Retention of Configuration at the Titanium Atom upon Oxo–Peroxo Ligand Substitution of Titanium(IV) Porphyrins

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Summary N.m.r. spectra of oxo- and peroxo-titanium(IV) complexes of a suitably substituted tetraphenylporphyrin suggest that formation of the peroxo-species from the oxo-compound and hydrogen peroxide takes place with retention of configuration; labelling experiments indicate that this ligand exchange is a true substitution, *i.e.* the O–O bond of H_2O_2 remains intact in the peroxo complex.

PEROXO complexes are formed when oxotitanium(IV) complexes react with hydrogen peroxide. The thermodynamic aspects of this ligand exchange[1] and the structure of the peroxotitanium(IV) products[2,3] have been the subjects of numerous studies. Little is known, however, about the mechanisms of these substitution reactions. We now report the stereochemical course of this reaction with titanium(IV) porphyrin complexes.

A porphyrin bearing face-differentiating substituents, H_2dip (Figure), was prepared according to a published procedure.[4] Treatment of this free base with titanium tetrachloride–pyridine in refluxing dimethylformamide,[5]

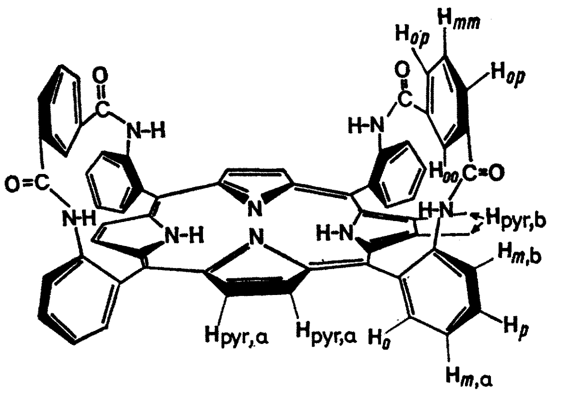
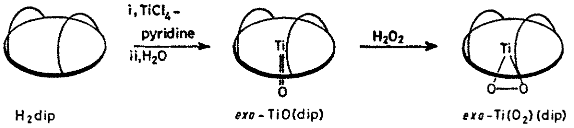


FIGURE. The structure of the ligand H_2dip. The proton labels are used for n.m.r. assignments in the text.

followed by hydrolysis and chromatography on silica gel gave the expected oxotitanium(IV) complex TiO(dip) in 70% yield. All available evidence suggests that only one of the two possible isomers is formed under these conditions. T.l.c. showed a single spot, and ^{1}H n.m.r. spectroscopy revealed a simple pattern of peaks consistent with the presence of only one isomer: δ 9·61 (s, $H_{pyr,\,a}$), 8·88 (s, $H_{pyr,\,b}$), 8·77 (d, $H_{m,b}$), 8·71 (d, H_o), 7·98 (t, H_p), 7·81 (t, $H_{m,a}$), 7·23 (d, H_{op}), 6·97 (s, N–H), 6·84 (t, H_{mm}), and 6·40 (s, H_{oo}) (see Figure for assignments). The possibility of a fast intermolecular exchange between the two isomers, resulting in an averaging between the two sets of resonances, can be ruled out by previous experiments which showed that oxotitanium(IV) porphyrin complexes are substitutionally inert.[5] Indeed, the *ortho*-phenyl protons of oxotitanium(IV) tetraphenylporphyrin, TiO(tpp), exhibit two distinct resonances (δ 8·17 and 8·57), reflecting a magnetic inequivalence of the two faces of the porphyrin induced by the presence of a single axial ligand.[5,6]

The TiO(dip) complex is assigned the *exo* configuration (Scheme) on the following grounds. In the simple oxo- and peroxo-titanium(IV) tetraphenylporphyrin complexes, TiO(tpp) and Ti(O_2)(tpp), we assign the set of *ortho*-phenyl protons located on the face devoid of axial ligand to the resonances at higher field (δ 8·17 and 8·16, respectively), while those on the liganded face are at lower field (δ 8·57 and 8·41, respectively). The resonance for TiO(dip) (δ 8·71) therefore suggests that the *ortho* protons are on the liganded face, *i.e.* the *exo* configuration. Moreover, a Ti–O stretching frequency is observed at 980 cm^{-1} in the i.r. spectra of both TiO(tpp) and TiO(dip), reflecting identical environments for the oxo ligand.

Treatment of *exo*-TiO(dip) with hydrogen peroxide in dichloromethane according to a published procedure[3] gave a single isomer of Ti(O_2)(dip) in essentially quantitative yield. The ^{1}H n.m.r. spectrum of this peroxo complex is strikingly similar to that of *exo*-TiO(dip): δ 9·40 (s, $H_{pyr,\,a}$), 8·84 (s, $H_{pyr,\,b}$), 8·77 (d, $H_{m,\,b}$), 8·63 (d, H_o), 7·96 (t, H_p), 7·79 (t, $H_{m,\,a}$), 7·27 (d, H_{op}), 6·94 (s, N–H), 6·88 (t, H_{mm}), and 6·38 (s, H_{oo}). The small shifts obtained upon oxo–peroxo ligand exchange in this system are in the range observed for Ti(O_2)(tpp) and TiO(tpp),[3] and allow the safe conclusion that the product has retained the *exo* configuration (Scheme). That *exo*-Ti(O_2)(dip) is the kinetic product is suggested by the fact that Ti(O_2)(tpp) is configurationally stable; the two resonances for the *ortho*-phenyl protons are preserved in the presence of an excess of hydrogen peroxide.



SCHEME

Isotopically labelled reagents were used to investigate further the mechanism of this oxo–peroxo ligand substitution. Ti^{18}O(tpp) (ν_{Ti-O} 940 cm^{-1}) was obtained by equilibration of TiO(tpp) (ν_{Ti-O} 980 cm^{-1}) with excess of $H_2{}^{18}O$ (99% isotopic purity) over a period of several days. Treatment of this labelled complex with unlabelled H_2O_2 (5 M solution in H_2O) gave only unlabelled Ti(O_2)(tpp) (ν_{O-O} 906 cm^{-1}), equation (1). A control experiment

$$\mathrm{Ti^{18}O(tpp)} + \mathrm{H_2O_2} \rightarrow \mathrm{Ti(O_2)(tpp)} \qquad (1)$$

showed that under these conditions of high water concentration Ti^{18}O(tpp) does not lose its label to a significant extent (<5% decrease) during the time necessary for reaction (1).

Similarly, reaction of unlabelled TiO(tpp) with doubly labelled $H_2{}^{18}O_2$ (85% isotopic purity, 0·25 M solution in $H_2{}^{16}O$) afforded doubly labelled Ti($^{18}O_2$)(tpp) (ν_{O-O} 857 cm^{-1}) but no singly labelled peroxo complex, equation (2). The observed isotopic shifts are consistent with

$$\mathrm{TiO(tpp)} + \mathrm{H_2{}^{18}O_2} \rightarrow \mathrm{Ti(^{18}O_2)(tpp)} \qquad (2)$$

calculations based on diatomic harmonic oscillator models.[7] The obvious conclusion is that the O–O bond of H_2O_2 remains intact throughout the ligand substitution process.

Two stereochemical aspects thus emerge for the oxo–peroxo ligand exchange on titanium(IV) in this system: the integrity of the oxygen–oxygen bond and the retention of configuration at the titanium atom. These features may be rationalized by an associative mechanism in which the intermediate has both the entering and the leaving ligands adjacent to one another on a single face of the porphyrin. Substitution might be favoured by such a mechanism because oxo and peroxo ligands are poor leaving and entering groups and would require some assistance from proton exchange in a cyclic transition state.

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