Syntheses and Photochemistry of Fluorinated and Chlorinated Titanium Porphyrinates: Crystal Structure of Oxotitanium *meso*-Tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate

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The syntheses of oxotitanium(IV) *meso*-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate O=Ti($TPPF_{20}$) (**1**), oxotitanium(IV) *meso*-tetrakis(2,6-difluorophenyl)porphyrinate O=Ti($TPPF_8$) (**3**), and oxotitanium(IV) *meso*-tetrakis(2,6-dichlorophenyl)porphyrinate O=Ti($TPPCl_8$) (**5**) from titanium tetrachloride and the corresponding porphine are described. The structure of **1** was determined by single-crystal X-ray diffraction. The reaction of oxotitanium porphyrinates with aqueous hydrogen peroxide leads to the corresponding light-sensitive peroxotitanium(IV) complexes: Ti(O_2)($TPPF_{20}$) (**2**), Ti(O_2)($TPPF_8$) (**4**), Ti(O_2)($TPPCl_8$) (**6**). All complexes are efficient and stable photosensitizers for the generation of singlet oxygen.

The activation of oxygen and hydrogen peroxide for the production of oxygenated hydrocarbons is of current interest[1]. We are interested in determining the catalytic properties of titanium porphyrinates for the production of fine chemicals.

Since the preparation of O=Ti(*meso*-DME) in 1968 by Tsutsui[2,3] the syntheses of several titanyl porphyrinates were reported starting from titanyl acetylacetone[4], titanocene dichloride[5,6] or titanium tetrachloride[7,8]. These air-stable compounds are the starting material for the synthesis of dihalogeno, sulfo, seleno, or organoimido titanium(IV) porphyrinates[9,10,11] and low-valent titanium porphyrinate complexes as well[12]. Only few stereochemical data of the coordination sphere of titanylporphyrinates are known[13]. The X-ray crystal structures of O=Ti(OEP) and O=Ti($OEPMe_2$) were reported[14,15]. The complex O=Ti(TPP) was studied by EXAFS[16,17].

In this paper we report on the synthesis, structural characterization, and photocatalytic properties of some fluorinated and chlorinated oxotitanium *meso*-tetraarylporphyrinates and their conversion to the corresponding peroxo complexes.

Syntheses and Characterization of Oxotitanium Porphyrinates

As illustrated in equation (1) the treatment of $H_2(P)$ with an excess of $TiCl_4$ results in the formation of the oxotitanium complexes O=Ti(P) **1**, **3**, and **5** in a two-step one-pot procedure. After refluxing in toluene for 28 hours and acid hydrolysis an overall yield of 82–90% based on the free porphyrin was obtained. To avoid undesired reactions at the perfluorinated phenyl groups toluene was chosen as inert solvent instead of a DMF/pyridine mixture[14]. Only O=Ti($TPPF_8$) **3** is mentioned in the literature but without any details of its preparation or characterization[18].

Scheme 1. Reaction conditions and yields

$$TiCl_4 + H_2(P) \xrightarrow{a,b} O{=}Ti(P) \qquad (1)$$

$$O{=}Ti(P) + H_2O_2 \xrightarrow{c} Ti(O_2)(P) \qquad (2)$$

a) Toluene, argon, 28 h reflux. – b) H_2O/HCl. – c) CH_2Cl_2, 4 h; O=Ti($TPPF_{20}$) **1** (90%), Ti(O_2)($TPPF_{20}$) **2** (85%), O=Ti($TPPF_8$) **3** (92%), Ti(O_2)($TPPF_8$) **4** (85%), O=Ti($TPPCl_8$) **5** (81%), Ti(O_2)($TPPCl_8$) **6** (85%).

As reported earlier[14,19,20] the reaction of titanium porphyrinates with an excess of hydrogen peroxide (30% in water) yields peroxotitanium(IV) porphyrinates[21]. Equation (2) shows the syntheses of the light-sensitive new complexes Ti(O_2)(P) **2**, **4**, and **6**. The yield is 85–92%. Visible light has to be excluded during the preparation and purification procedure. Especially in solution decomposition to **1**, **3** or **5** takes place.

The ^1H-NMR spectra confirm the expected diamagnetism of **1**–**6**. The β-pyrrole resonances appear as sharp singlets between δ = 9.23 and 8.95 (**1**, **3**, **5**) or δ = 9.16 and 8.85 (**2**, **4**, **6**). These chemical shifts are very similar to those of the unsubstituted complexes O=Ti(TPP) (δ = 9.24) and Ti(O_2)(TPP) (δ = 9.16). The presence of the oxotitanium and peroxotitanium group causes the nonequivalence of *ortho* and *meta* hydrogen atoms (fluorine atoms) on the phenyl rings. This indicates a rotation barrier of the phenyl

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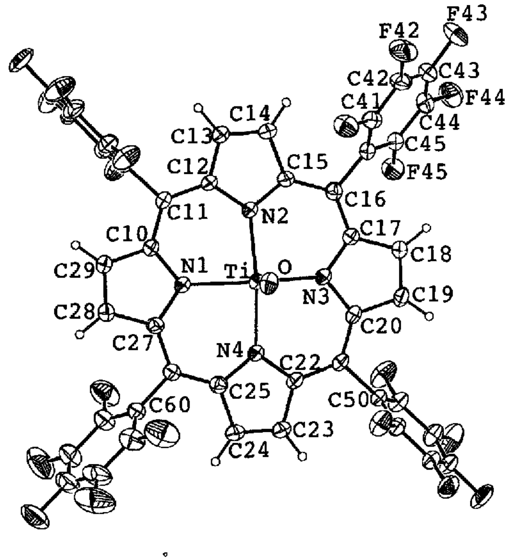
ring. The differences in the chemical shifts of fluorines are small between oxotitanium and peroxotitanium complexes.

The oxotitanium moiety causes an intense absorption in the infrared spectrum between 945 and 984 cm^{-1}. The peroxotitanium group shows three absorptions around 904 (O−O stretching mode), 645 and 612 cm^{-1} (symmetric and asymmetric Ti−O stretching modes). The UV-Vis spectra are very similar to the very intense Soret band between 415 and 421 nm and three to four Q bands around 545 nm. The SIMS spectra show the incorporation of the oxo- and peroxotitanium group into the macrocycle. Mainly the ejection of one or two oxygen atoms is observed.

Crystal Structure of 1

The oxo complex $O{=}Ti(TPPF_{20})$ **1** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The titanium atom is pentacoordinated by the oxygen atom and the four nitrogen atoms (Figure 1). The point group symmetry of this coordination polyhedron is C_{4v} with nearly planarity of the porphyrin core. The dihedral angle between the nitrogen plane and the phenyl rings varies from 60 to 90 deg. The titanium−oxygen distance is 1.616(3) Å and the average titanium−nitrogen distance 2.098(3) ± 0.013 Å. The titanium atom lies 0.527(1) Å above the plane defined by the four nitrogen atoms and 0.586(1) Å above the mean plane of the porphine skeleton. This structure is close to the structure of O=Ti(OEP)[14]. Compared to the unsubstituted O=Ti(TPP) the introduction of fluorine atoms into the phenyl groups has no significant influence on the coordination polyhedron of titanium and on the bond lengths between titanium and oxygen or nitrogen.

Figure 1. PLATON[32] view of **1**. The vibrational ellipsoids are drawn at the 50% probability level



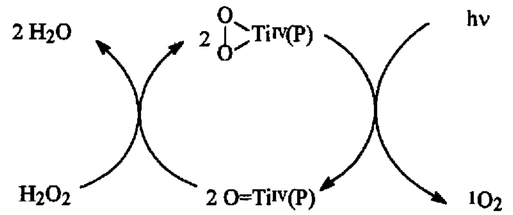
Selected bond lengths [Å]: Ti−O 1.616(3), $Ti-N_1$ 2.105(3), $Ti-N_2$ 2.102(3), $Ti-N_3$ 2.085(3), $Ti-N_4$ 2.098(3). Selected bond angles [deg]: $O-Ti-N_1$ 106.4(1), $O-Ti-N_2$ 105.4(1), $O-Ti-N_3$ 102.1(1), $O-Ti-N_4$ 104.3(1), N_1-Ti-N_2 86.5(1), N_1-Ti-N_3 151.5(1), N_1-Ti-N_4 86.1(1), N_2-Ti-N_3 85.7(1), N_2-Ti-N_4 150.3(1), N_3-Ti-N_4 87.3(1)[33].

Reactions of Oxotitanium Porphyrinates

In the presence of oxygen all complexes **1**−**6** are efficient sensitizers for the photooxygenation of cyclic olefins. Cyclohexene and *cis*-cyclooctene were converted into the corresponding allyl hydroperoxide ("Schenck en reaction"[22]) and small amounts of enol, enone, or epoxide. In the presence of DABCO no reaction takes place. This confirmes the existence of singlet oxygen. The stability of these titanium porphyrinates against oxidative degradation during the irradiation is considerably higher than in the case of O=Ti(TPP). Especially the fluorinated porphyrins are most effective. The perfluorinated complex **1** is more labile than **3**. This may be attributed to the sensitivity of **1** to nucleophilic attack on the phenyl group through the oxidation products. The generation of superoxide is also possible[23].

The production of singlet oxygen during the irradiation of peroxotitanium(IV) porphyrinates was suggested by several authors[24]. Recently, the formation of oxotitanium *meso*-tetraphenyl *N*-oxide was observed during the photolysis of peroxotitanium *meso*-tetraphenylporphyrinate[25]. This behavior suggests the possibility of the photoactivation of hydrogen peroxide or hydroperoxides according to Figure 2. But the irradiation of cyclohexene in the presence of H_2O_2 (30%) and the complexes **1**, **3**, or **5** dissolved in dichloromethane leads to a rapid degradation of the catalysts. Only small amounts of oxygenated products could be detected by GC.

Figure 2. Photocatalytic activation of hydrogen peroxide



Experimental

The NMR spectra were recorded with a Bruker AC300 spectrometer. Chemical shifts (δ) for the ^1H-NMR spectrum (300 MHz) are reported relative to residual protons in deuterated chloroform or dichloromethane and the ^{19}F-NMR spectra (282 MHz) relative to trifluoromethane as external standard. − The IR spectra were measured with a Nicolet 510/P spectrometer in a KBr matrix. − The UV-Vis spectra were recorded with the Perkin-Elmer Lambda 14 spectrometer. − The Finnigan MAT 95 served for the detection of the SIMS spectra (Cs^+, 20 kV, mixture of dithioerythrol/dithiothreithol as matrix)[26]. − Titanium tetrachloride (Fluka) was distilled under argon before use. Hydrogen peroxide (30%, Merck) was used as purchased. The porphine H_2TPPF_{20} was synthesized from 2,3,4,5,6-pentafluorobenzaldehyde and pyrrole in the presence of boron trifluoride−diethyl ether and subsequent oxidation with *p*-chloranil or 2,3-dichloro-5,6-dicyanobenzoquinone according to a procedure published by Volz et al.[27]. By a similar procedure H_2TPPF_8[28] and H_2TPPCl_8[29] can be obtained.

Synthesis of Oxotitanium Porphyrinates: To a refluxing solution of the porphine (0.15 mmol) in 200 ml dry toluene $TiCl_4$ (1.9 ml) was added dropwise with stirring under argon. The reaction mixture was heated for 28 hours and hydrolyzed by adding chloroform (250 ml) and diluted HCl (200 ml) after cooling to room temp. The color of the solution changed from deep green to red. The aqueous layer was extracted several times with chloroform. The combined organic phases were washed with water, satd. $NaHCO_3$ solution, and again with water. The solvent was evaporated in vacuo to afford a solid which was chromatographed on silica gel with dichloromethane as solvent. Traces of unreacted porphine were eluted first as a deep purple band. The compounds show in solution a purple red color. After evaporation of the solvent and drying deep red crystals were obtained in 81 to 90% yield.

O=Ti(TPPF$_{20}$) (**1**): Yield 90%; R_f (CH_2Cl_2) = 0.56. – ^{1}H NMR ($CDCl_3$): δ = 9.23 (s, $H_{Pyrrole}$). – ^{19}F NMR ($CDCl_3$): δ = –135.0 (d, J = 20.9 Hz, F_{ortho}), –137.0 (d, J = 20.3 Hz, F_{ortho}), –150.6 (t, J = 21.4 Hz,F_{para}), –160.7 (m, F_{meta}), –161.3 (m, F_{meta}). – IR (KBr): $\tilde{\nu}$ = 945 (ν_{TiO}) cm^{-1}. – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 393 sh (4.71), 416 (5.65), 504 (3.45), 545 (4.34), 580 (3.86), 639 (3.08) nm. – SIMS *m/z* (%): 1037 (100) [M(^{47}Ti) + H], 1020 (17) [M(^{47}Ti) – O]. – $C_{44}H_8F_{20}N_4OTi$ (1036.44 g/mol) calcd. C 50.99, H 0.78, N 5.40; found C 51.30, H 1.04, N 5.22.

O=Ti(TPPF$_8$) (**3**): Yield 92%; R_f (CH_2Cl_2) = 0.25. – ^{1}H NMR ($CDCl_3$): δ = 9.17 (s, 8$H_{Pyrrole}$), 7.83 (tt, J = 8.3 Hz/2.2 Hz, 4H_{para}), 7.49 (t, J = 8.3 Hz, 4H_{meta}), 7.36 (t, J = 8.3 Hz, 4H_{meta}). – ^{19}F NMR ($CDCl_3$): δ = –106.7 (s, 4F_{ortho}), –108.75 (s, 4F_{ortho}). – IR (KBr): $\tilde{\nu}$ = 977 sst (ν_{TiO}) cm^{-1}. – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 396 sh (4.75), 417 (5.70), 501 (3.67), 547 (4.46), 581 (3.67) nm. – SIMS *m/z* (%): 821 (100) [M(^{47}Ti) + H], 804 (10) [M(^{47}Ti) – O]. – $C_{44}H_{20}F_8N_4OTi$ (820.55 g/mol) calcd. C 64.40, H 2.46, N 6.83; found C 64.45, H 2.55, N 6.59.

O=Ti(TPPCl$_8$) **5**: Yield 81%; R_f (CH_2Cl_2) = 0.23. – ^{1}H-NMR (CD_2Cl_2): δ = 9.02 (s, 8$H_{Pyrrole}$), 7.96 (m, 4H_{para}), 7.82 (m, 8H_{meta}). – IR (KBr): $\tilde{\nu}$ = 984 m (ν_{TiO}) cm^{-1}. – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 402 sh (4.71), 422 (5.75), 510 (3.40), 552 (4.45), 587 (3.50), 638 (3.28) nm. – SIMS *m/z* (%): 953 (100) [M(^{47}Ti)]. – $C_{44}H_{20}Cl_8N_4OTi$ (952.19 g/mol) calcd. C 55.45, H 2.12, N 5.88; found C 54.42, H 1.94, N 5.72.

Synthesis of Peroxotitanium Porphyrinates: During all procedures visible light had to be excluded. A solution of **1** (0.10 mmol) and H_2O_2 (30%, 0.25 g) in dichloromethane (15 ml) was stirred during 4 hours. The organic layer was treated several times with water until no peroxide could be detected (KI). The solution was dried with Na_2SO_4, concentrated and the residue was chromatographed on silica gel with dichloromethane. The peroxo compounds were eluted as a red fraction. After evaporation of the solvent from the elvate and drying of the residue red crystals (85–92%) were obtained.

Ti(O_2)(TPPF$_{20}$) (**2**): Yield 85%; R_f (CH_2Cl_2) = 0.70. – ^{1}H NMR ($CDCl_3$): δ = 9.15 (s, $H_{Pyrrole}$). – ^{19}F NMR ($CDCl_3$): δ = –135.4 (d, J = 18.9 Hz, 4F_{ortho}), –137.1 (d, J = 21.4 Hz, 4F_{ortho}), –150.5 (t, J = 20.2 Hz, 4F_{para}), –160.6 (m, 4F_{meta}), –161.1 (m, 4F_{meta}). – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 393 sh (4.25), 415 (5.47), 538 (3.82), 542 (4.20), 570 (3.97) nm. – IR (KBr): $\tilde{\nu}$ = 903 (ν_{OO}), 763, 642 (ν_{TiO_2}), 612 (ν_{TiO_2}) cm^{-1}. – SIMS: *m/z* (%): 1052 (18) [M(^{47}Ti)], 1036 (100) [M(^{47}Ti) – O], 1020 (11) [M(^{47}Ti) – O_2]. – $C_{44}H_8F_{20}N_4O_2Ti$ (1052.44 g/mol) calcd. C 50.12, H 0.76, N 5.31; found C 51.04, H 1.05, N 5.10.

Ti(O_2)(TPPF$_8$) (**4**): Yield 85%; R_f (CH_2Cl_2) = 0.52. – ^{1}H NMR ($CDCl_3$): δ = 9.10 (s, 8$H_{Pyrrole}$), 7.82 (m, 4H_{para}), 7.44 (tr, J = 8.3 Hz, 4H_{meta}), 7.35 (t, J = 8.3 Hz, 4H_{meta}). – ^{19}F NMR ($CDCl_3$9: δ = –107.05 (s, 4F_{ortho}), –108.82 (s, 4F_{ortho}). – IR (KBr): $\tilde{\nu}$ = 904 m (ν_{OO}), 642 w ($\nu_{Ti\text{-}O_2}$), 614 w ($\nu_{Ti\text{-}O_2}$) cm^{-1}. – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 396 sh (4.52), 417 (5.44), 531 (3.83), 543 (4.16), 569 (3.69) nm. – SIMS *m/z* (%): 835 (3.1) [M(^{47}Ti)], 821 (100) [M(^{47}Ti) – O]. – $C_{44}H_{20}F_8N_4O_2Ti$ (836.55 g/mol) calcd. C 63.17, H 2.41, N 6.70; found C 63.23, H 2.36, N 6.68.

Ti(O_2)(TPPCl$_8$) (**6**): Yield 85%; R_f (CH_2Cl_2) = 0.61. – ^{1}H NMR (CH_2Cl_2): δ = 8.95 (s, 8H_{Pyrrol}), 7.92 (dd, J = 7 Hz/2 Hz, 4H_{para}), 7.82 (m, 8H_{meta}). – IR (KBr): $\tilde{\nu}$ = 904 m (ν_{OO}), 650 w (ν_{TiO_2}), 610 w (ν_{TiO_2}) cm^{-1}. – UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 400 sh (4.34), 421 (5.31), 534 sh (3.70), 548 (4.30), 575 (3.58) nm. – SIMS *m/z* (%): 969 (42.2) [M(^{47}Ti) + H], 951 (100) [M(^{47}Ti) – O]. – $C_{44}H_{20}Cl_8N_4O_2Ti$ (96.19 g/mol) calcd. C 54.58, H 2.08, N 5.79; found C 52.90, H 2.10, N 5.54.

Crystallographic Data Collection: Single crytals of **1** were obtained from dichloromethane, ethanol, or acetone. Single crystals generated from the former solvent suffers from rapid loss of clathrated dichloromethane whereas those obtained from the latter two solvents are sufficiently stable for an X-ray data collection. From ethanol the product crystallizes in the space group $P2_1/n$ with the approximate lattice constants a = 13.04, b = 12.52, c = 13.61 Å and β = 114.5 deg. The molecules are disordered around $\bar{1}$ center; no complete intensity data collection and no precise cell determination were performed. Crystals from acetone clathering the solvent in a 1:1 molar ratio belong to the space group $P2_1/c$.

Crystal Data: $C_{47}H_{14}F_{20}N_4O_2Ti$: M = 1094.53 g mol^{-1}, monoclinic $P2_1/c$, a = 14.059(3), b = 11.517(4), c = 26.78(1) Å, β = 102.07(3) deg., V = 4240(3) Å^3, Z = 4, $d_{calcd.}$ = 1.714 g cm^{-3}, λ(Cu-K_α) = 0.54184 Å, μ = 29.60 cm^{-1}, F(000) = 2168, T = 20°C. – *Data Collection and Processing:* CAD4 diffractometer, omega mode, graphite-monochromated Cu-K_α radiation; 12267 reflections measured (5.0 < Θ < 70.0 deg) in the $+h \pm k \pm l$ hemisphere. 5443 unique reflections with $I > 1.0\ \sigma(I)$ which were used for further computations. The data were corrected for anisotropic decay. An empirical absorption correction based on psi-scans was applied[30] (min. transmission 0.77, max. transmission 1.00).

Structure Determination: The structure was solved by direct methods. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were calculated in idealized positions with isotropic thermal parameters of B(H) = 1.3 B(C) and allowed to ride on their C atoms. Refinement converged with 668 parameters by using a statistical weighing scheme $w = 1/[\sigma^2(F_o)]$ at values of R = 0.059 and Rw = 0.063 with a goodness-of-fit of 1.194. A coefficient for secondary extinction was included and refined to 0.511 · 10^{-6}. Calculations were performed by using the SDP system of programs[31].

CAS Registry No.: H_2TPPCl$_8$ [37083-37-7]; H_2TPPF$_8$ [104322-39-6]; H_2TPPF$_{20}$ [25440-14-6]; O=TiTPPF$_8$ [119889-96-2]; $TiCl_4$ [7550-45-0]; H_2O_2 [7722-84-1]; O_2 [7782-44-7]; cyclohexene [110-83-8]; *cis*-cyclooctene [931-87-3].

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