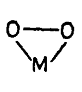
The First Peroxometalloporphyrin with Dioxygen Symmetrically Bonded by Both Atoms; Synthesis and *X*-Ray Crystal Structure of Peroxotitaniumoctaethylporphyrin

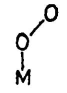
By ROGER GUILARD, MAX FONTESSE, and PIERRE FOURNARI*
(*Laboratoire de Polarographie Organique, associé au C.N.R.S., LA* 33, 6 *Boulevard Gabriel*-21000 *Dijon, France*)
and CLAUDE LECOMTE and JEAN PROTAS
(*Laboratoire de Minéralogie et Cristallographie, Equipe de Recherches associée au C.N.R.S., n°* 162, *Faculté des Sciences, Centre de 2ème Cycle, case officielle n°* 140, 54037 *Nancy Cedex, France*)

Summary Treatment of oxotitaniumoctaethylporphyrin with benzoyl peroxide leads to a complex which is shown to have a peroxo-bonding structure by *X*-ray diffraction; the oxygen atoms of the dioxygen are both bonded to the metal.

WE have recently[1] pointed out that the action of titanium tetrachloride on various porphyrins (PH_2) gives oxotitaniumporphyrins (PTiO) in good yield. Collmann *et al.*[2] have shown that dioxygen complexes can be obtained, starting from iron(II) porphyrins. *A priori*, the dioxygen complex could have either structure (**1**) or (**2**) (M = Fe) and the compound obtained by Collmann *et al.* was of type (**2**). We have attempted to determine whether the oxotitaniumporphyrins would lead to a structure of type (**1**) or (**2**) (M = Ti).



(1)



(2)

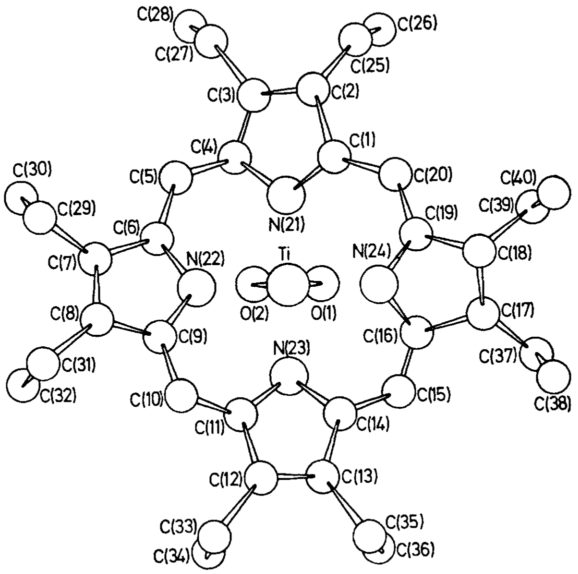
The titanium–oxygen bond was not very reactive; however, starting from oxotitaniumoctaethylporphyrin (OEPTi-O) we have obtained a product with a structural arrangement of type (**1**), and we now report its preparation and crystal structure.

To a stirred solution of OEPTiO (0·5 mmol) in 1,2,4-trichlorobenzene (200 ml) at 90 °C benzoyl peroxide (2 mmol) dissolved in the same solvent (100 ml) was added dropwise. The solution was then stirred for 8 h at 90 °C and concentrated *in vacuo*, and a solution of the residual oil in light petroleum was chromatographed on silica gel. The last traces of 1,2,4-trichlorobenzene were eluted by light petroleum, and CH_2Cl_2–light petroleum (3:2) was then used as eluant. Evaporation and recrystallisation from toluene yielded red crystals (33%). The same product was also obtained when OEPTiO was treated with hydrazine hydrate, and also when the chlorohydrate of OEPTiO was treated with PhLi.

Elemental analyses indicated the formula $C_{36}H_{44}N_4O_2Ti$ ($OEPTiO_2$); its spectral data are as follows: ν_{O-O} 898 cm^{-1}; ν_{Ti-O} 645 and 600 cm^{-1}; δ ($CDCl_3$; Me_4Si) 1·90 (t, Me), 4·08 (q, CH_2), and 10·35 (s, *meso*-H).

Crystal data: Preliminary Weissenberg photographs showed that the crystal symmetry was monoclinic, space group $P2_1/c$, with $a = 14{\cdot}60 \pm 0{\cdot}02$, $b = 23{\cdot}27 \pm 0{\cdot}03$, $c = 9{\cdot}79 \pm 0{\cdot}01$ Å, $\beta = 105{\cdot}0 \pm 0{\cdot}02$, $Z = 4$, $D_c = 1{\cdot}25$ g cm^{-3}.

Three-dimensional intensity data were collected on a three-circle automatic diffractometer (CAD 3 Nonius), with Cu-K_α radiation. The structure was determined by direct methods, using the MULTAN programme.[3] Diagonal least-squares refinement of the non-hydrogen atoms for the 2600 non-zero reflections with $\sigma(I)/I < 0{\cdot}20$ (with anisotropic thermal parameters) gives an R index of 0·106.



FIGURE

The Figure shows a perspective view of the complex. The co-ordination around the titanium atom is of particular interest: it lies at 0·62 Å from the plane of the four nitrogen atoms, towards the oxygen atoms. The oxygen atoms O(1) and O(2) are 2·29 Å from this plane in an eclipsed position with respect to the N(22) and N(24) atoms. No Ti–N distances are significantly different from each other [av. Ti–N = 2·108 (8) ± 0·021 Å] and all agree with those found in the oxotitaniumoctaethylporphyrin complex.[4] The Ti–O(1) and Ti–O(2) bond lengths are 1·829(8) and 1·822(8) Å respectively; the O(1)–O(2) distance is 1·458(9) Å and the O(1)–Ti–O(2) bond angle 47°. These results show the existence of peroxo-bonding to the titanium atom, which is confirmed by the ν_{Ti-O} and ν_{O-O}, i.r. absorptions, which are in agreement with those reported by Wendling[5] for M_2-$TiCl_4O_2,H_2O$.

The pyrrole rings are planar (within ±0·03 Å) and are not significantly tilted with respect to each other. The bond distances and angles in the porphinato-core agree with those found in other porphyrin compounds.

(*Received*, 8*th December* 1975; *Com.* 1366.)

[1] P. Fournari, R. Guilard, M. Fontesse, J. M. Latour, and J. C. Marchon, *J. Organometallic Chem.*, in the press.

[2] J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 1427.

[3] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[4] C. Lecomte, J. Protas, and R. Guilard, *Compt. rend.*, 1975, 921.

[5] E. Wendling, *Bull. Soc. chim. France*, 1967, 16.