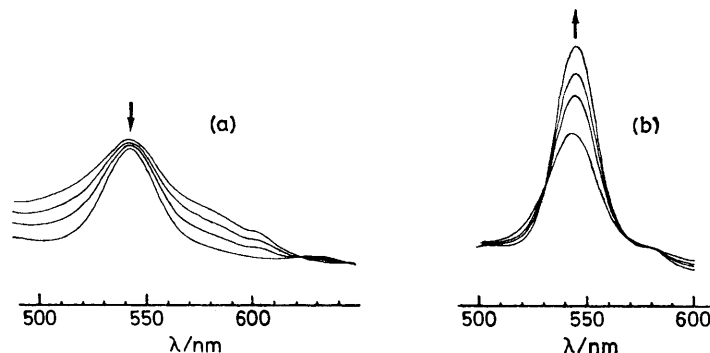
FIGURE 2. Changes occurring in the visible spectrum of a $1\cdot25 \times 10^{-4}$M solution of TPPCr in toluene during its titration with air-saturated toluene. Spectral changes are in the directions of the arrows. The traces are for ratios of (moles of O_2 added)/(moles of TPPCr initially present), respectively, of (a), 0, 0·09, 0·17, 0·26, and (b) 0·30, 0·39, 0·43, 0·50.

The stoicheiometry of the reaction between TPPCr and O_2 in toluene has been established by titrating a solution of TPPCr with toluene, saturated with air, and monitoring the reaction spectrophotometrically. Figure 2a shows the spectral changes occurring until the ratio of TPPCr to O_2 reaches 4 : 1.‡ Further addition of O_2 results in the spectral changes shown in Figure 2b. When the TPPCr to O_2 ratio of 2 : 1 is reached, the reaction is complete.

These results imply that there are two distinct stages in the reaction leading to the formation of TPPCrO. In the initial stage, the reaction stoicheiometry strongly supports the formation of a μ-oxo-chromium(III) intermediate according to the equation (1). After all the TPPCr has been

$$4\text{TPPCr} + O_2 \rightarrow 2\{\text{TPPCr}\}_2O \qquad (1)$$

consumed, the second stage of the reaction (Figure 2b) begins with $\{\text{TPPCr}\}_2O$ and O_2 reacting to give TPPCrO [equation (2)].

$$2\{\text{TPPCr}\}_2O + O_2 \rightarrow 4\text{TPPCrO} \qquad (2)$$
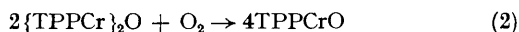
Further support for the formation of $\{\text{TPPCr}\}_2O$ has been obtained by treating a sample of TPPCr with excess of TPPCrO and titrating the resultant solution with O_2 as before. The spectral changes were uniform throughout the titration and paralleled *exactly* those shown in Figure 2b. These observations are consistent with $\{\text{TPPCr}\}_2O$ being formed according to equation (3).

$$\text{TPPCr}^{IV}O + \text{TPPCr}^{II} \rightarrow \{\text{TPPCr}\}_2O \qquad (3)$$
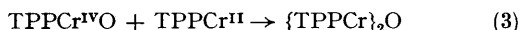
Although ferryl porphyrin complexes have been implicated as reactive intermediates during the autoxidation of PFe in toluene,[1] no *direct* experimental evidence has been obtained for their existence. Therefore, the isolation and complete characterisation of TPPCrO, from the reaction between TPPCr and O_2, provides a strong chemical precedent for the suggested PFeO intermediate. Further, equation (3) is analogous to that proposed for the mechanism of formation of $\{\text{PFe}\}_2O$, from PFe and PFeO.[1]

In comparing the autoxidations of TPPCr and PFe, we note that μ-oxo-species are formed in both cases. However, a further reaction of $\{\text{TPPCr}\}_2O$ with O_2 readily occurs, implying it is a stronger reducing agent than $\{\text{TPPFe}\}_2O$. $\{\text{TPPFe}\}_2O$ is known to undergo reversible one-electron oxidations at 0·79 and 1·03 V (*vs.* standard calomel electrode and in $R_4NClO_4-CH_2Cl_2$).[14]

The proposition that TPPCrO and PFeO complexes are involved as intermediates in the respective autoxidations of TPPCr and PFe in toluene has clearly been strengthened by the isolation and characterisation of TPPCrO. TPPCrO is the first well defined oxidation product of a chromium(II) porphyrin and, to date, the only high-valent chromium metalloporphyrin to be structurally characterised. We are currently investigating the mechanism of formation and reactivity of TPPCrO.

‡ At TPPCr : O_2 = 4 : 1, the visible spectrum shows λ_{max} 412 and 542 nm.

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