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Molecular Structure of Methoxotitanium (III) Tetraphenylporphyrin, A Slightly Bent Methoxo Complex

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Methoxotitanium (III) tetraphenylporphyrin was obtained by reaction of fluorotitanium (III) tetraphenylporphyrin and sodium methylthiolate in the presence of methanol, and was characterized by X-ray structural analysis. This methoxo complex crystallizes in the monoclinic space group $P2_1/c$ *with four molecules in a unit cell of dimensions* $a = 10.15(1)$ Å, $b = 16.29(2)$ Å, $c = 23.62(2)$ Å, *and* $\beta = 117.7(1)°$. *The structure was solved by standard heavy-atom techniques. Least-squares refinement has led to a final value of the conventional* R *index of 0.105 based on 1766 reflections. The titanium atom is coordinated to the four nitrogen atoms and to the oxygen atom. The methoxo ligand is significantly deviated from the usual bent geometry. The three atoms Ti, O, and C are nearly collinear (Ti–O–C angle; 171(1)°), and the Ti–O bond distance is very short (1.77(1) Å). The slightly bent configuration of the axial bonding system is accounted for by significant π-donation from the methoxo ligand to the electron-deficient metal.*

Introduction

Three main features seem necessary for a first-row transition metal porphyrin complex to form an adduct with the dioxygen molecule: a vacant coordination site, some unpaired d electron density on the metal, and a low redox potential [1]. Five-coordinate titanium(III) porphyrins, which have a single 3d electron, are the simplest complexes meeting these three requirements. Accordingly, various complexes of titanium(III) tetraphenylporphyrin having the general formula TiX(tpp), where X is an axial anionic ligand such as halide, thiolate, or aryl [1–4], have been synthesized in our laboratories during the last few years, and their dioxygen bonding ability has been evaluated. Indeed, all of these five-coordinate titanium (III) complexes exhibit a high affinity for dioxygen. When exposed to an oxygen atmosphere, their solutions autoxidize to the corresponding oxo- and/or peroxotitanium (IV) complex, TiO(tpp) and $Ti(O_2)$(tpp), respectively. Whether the oxo- or the peroxo-complex is obtained is directly related to the oxidizability of the anion X. When X is difficult to oxidize, *e.g.* with TiF(tpp), dioxygen is reduced mainly to the peroxo-complex $Ti(O_2)$(tpp) which is a kinetic product of the reaction [1, 2]. In contrast, when X is a strong one-electron reductant, such as thiolate or aryl, the oxygen–oxygen bond is cleaved and the oxo-complex TiO (tpp) is obtained [1, 4].

Structural determinations of titanium (III) tetraphenylporphyrin complexes have been undertaken to try and set out possible correlations between stereochemical parameters and autoxidation patterns. Herein we report the molecular structure of methoxotitanium (III) tetraphenylporphyrin. This complex was obtained by reaction of fluorotitanium (III) tetraphenylporphyrin with sodium methylthiolate and methanol in benzene solution. Elemental analysis of the microcrystalline product indicated virtual absence of sulfur, suggesting that the expected fluoride → thiolate axial ligand change was complicated by further reaction of the titanium (III) complex with methanol, a component of the solvent mixture which was necessary for solubilization of sodium methylthiolate. As large crystals could be obtained, X-ray structure determination was used to confirm methoxide axial ligation. Indeed, assignment of the formula $Ti(OCH_3)$(tpp) was corroborated by the successful structure solution. Moreover, some rather unusual features were found for the axial bonding system in $Ti(OCH_3)$(tpp), and reactivity studies will be reported in a separate paper.

Experimental

Synthesis

Tetraphenylporphyrin was prepared by a literature method [5]. Titanium insertion from $TiCl_4$ lead to the oxo-complex TiO(tpp) [6]. Reaction of the

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latter with gaseous HF gave TiF_2(tpp) [7]. All subsequent operations were performed in a glove box under argon containing 1–5 ppm of O_2. Stirring a suspension of 200 mg of TiF_2(tpp) in 300 ml of benzene with excess zinc amalgam for 24 hours gave, after filtration, a red solution containing pure TiF (tpp) [2]. To 50 ml of this solution were added 120 mg of $NaSCH_3$ and 0.5 ml of methanol. The mixture was brought to reflux for 15 min. Evaporation of the solvent to about 20 ml gave purple crystals of $Ti(OCH_3)$(tpp). The latter was characterized by its electron paramagnetic resonance ($g = 1.976$; $a_N = 2.3$ G) and UV-visible (λ_{max} in C_6H_6: 426, 522, 552, 589) spectra, and by elemental analysis. *Anal.* Calcd: C, 78.14; H, 4.52; N, 8.10; Ti, 6.93. Found: C, 76.79; H, 4.08; N, 8.07; Ti, 6.81; S, 0.29%.

X-Ray Crystallography

Single crystals were obtained as follows: 80 mg of $Ti(OCH_3)$(tpp) were dissolved in 15 ml of toluene, and a mixture of 60 ml of n-hexane and 5 ml of methanol was slowly added. Crystals with parallepiped geometry were collected after a few weeks and mounted in glass capillaries under argon. Preliminary precession photography established a monoclinic unit cell, with systematic absences consistent with space group $P2_1/c$. Crystal data are given in Table I.

TABLE I. Crystal Data.

$C_{45}H_{31}N_4OTi$	mol. wt.: 691.17
$a = 10.15(1)$ Å	space group: $P2_1/c$
$b = 16.29(2)$ Å	$Z = 4$
$c = 23.62(2)$ Å	$V = 3457.50$ Å^3
$\beta = 117.7(1)°$	$d_{calcd} = 1.33$ g/cm^3

Diffracted intensities were collected by using an ENRAF-NONIUS CAD-4 diffractometer with prefiltered Cu K_α radiation. A total of 4889 independent reflections were measured out to $2\theta \leqslant 55°$. Two standard reflections, measured every 500 reflections, showed a small (*ca.* 6%) decrease in intensity. A total of 1766 reflections having $F_o \geqslant 3\,(F_o)$ were taken to be observed.

The structure was solved by standard heavy-atom techniques. The Ti atom was located from a three-dimensional Patterson map. The other non-hydrogen atoms were found by successive Fourier syntheses. Initial refinement using isotropic B factors was started, and led to convergence. A difference Fourier map gave the approximate positions of several hydrogen atoms of the molecule (17 out of 31). However, the latter were not included in the refinement. Subsequent cycles of refinement, by the usual full-matrix least-squares method, used anisotropic B factors for all non-hydrogen atoms. The final value of the discrepancy indexes were 0.1055 for $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and 0.1307 for $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. No absorption correction was made. A list of calculated and observed structure factors has been deposited with the Editor.

Results and Discussion

The molecular structure of $Ti(OCH_3)$(tpp) confirms its formulation as a five-coordinate neutral complex (Fig. 1), and makes plausible its preparation by the sequence of reactions 1 and 2:

$$TiF(tpp) + NaSCH_3 \longrightarrow Ti(SCH_3)(tpp) + NaF\downarrow \quad (1)$$

$$Ti(SCH_3)(tpp) + CH_3OH \rightleftharpoons Ti(OCH_3)(tpp) + CH_3SH \quad (2)$$

Axial ligand substitution by reaction of methanol with $Ti(SCH_3)$(tpp) is not entirely unexpected in view of the oxophilicity of titanium.

Table II shows a list of positional and thermal parameters in the unit cell of the complex. Tables III and IV give the values of the bond distances and angles in the porphyrin core of the complex. Bond lengths are slightly longer but are otherwise close to the average dimensions of the porphyrin skeleton [8].

An interesting feature of the structure is that the methyl group of the methoxo ligand is precisely located, and not statistically disordered as could have been expected from the quasi-fourfold symmetry of the porphyrin ring. Examination of the geometry of the ligand atoms around the titanium ion reveals an uncommon feature. The methoxo ligand is significantly deviated from the usual bent geometry. The three atoms Ti, O, and C are nearly collinear (Ti–O–C angle: 171(1)°), and the Ti–O bond distance is very short (1.77(1) Å). A typical single Ti–O bond is assumed [9] to have a length of *ca.* 2.0 Å. Observation of a shorter bond distance suggests some multiple bond character due to donation of electron density from filled oxygen p_π orbitals to unfilled d orbitals on the electron-deficient metal. Recent examples of alkoxide complexes in which π-donation to titanium results in a short titanium–oxygen distance have been described and discussed by Caulton [10]. Thus, in the 12 electron pinacolato complex $[CpTiCl_2]_2O_2C_2(CH_3)_4$, a Ti–O distance of 1.750 Å is observed. A corollary consequence of the strong multiple Ti–O bonding in this complex is the 166.2° Ti–O–C angle, the most obtuse then found for an alkoxide ligand. The pinacolato ligand in this complex is considered donating at least three electrons to the metal [10]. The 11 electron methoxo complex $Ti(OCH_3)$(tpp) is even more electron deficient, and it exhibits an even more obtuse Ti–O–C angle suggesting increased π-donation. The strongest cases of π-donation, and correspondingly

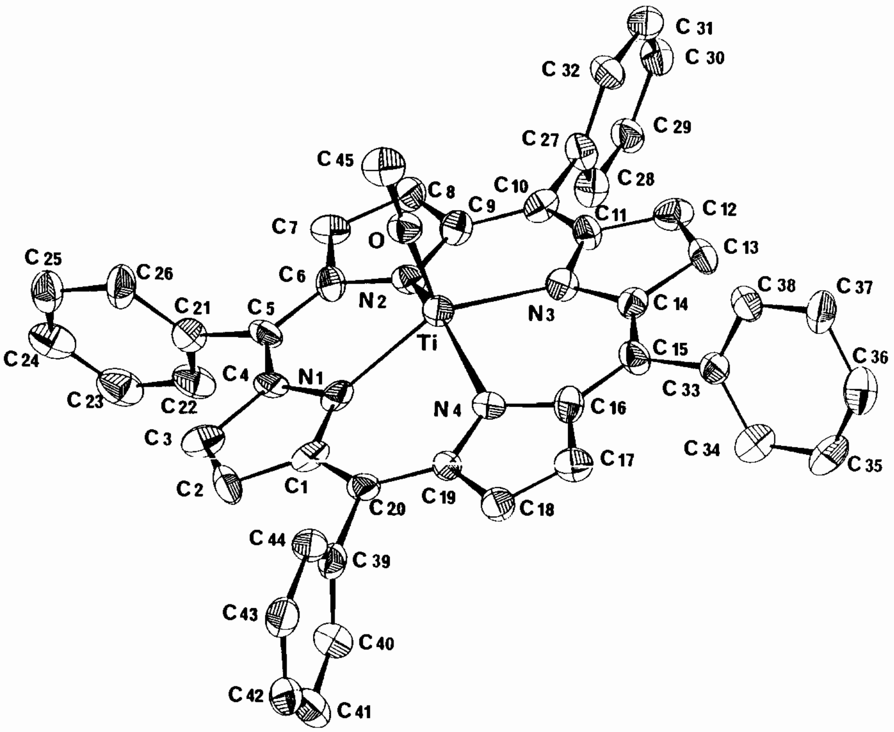

Fig. 1. Computer-drawn model of Ti(OCH$_3$) (tpp). The label assigned to each atom is displayed. Thermal ellipsoids are contoured at the 50% probability level.

TABLE II. Positional and Thermal Parameters in the Unit Cell of Ti(OCH$_3$)(tpp).[a, b]

	10^4x	10^4y	10^4z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Ti	3032(10)	3221(5)	1552(7)	168(1)	47(1)	21(1)	−2(6)	25(2)	−2(4)
O	4771(5)	2771(1)	1740(8)	165(7)	57(7)	30(5)	0(4)	28(8)	−3(3)
N(1)	1412(0)	2268(3)	1199(1)	196(8)	53(4)	13(4)	17(1)	19(5)	9(6)
N(2)	2749(0)	3140(7)	2380(0)	161(9)	52(1)	20(3)	1(5)	17(4)	−9(9)
N(3)	3445(9)	4483(7)	1764(5)	172(2)	56(2)	25(2)	−8(8)	37(2)	3(8)
N(4)	2021(3)	3602(10)	576(9)	124(1)	54(8)	26(1)	−4(2)	17(2)	−1(10)
C(1)	689(8)	1926(5)	601(5)	219(4)	70(3)	5(2)	30(8)	19(1)	9(3)
C(2)	−30(2)	1156(9)	608(8)	197(9)	40(7)	51(7)	−30(2)	53(6)	−9(1)
C(3)	244(3)	1028(3)	1222(9)	224(8)	90(4)	16(6)	18(10)	24(9)	3(1)
C(4)	1176(7)	1714(6)	1583(1)	168(6)	55(7)	10(10)	−6(1)	−4(1)	12(3)
C(5)	1576(9)	1770(7)	2236(2)	128(9)	52(1)	28(2)	−18(7)	15(4)	−14(6)
C(6)	2332(4)	2443(4)	2606(9)	183(1)	49(9)	38(1)	−17(9)	44(8)	10(10)
C(7)	2785(3)	2557(2)	3296(4)	178(3)	75(2)	12(3)	0(2)	21(5)	−7(1)
C(8)	3456(9)	3334(5)	3468(6)	211(7)	45(5)	29(3)	5(4)	29(4)	−6(1)
C(9)	3379(0)	3678(4)	2894(8)	201(8)	53(9)	28(9)	2(6)	42(7)	4(8)
C(10)	3941(3)	4485(3)	2897(6)	175(2)	62(10)	21(5)	15(9)	44(3)	11(6)
C(11)	3960(10)	4829(3)	2379(5)	202(2)	40(2)	29(1)	−15(0)	38(7)	−5(2)
C(12)	4440(8)	5657(9)	2372(10)	179(2)	85(5)	25(9)	0(3)	29(4)	10(1)
C(13)	4208(8)	5837(3)	1749(9)	194(3)	40(7)	42(1)	−25(7)	42(3)	−9(5)
C(14)	3519(7)	5102(3)	1375(7)	144(6)	46(5)	30(5)	7(4)	35(1)	4(3)
C(15)	3053(1)	5011(7)	705(1)	213(2)	48(6)	23(5)	−25(0)	28(2)	−8(4)
C(16)	2344(9)	4329(8)	357(2)	206(10)	47(2)	35(1)	−3(8)	51(0)	6(5)
C(17)	1766(2)	4267(9)	−342(4)	211(5)	71(3)	25(2)	0(5)	32(5)	−4(7)
C(18)	1036(2)	3526(5)	−535(5)	223(1)	59(1)	23(10)	−15(0)	20(6)	3(6)
C(19)	1208(8)	3131(4)	47(5)	177(5)	37(5)	24(8)	−1(3)	12(4)	−6(3)
C(20)	633(6)	2347(4)	71(9)	151(8)	45(7)	28(3)	14(0)	3(4)	−11(9)

(Continued overleaf)

TABLE II. *(Continued)*

C(21)	1106(1)	1116(6)	2561(4)	213(1)	64(8)	19(4)	−20(6)	31(7)	4(7)
C(22)	−109(4)	1296(9)	2663(0)	155(6)	97(8)	36(1)	−36(9)	40(8)	−3(10)
C(23)	−609(10)	658(2)	2932(3)	250(9)	115(3)	30(9)	−47(7)	34(4)	−4(2)
C(24)	226(8)	−55(10)	3117(8)	238(2)	110(3)	18(7)	−34(2)	32(5)	−15(9)
C(25)	1462(10)	−235(1)	3052(4)	326(9)	48(10)	33(2)	−12(7)	50(4)	−2(6)
C(26)	1974(5)	397(8)	2763(1)	369(1)	45(4)	35(1)	−16(3)	50(8)	5(10)
C(27)	4487(8)	4985(2)	3512(3)	261(6)	52(8)	17(4)	−30(2)	38(2)	−7(5)
C(28)	3425(10)	5224(6)	3689(10)	265(5)	57(3)	29(9)	2(3)	52(5)	0(7)
C(29)	3945(3)	5675(4)	4276(9)	216(7)	56(9)	27(2)	−23(9)	24(2)	−1(2)
C(30)	5405(5)	5918(2)	4619(9)	208(7)	52(1)	44(0)	−6(4)	54(9)	−3(8)
C(31)	6462(2)	5661(7)	4420(5)	259(2)	63(4)	23(8)	−6(7)	8(3)	0(3)
C(32)	5974(6)	5189(9)	3840(0)	193(8)	59(6)	37(1)	−27(8)	27(7)	−4(5)
C(33)	3268(10)	5719(10)	353(4)	182(1)	47(1)	25(8)	−10(9)	23(5)	4(0)
C(34)	4671(1)	5944(9)	467(8)	220(6)	51(4)	38(2)	−30(1)	27(4)	−1(1)
C(35)	4925(10)	6599(0)	130(6)	308(8)	44(7)	45(4)	2(5)	57(6)	8(8)
C(36)	3632(1)	7012(6)	−323(2)	321(6)	57(8)	51(4)	0(3)	96(3)	6(1)
C(37)	2215(5)	6794(1)	−435(3)	299(9)	75(0)	33(2)	55(9)	49(8)	15(10)
C(38)	2030(9)	6142(10)	−80(6)	237(2)	77(7)	35(8)	31(9)	52(7)	7(7)
C(39)	−308(5)	1965(5)	−592(8)	222(4)	42(5)	31(6)	0(5)	38(4)	7(8)
C(40)	−1857(1)	2048(10)	−873(1)	206(3)	73(9)	41(0)	−15(9)	35(5)	−5(9)
C(41)	−2685(2)	1751(10)	−1519(1)	281(4)	80(8)	34(4)	−63(3)	35(3)	−6(7)
C(42)	−2032(3)	1363(5)	−1840(8)	237(4)	49(6)	41(2)	0(1)	39(7)	−5(4)
C(43)	−498(4)	1259(6)	−1539(8)	296(5)	52(8)	37(4)	9(4)	44(1)	2(4)
C(44)	436(0)	1599(7)	−903(2)	236(8)	60(6)	21(10)	−8(1)	12(2)	−3(3)
C(45)	6147(1)	2444(4)	1798(3)	234(1)	88(6)	40(6)	8(7)	45(9)	−5(7)

[a] Estimated standard deviations are given in parentheses and correspond to the last significant figure. The thermal ellipsoid is given by exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] $B_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$.

TABLE III. Bond Lengths (Å) of the Porphyrin Core of Ti(OCH_3)(tpp).[a]

Ti–O	1.77(1)	C(4)–C(5)	1.40(2)
Ti–N(1)	2.13(2)	C(5)–C(6)	1.39(2)
Ti–N(2)	2.11(1)	C(6)–C(7)	1.48(2)
Ti–N(3)	2.11(2)	C(7)–C(8)	1.41(2)
Ti–N(4)	2.13(1)	C(8)–C(9)	1.44(2)
O–C(45)	1.44(2)	C(9)–C(10)	1.43(2)
N(1)–C(1)	1.37(2)	C(10)–C(11)	1.35(2)
N(1)–C(4)	1.38(2)	C(11)–C(12)	1.44(2)
N(2)–C(6)	1.40(2)	C(12)–C(13)	1.41(2)
N(2)–C(9)	1.39(2)	C(13)–C(14)	1.46(2)
N(3)–C(11)	1.41(2)	C(14)–C(15)	1.44(2)
N(3)–C(14)	1.39(2)	C(15)–C(16)	1.37(2)
N(4)–C(16)	1.39(2)	C(16)–C(17)	1.48(2)
N(4)–C(19)	1.37(2)	C(17)–C(18)	1.38(2)
C(1)–C(2)	1.46(2)	C(18)–C(19)	1.46(2)
C(2)–C(3)	1.36(2)	C(19)–C(20)	1.42(2)
C(3)–C(4)	1.46(2)	C(20)–C(1)	1.40(2)

[a] Figures in parentheses are estimated standard deviations in the last significant figure.

lowest limits for a Ti–O bond distance, are to be found in oxotitanium (IV) porphyrins. Thus oxotitanium (IV) octaethylporphyrin [11] has a Ti–O bond length of 1.613 Å.

Table V gives structural characteristics of the axial methoxo bonding system in four first-row transition metal-porphyrin complexes, Ti(OCH_3)(tpp), Fe(OCH_3)(tpp) [12], Fe(OCH_3)(mpIXdme) [13], and Co(OCH_3)(py)(tpp) [14]. A shortening of the metal–oxygen bond distance as the number of valence electrons decreases, and a correlative opening of the metal–oxygen–carbon angle are observed. This suggests the order of decreasing π-donation Ti > Fe > Co for the axial methoxo bonding system in the three complexes. A similar phenomenon has been found in nitrosyl complexes of Mn, Fe and Co tetraphenylporphyrins [15, 16]. On the basis of observed trends in metal–nitrogen M–N(NO), distances and M–N–O angles in these complexes, Scheidt suggested the order Mn > Fe > Co for π interaction in the axial NO bonding system [16]. Indeed, the variable stereochemistry of nitrosylmetalloporphyrins is consistent with the well-known ability of the nitric oxide ligand to exist in more than one electronic and structural configuration [17]. Similarly, in view of Caulton's [10] and our studies, it now appears that alkoxides also can behave as 'non-innocent' ligands.

Finally, it can be noted that an electron-deficient complex such as Ti(OCH_3)(tpp) may approach the stable 18 electron configuration by two alternative mechanisms: dimer formation with bridging methoxide groups, or π-donation from a single axial methoxo ligand. Dimerization probably would result in some steric strain due to the presence of two methoxide groups within the space between the two

TABLE IV. Bond Angles (Deg) in the Coordination Group and Porphinato Skeleton of Ti(OCH_3)(tpp).[a]

O–Ti–N(1)	107.1(5)	C(5)–C(6)–C(7)	126(2)
O–Ti–N(2)	107.0(5)	C(6)–C(7)–C(8)	107(2)
O–Ti–N(3)	106.3(5)	C(7)–C(8)–C(9)	106(2)
O–Ti–N(4)	108.4(5)	N(2)–C(9)–C(8)	112(2)
N(1)–Ti–N(2)	84.5(6)	N(2)–C(9)–C(10)	127(2)
N(1)–Ti–N(4)	83.8(6)	C(8)–C(9)–C(10)	120(2)
N(2)–Ti–N(3)	86.5(6)	C(9)–C(10)–C(11)	123(2)
N(3)–Ti–N(4)	85.1(6)	N(3)–C(11)–C(10)	128(2)
N(1)–Ti–N(3)	146.6(5)	N(3)–C(11)–C(12)	109(2)
N(2)–Ti–N(4)	144.6(5)	C(10)–C(11)–C(12)	123(2)
Ti–O–C(45)	171(1)	C(11)–C(12)–C(13)	108(2)
C(1)–N(1)–C(4)	104(1)	C(12)–C(13)–C(14)	105(2)
C(6)–N(2)–C(3)	106(2)	N(3)–C(14)–C(13)	111(2)
C(11)–N(3)–C(14)	106(2)	N(3)–C(14)–C(15)	124(2)
C(16)–N(4)–C(19)	107(2)	C(13)–C(14)–C(15)	125(2)
N(1)–C(1)–C(2)	112(2)	C(14)–C(15)–C(16)	124(2)
N(1)–C(1)–C(20)	120(2)	N(4)–C(16)–C(15)	128(2)
C(2)–C(1)–C(20)	128(2)	N(4)–C(16)–C(17)	109(2)
C(1)–C(2)–C(3)	107(2)	C(15)–C(16)–C(17)	123(2)
C(2)–C(3)–C(4)	105(2)	C(16)–C(17)–C(18)	108(2)
N(1)–C(4)–C(3)	113(1)	C(17)–C(18)–C(19)	105(2)
N(1)–C(4)–C(5)	129(2)	N(4)–C(19)–C(18)	112(2)
C(3)–C(4)–C(5)	118(2)	N(4)–C(19)–C(20)	124(2)
C(4)–C(5)–C(6)	122(2)	C(18)–C(19)–C(20)	125(2)
N(2)–C(6)–C(5)	125(2)	C(19)–C(20)–C(1)	129(2)
N(2)–C(6)–C(7)	109(2)		

[a] Figures in parentheses are estimated standard deviations in the last significant figure.

TABLE V. Stereochemical Parameters of the Axial Methoxo Bonding System in Methoxometalloporphyrins.

Metalloporphyrin	Distance, Å		MOC angle, deg.	Ref.
	M–N	M–O		
Ti(OCH_3)(tpp)	2.12(2)	1.77(1)	171(1)	this work
Fe(OCH_3)(tpp)[a]		1.817(3)	129(1)	12
Fe(OCH_3)(mpIXdme)[b]	2.073(6)	1.842(4)	125.9(6)	13
Co(OCH_3)(py)(tpp)[c]	1.96(1)	1.92(7)	121(4)	14

[a] At 100 K. [b] Methoxoiron (III) mesoporphyrin IX dimethyl ester. [c] Methoxocobalt (III) pyridine tetraphenylporphyrin.

porphyrin rings, and thus π-donation is preferred. In such a mononuclear structure, bonding of a methanol molecule at the vacant coordination site would help to get closer to the 18 electron configuration. However, *trans* effect from the strongly bound methoxide probably prevents formation of a stable six-coordinate complex. In the case of the closely related fluorotitanium (III) tetraphenylporphyrin complex TiF (tpp), electron paramagnetic resonance spectroscopy indicates that various N-, P-, O-, and S-donor ligands can bind the titanium ion to give six-coordinate complexes of the type TiF(L)(tpp) [2]. However O-donor ligands such as ethanol bind weakly (consistent with the 'hard' character of the metal), and only at low temperatures ($t < 0$ °C) do they form to a significant extent [18]. Thus crystallization at ambient temperatures always affords the five-coordinate complex.

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