

Synthesis and Characterization of a New Series of Titanium(IV) Porphyrins Co-ordinated to a Disulphur or a Diselenium Ligand

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The preparation and physicochemical properties of the new titanium(IV) porphyrin complexes (Por)Ti(Y<sub>2</sub>) where Y = S or Se and Por = porphyrinato dianion are reported and the structure of the (TpTP)Ti(S<sub>2</sub>) (TpTP = tetrakis-*p*-tolylporphyrin) complex has been solved by single crystal X-ray diffraction.

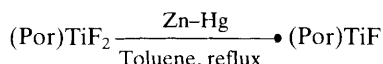
To date<sup>1</sup> only few reports have focused on the synthesis and properties of titanium(IV) porphyrins which are of potential interest in catalysis. The poor reactivity and high stability of oxotitanium porphyrins explain why they have received little attention. Peroxo<sup>2</sup> and dihalogeno<sup>3</sup> titanium porphyrins are more reactive and the former complexes were the first metalloporphyrins with a dioxygen moiety bonded 'side-on' to the metal, while the latter complexes are remarkable precursors of low-valent titanium porphyrins. We now report the synthesis and physicochemical characterization of a new series of titanium(IV) complexes, (Por)Ti<sup>IV</sup>(Y<sub>2</sub>),<sup>†</sup> where Y = S or Se, and we present an X-ray structure determination of the (TpTP)Ti(S<sub>2</sub>) complex.

Reduction by zinc amalgam (1 g) of a dry oxygen-free toluene solution (180 ml) containing 500 mg of (Por)TiF<sub>2</sub> led, after 6 h under reflux, to a pink solution of (Por)TiF. To this titanium(III) porphyrin, 500 mg of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiY<sub>2</sub> (Y = S or Se) were added and the mixture was heated under reflux for 8 h (Scheme 1). The progress of the reaction is easily monitored by u.v.-visible spectroscopy.

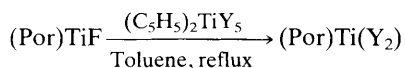
The solvent was evaporated under reduced pressure and the crude product was chromatographed on an alumina column with toluene as eluant. The resulting dark-red solution was

evaporated to dryness, and the solid residue recrystallized from toluene to give a 70% yield of (Por)Ti(Y<sub>2</sub>) where Y = S or Se. Unlike the starting materials, these new disulphur and diselenium compounds appear very stable.

The electronic absorption spectrum of the synthesized compounds belongs to the hyperclass showing a Soret band split into two bands, one of which appears between 363 and 389 nm and the other in the range 417–437 nm in toluene solution. I.r. spectra in CsI pellets show a strong vibrational band between 549 and 553 cm<sup>-1</sup> for the sulphur complexes and in the range 433–440 cm<sup>-1</sup> for the selenium complexes. Such vibrational modes are attributed to the Ti(Y<sub>2</sub>) group.<sup>4–10</sup>



Por: TPP; TmTP; TpTP; TpCF<sub>3</sub>PP; TMP; and OEP



Scheme 1. Y = S or Se

<sup>†</sup> Abbreviations used: Por, any porphyrin; (TPP)H<sub>2</sub>, tetraphenylporphyrin; (TpTP)H<sub>2</sub>, tetrakis(*p*-tolyl)porphyrin; (TmTP)H<sub>2</sub>, tetrakis(*m*-tolyl)porphyrin; (TMP)H<sub>2</sub>, tetramesitylporphyrin; (TpCF<sub>3</sub>PP)H<sub>2</sub>, tetrakis(*p*-trifluoromethylphenyl)porphyrin; (OEP)H<sub>2</sub>, octaethylporphyrin.

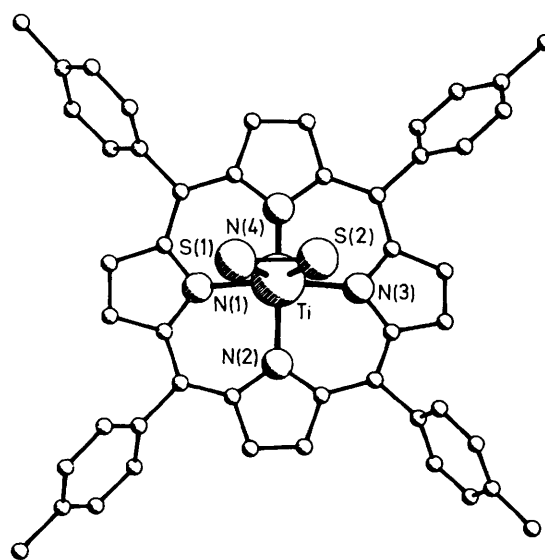


Figure 1. PLUTO view of (TpTP)Ti(S<sub>2</sub>). Selected bond lengths and angle: Ti-S(1) 2.283(2), Ti-S(2) 2.311(3), Ti-N(1) 2.134(5), Ti-N(2) 2.085(5), Ti-N(3) 2.125(5), Ti-N(4) 2.089(5), S(1)-S(2) 2.042(3) Å; S(1)-Ti-S(2) 52.79(9)°.

<sup>1</sup>H N.m.r. data are typical of diamagnetic compounds and agree well with the metal centre in the IV oxidation state.‡

The structure of (TpTP)Ti(S<sub>2</sub>) was established by single crystal X-ray analysis (Figure 1).§ The S<sub>2</sub><sup>2-</sup> ligand is bonded 'side-on' to the metal as the oxygen atoms in the peroxo analogue (OEP)Ti(O<sub>2</sub>)<sup>11</sup> and the sulphur atoms are also in an eclipsed position with respect to the N(1) and N(3) atoms of the macrocycle.

As previously reported,<sup>12,13</sup> this eclipsed conformation is more stable, owing mainly to the bonding interaction between the d<sub>xy</sub> metal orbital with a π\* molecular orbital of the diatomic ligand. The S-S distance of 2.042(3) Å should be compared with those found for S<sub>2</sub> (1.89 Å), S<sub>2</sub><sup>-</sup> (2.00 Å), and S<sub>2</sub><sup>2-</sup> (2.13 Å).<sup>14</sup> This rather short value is consistent with a charge delocalization from the S<sub>2</sub><sup>2-</sup> ligand to the metal. The Ti-S(1) and Ti-S(2) bond lengths are 2.283(2) and 2.311(3) Å

‡ (TpTP)Ti(S<sub>2</sub>), <sup>1</sup>H n.m.r. δ (C<sub>6</sub>D<sub>6</sub>, from Me<sub>4</sub>Si as reference): 9.11 (s, pyrrole H), 8.12 and 7.91 (d, Ar *o*-H), 7.25 (m, Ar *m*-H), and 2.38 (s, Ar *p*-Me).

§ *Crystal data*: C<sub>48</sub>H<sub>36</sub>N<sub>4</sub>TiS<sub>2</sub>·1/2(C<sub>7</sub>H<sub>8</sub>), *M* = 826.9, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 14.688(2), *b* = 14.822(2), *c* = 19.308(4) Å, β = 90.51(2)°, *U* = 4203 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.307 g cm<sup>-3</sup>, μ(Mo-Kα) = 2.57 cm<sup>-1</sup>. A total of 5525 unique reflections were measured on an Enraf-Nonius CAD4 diffractometer at 20 °C. The data were corrected for Lorentz, polarization, and decay effects. 2858 Reflections were considered observed [*I* > 3σ(*I*)] and used to solve the structure (Patterson syntheses). During refinement, a disordered toluene molecule of solvation was found near an inversion centre. Hydrogen atoms attached to trigonal carbon atoms were included in their idealized positions in the structure factors calculation but were not refined. Least squares refinement with all thermal parameters assigned anisotropic (except for the toluene solvate and hydrogen atoms) resulted in the final residuals *R* = 0.049, *R*<sub>w</sub> = 0.051 and G.O.F. = 1.41. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

respectively and this difference could be due to crystal packing effects. As expected from the co-ordination geometry, two significantly different bond lengths are found for Ti-N: Ti-N(1) [2.134(5) Å], Ti-N(3) [2.125(5) Å]; Ti-N(2) [2.085(5) Å], Ti-N(4) [2.089(5) Å]. The titanium atom lies at 0.659(1) Å from the plane of the four nitrogen atoms. This distance is slightly larger than the corresponding distance observed for the peroxo derivative [Δ4N = 0.620(6) Å].

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