Dihalide Complexes of Titanium(IV) Tetraphenylporphyrin. Precursors to Low-valent Titanium Porphyrins

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Summary Reaction of the hydrogen halides HF, HCl, and HBr with oxotitanium(IV)tetraphenylporphyrin gives the corresponding dihalogeno titanium(IV) complexes which show a novel pattern of reduction: the difluoride complex provides the first example of a titanium(IV) porphyrin in which the site of the first reduction is the metal ion rather than the porphyrin ring or the axial ligand.

Recently several syntheses of titanium(IV) porphyrins with an axial oxo[1] or peroxo[2] ligand have been reported, but reduction of these complexes has not provided a satisfactory route to low-valent titanium porphyrins. Insertion of Ti into a free-base porphyrin invariably leads to an oxotitanium(IV) complex unless oxygen and/or moisture is rigorously excluded. Previous studies have shown that these oxo complexes are highly stable and the metal centre cannot be reduced; the two one-electron reduction steps which have been observed have been assigned to redox reactions of the porphyrin ring.[1c] In peroxotitanium(IV) porphyrin complexes the site of the first reduction is the edge-bound dioxygen ligand which undergoes a two-electron, irreversible cleavage of the O–O bond leading to the corresponding oxotitanium(IV) complex.[2] We now report the isolation and characterisation of dihalogeno-complexes of titanium(IV) tetraphenylporphyrin ($\mathrm{TPPTi^{IV}X_2}$) (X = F, Cl, or Br) and the easy electrochemical reduction of $\mathrm{TPPTi^{IV}F_2}$ to a titanium(III) porphyrin complex.

Gaseous HF diluted with dinitrogen† was bubbled through hexane in a polyethylene bottle. Dropwise addition of a solution of TPPTiO in dichloromethane, followed by filtration on a polyethylene funnel afforded a 78% yield of green microcrystalline $\mathrm{TPPTiF_2}$.‡ The corresponding green dichloro- and dibromo-complexes were obtained in good yield ($\mathrm{TPPTiCl_2}$: 81%; $\mathrm{TPPTiBr_2}$: 73%) by similar procedures using conventional glassware.‡ Far-i.r. spectra in CsI pellets show the bands expected[3] for titanium–terminal halogen stretching vibrations [ν(Ti–F): 647; ν(Ti–Cl): 358; ν(Ti–Br): 280 cm^{-1}]. In every case the band at 980 cm^{-1} assigned to the titanium–oxygen stretching vibration of the starting complex[1c] has disappeared. The postulated mononuclear nature of the $\mathrm{TPPTiX_2}$ complexes cannot be verified without a single-crystal *X*-ray structure analysis or a molecular weight determination, and measurements of molecular weights are prevented by low solubilities and extreme propensities of solutions towards hydrolysis. An *X*-ray crystallographic study is in progress to elucidate this point and to ascertain the geometry of the $\mathrm{TiX_2}$ group.§ Electronic absorption spectra of dichloromethane solutions made from the crystalline dihalogeno-complexes reveal the presence of TPPTiO in addition to $\mathrm{TPPTiX_2}$. Bubbling the appropriate hydrogen halide through the solution quickly restores the spectrum of pure $\mathrm{TPPTiX_2}$. These observations indicate a ready equilibrium between $\mathrm{TPPTiX_2}$, traces of residual water, and TPPTiO [equation (1)].

$$\mathrm{TPPTiX_2 + H_2O \rightleftharpoons TPPTiO + 2\,HX} \qquad (1)$$

High resolution ^{1}H n.m.r. spectra of $\mathrm{TPPTiX_2}$ (X = Cl or Br) in $\mathrm{CD_2Cl_2}$ solutions in the presence of excess HX recorded at 250 MHz in the pulsed Fourier transform mode with 200 accumulations exhibit the sharp lines expected for diamagnetic tetraphenylporphyrin complexes [$\mathrm{TPPTiCl_2}$, δ ($\mathrm{Me_4Si}$) 9·07 (pyrrole H), 8·29 (phenyl *ortho* H), and 7·86—7·83 (phenyl *meta* + *para* H); $\mathrm{TPPTiBr_2}$: 9·12, 8·30, and 7·86—7·83]. The resonance of the *ortho* phenyl protons is a single line in both cases,¶ indicating either symmetrical axial ligation with two halogeno-ligands in a *trans* configuration, or rapid porphyrin inversion induced by halogen exchange between HX and $\mathrm{TPPTiX_2}$ in a *cis* configuration.[4] The spectrum of the less readily hydrolysed $\mathrm{TPPTiF_2}$ complex recorded in the absence of HF also exhibits a single line for the *ortho* phenyl protons, thus supporting the former hypothesis§ [$\mathrm{TPPTiF_2}$, δ ($\mathrm{Me_4Si}$) 9·00, 8·30, and 7·82—7·80).

The current–potential curve of a $\mathrm{TPPTiF_2}$ solution (*ca.* 5×10^{-4} M) in $\mathrm{CH_2Cl_2}$ with $\mathrm{Bu_4NPF_6}$ (10^{-1} M) with a rotating platinum electrode exhibits four reduction waves of unequal intensities with $E_{\frac{1}{2}}$ −0·45, −1·14, −1·53, and −1·98 V *vs.* aqueous SCE. The first three reduction steps show reversible behaviour in cyclic voltammetry. The second and third wave, whose limiting current increase on addition of TPPTiO correspond to ring reduction reactions of TPPTiO[1c] formed by reaction with residual water according to equation (1). Exhaustive electrolysis at a controlled potential on the first wave (−0·9 V) requires 1 F per mol of $\mathrm{TPPTiF_2}$, and it yields a purple, oxygen-sensitive solution whose voltammogram exhibits an anodic wave

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† Use of a stream of pure HF resulted in demetallation of the porphyrin.

‡ Satisfactory elemental analyses were obtained.

§ Preliminary results of an *X*-ray study of $\mathrm{TPPTiBr_2}$ by Drs. C. Lecomte and J. Protas lead to a body-centred tetragonal lattice. The probable space group is *I4/m*. The two-molecule unit cell has the constants: *a* = 13·76 Å, *c* = 9·88 Å. $\mathrm{TPPTiBr_2}$ is thus isotypic to $\mathrm{TPPSnCl_2}$ whose *trans* configuration is well documented. See: D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1972, **94**, 6689.

¶ Small splittings due to *ortho* and *meta* couplings are observed.

at $E_{\frac{1}{2}}$ $-0{\cdot}45$ V, a value identical to that of the first half-wave potential of the starting $TPPTiF_2$ solution. Such behaviour indicates little structural change between $TPPTiF_2$ and its one-electron reduction product, which is tentatively formulated as the titanium(III) complex TPPTiF. Support for this assignment comes from the observed reaction with dioxygen [equation (2)]: after exposure of the reduced solution to air, the voltammogram

$$2\,TPPTi^{III}F + O_2 \rightarrow TPPTi^{IV}(O_2) + TPPTi^{IV}F_2 \quad (2)$$

and u.v.–visible spectrum are similar to those of a 1:1 mixture of $TPPTiF_2$ and $TPPTi(O_2)$.

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