

# Synthesis and Crystal Structure of a Tetrameric Titanium Methoxochloro Complex, $Ti_4(OCH_3)_{14}Cl_2$

Kirsi Hyvärinen,<sup>†</sup> Martti Klinga and Markku Leskelä

Inorganic Chemistry Laboratory, PO Box 55, FIN-00014 University of Helsinki, Finland

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The titanium alkoxo complex, bis(chloro- $\mu_3$ -methoxo)tetra( $\mu$ -methoxo)octamethoxotetratitanium(IV),  $Ti_4(OCH_3)_{14}Cl_2$ , was formed by reaction of methyl-dimethoxysilane with n-butyl lithium followed by reaction with titanium tetrachloride. Titanium atoms are connected to each other by methoxy bridges forming a tetramer. The distorted octahedral coordination is completed by terminal methoxy groups or chloride ions. The colorless compound crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 10.673(3)$ ,  $b = 12.064(3)$ ,  $c = 12.295(3)$  Å,  $\beta = 110.89(2)^\circ$ .  $Z = 2$ . The data collection temperature was 193 K.

The chemistry of titanium(IV) alkoxides ( $Ti(OR)_4$ ) has been very widely studied.<sup>1–4</sup> Titanium alkoxides typically undergo hydrolysis easily, react with hydrolytic molecules, and have a tendency to increase the coordination number which, however, can be limited by the steric effects of the alkyl group. Therefore solid Ti alkoxides often have oligomeric or polymeric structures, for example  $(Ti(OMe)_4)_4$ ,  $(Ti(OEt)_4)_4$  or  $Ti_7O_4(OEt)_{20}$ .<sup>5–7</sup>

Our interest in Ti alkoxides stems from their use as precursors for the deposition of thin films from the gas phase and use as polymerization catalysts. In both applications monomolecular complexes instead of polymeric ones are preferred. The thin film precursors have to be volatile, and only monomolecular or small oligomeric complexes fulfill this requirement. We have successfully used Ti ethoxide and isopropoxide as precursors in the deposition of  $TiO_2$  films by atomic layer epitaxy.<sup>8,9</sup> Unsaturation in coordination is advantageous to catalysts, and a catalytically active complex must contain a ligand which is easily cleaved. Methods which have been used to preserve the structure of the Ti alkoxide monomolecular or small oligomeric complexes are (i) to increase the size of R, (ii) to make adducts with Lewis bases,<sup>10</sup> (iii) to have an organic ligand R' bound with a Ti–C  $\sigma$ -bond ( $TiR'(OR)_3$ )<sup>2</sup> or (iv) the use of mixed ligand complexes with halogens,  $(TiX_{4-n}(OR)_n)$ .<sup>11,12</sup> If  $n = 1$  monomolecular and catalytically active complexes may be obtained.<sup>13,14</sup>

In the present paper we report the crystal structure of

a tetrameric titanium alkoxo complex which has been synthesized as a byproduct in our studies on silicon-bridged alkoxo complexes of Group IV metals.

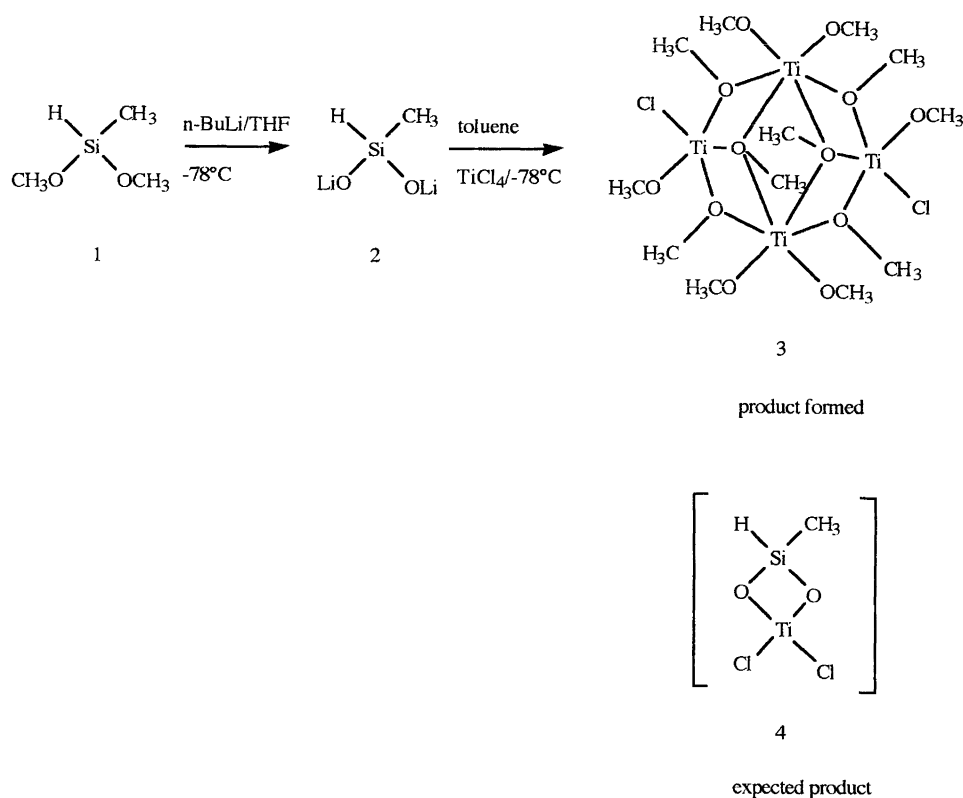
## Experimental

Because the reagents and the products were air- and moisture-sensitive all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) (Rathburn, HPLC grade), pentane (Rathburn, HPLC grade) and toluene (R.P. Normapur, p.a. grade) were purified by refluxing on  $LiAlH_4$  followed by distillation under an argon atmosphere. The n-butyl lithium used was a 1.6 M solution in hexane (Merck).

The titanium alkoxo complex was synthesized by the reaction of methyl-dimethoxysilane and n-butyl lithium followed by reaction with titanium tetrachloride (Scheme 1) as follows.

*Preparation of the crystal.* Methyl-dimethoxysilane (0.1 mol) was treated with 0.2 mol n-butyl lithium (1.6 M solution in hexane) in 120 ml of anhydrous tetrahydrofuran at  $-78^\circ C$ . The reaction was allowed to mix at  $-78^\circ C$  for 2 h and at room temperature overnight. Tetrahydrofuran was evaporated in vacuum, and the lithium salt was washed three times with anhydrous pentane. The solvent was changed to anhydrous toluene, and the reaction was treated with 0.5 mol titanium tetrachloride at  $-78^\circ C$  for a couple of hours and at room temperature overnight. The desired products were titanium alkoxo compound and lithium chloride. Lithium chloride was fil-

<sup>†</sup> To whom correspondence should be addressed. Fax: +358-0-40198.



Scheme 1. Preparation of  $\text{Ti}_4(\text{OCH}_3)_{14}\text{Cl}_2$ .

tered out, and the volume of the filtrate was evaporated in vacuum to  $2/3$  of the original volume. After a few days white crystals were formed at  $-8^\circ\text{C}$ .

*X-Ray measurements and calculations.* The manipulation of the air-sensitive crystal was made as described by Hope.<sup>15</sup> A single crystal was transferred from the mother liquid to the inert oil and cooled down to  $-80^\circ\text{C}$ . Details of the crystal analysis, data collection and structure re-

Table 1. Crystal data for  $\text{Ti}_4(\text{OCH}_3)_{14}\text{Cl}_2$ .

Compound	$[\text{Ti}_4(\text{OCH}_3)_{14}\text{Cl}_2]$
Formula	$\text{C}_{14}\text{H}_{42}\text{Cl}_2\text{O}_{14}\text{Ti}_4$
Formula mass	696.98
Space group	$P2_1/n$
Wavelength, (MoK $\alpha$ )/ $\text{\AA}$	0.71073
Crystal system	Monoclinic
Temperature/K	193(2)
$a/\text{\AA}$	10.673(3)
$b/\text{\AA}$	12.064(3)
$c/\text{\AA}$	12.295(3)
$\beta/^\circ$	110.89(2)
$V/\text{\AA}^3$	1479.0(7)
Z	2
$F(000)$	720
$D_c/\text{g cm}^{-3}$	1.565
$\mu/\text{cm}^{-1}$	12.76
Crystal size/mm	$0.18 \times 0.15 \times 0.12$
Scan mode	$\omega/2\theta$
$\theta_{\text{max}}/^\circ$	27.50
Weights	$[\sigma^2(F_o^2) + (0.44P)^2]^{-1}$ , where $P = (F_o^2 + 2F_c^2)/3$
No. of independent reflections	3553
No. of observed reflections	1207 [ $F > 4\sigma(F)$ ]
No. of variables	161
R	8.20
wR	14.31

Table 2. Atomic coordinates ( $\times 10^{-4}$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^{-2} \times 10^{-3}$ ) for  $\text{Ti}_4(\text{OCH}_3)_{14}\text{Cl}_2$ .

Atom	x	y	z	$U(\text{eq})^a$
Ti(1)	79(2)	4161(1)	2868(1)	44(1)
Ti(2)	1142(2)	6022(1)	5015(1)	41(1)
Cl(1)	2277(3)	4179(2)	2816(2)	70(1)
O(1)	-777(6)	4482(5)	1363(5)	53(2)
C(1)	-1004(11)	3958(8)	310(8)	69(3)
O(2)	52(6)	2670(5)	2815(5)	53(2)
C(2)	564(12)	1637(9)	2887(9)	79(4)
O(3)	778(5)	4253(4)	4783(4)	33(1)
C(3)	1864(9)	3546(7)	5449(7)	45(2)
O(4)	315(6)	5806(5)	3323(5)	42(2)
C(4)	420(10)	6630(8)	2514(8)	57(3)
O(5A) <sup>b</sup>	70(4)	752(1)	493(1)	47(6)
C(5)	1436(12)	8514(8)	5063(10)	80(4)
O(5B) <sup>b</sup>	117(6)	742(2)	502(2)	39(9)
O(6)	1583(5)	5768(5)	6710(4)	40(2)
C(6)	2852(9)	5967(9)	7549(8)	65(3)
O(7)	2827(6)	5977(5)	5133(5)	63(2)
C(7)	4019(11)	6295(11)	5030(11)	93(4)

<sup>a</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup> Atomic coordinates  $\times 10^{-3}$ .

Table 3. Bond lengths (in Å) for  $Ti_4(OCH_3)_{14}Cl_2$ .

Ti(1)–O(1)	1.790(6)	Ti(2)–O(3)	2.169(5)
Ti(1)–O(2)	1.799(7)	Ti(2)–O(3) <sup>i</sup>	2.176(5)
Ti(1)–O(6) <sup>i</sup>	2.020(6)	O(1)–C(1)	1.382(9)
Ti(1)–O(4)	2.053(6)	O(2)–C(2)	1.351(11)
Ti(1)–O(3)	2.204(5)	O(3)–C(3)	1.437(9)
Ti(1)–Cl(1)	2.370(3)	O(4)–C(4)	1.439(9)
Ti(2)–O(5B)	1.69(2)	O(5A)–C(5)	1.41(2)
Ti(2)–O(7)	1.753(6)	O(5B)–C(5)	1.35(2)
Ti(2)–O(5A)	1.86(2)	O(6)–C(6)	1.399(9)
Ti(2)–O(4)	1.966(6)	O(7)–C(7)	1.377(11)
Ti(2)–O(6)	1.990(5)		

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>  $-x, -y+1, -z+1$ .

finement are given in Table 1. The  $\omega$ - $2\theta$  data collection was carried out with a Rigaku AFC-7S diffractometer<sup>16,17</sup> using  $MoK\alpha$  ( $\lambda = 0.71073$  Å) radiation. The intensity data were corrected for Lorentz and polarization effects, but not for absorption ( $0.92 < T < 1.00$ ). The structure was solved and refined using SHELXTL<sup>18</sup> and SHELXL<sup>19</sup> programs, respectively. Scattering factors were those included in the program package SHELXL-93. All non-hydrogen atoms were anisotropically refined except for O(5), which was disordered with site occupancy factors 0.59(10) for O(5A) and 0.41(10) for O(5B). In the refinements hydrogen atoms were at their calculated positions ( $C-H = 0.96$  Å, riding model).

## Results and discussion

The atomic coordinates for the compound are presented in Table 2; bond lengths and angles are given in Tables 3 and 4. The product obtained was not that expected (Scheme 1), but a tetrameric methoxochloro compound,  $Ti_4(OCH_3)_{14}Cl_2$  (Fig. 1).

The steric effects around titanium and the high tendency of Ti to coordinate saturatively to oxygen were the main reasons that led to the formation of a tetramer. It seems that methoxy groups are sterically not bulky enough to form a monomeric titanium complex. The reason that product 4 (Scheme 1) was not formed was probably because *n*-butyl lithium reacted catalytically with the hydrogen atom of the starting material 1 producing a

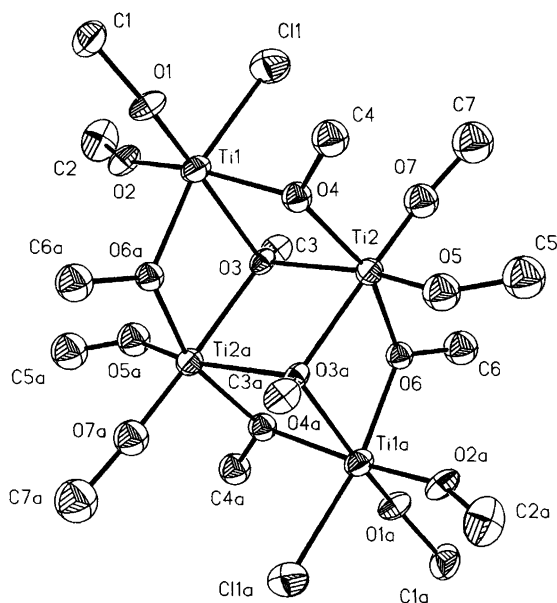


Fig. 1. One tetrameric unit of the title compound with atom labels. Only the major component of O(5) is represented. Symmetry-equivalent atoms are denoted with the label a. Hydrogen atoms are omitted for simplicity.

dimer of the starting material. This dimer reacted with titanium tetrachloride to give the titanium tetramer.

Oxygen atoms of the methoxy ligands form bridges between two or three titanium atoms. The tetrameric molecule has a center of symmetry and thus two independent Ti atoms. The framework  $Ti_4O_{14}Cl_2$  is similar to  $Ti_4O_{16}$  found in  $(Ti(OEt)_4)_4$  and  $(Ti(OMe)_4)_4$ .<sup>5,6</sup> All the titanium atoms in a tetramer are in the same plane because of the symmetry of the molecule. The polyhedra around the Ti atoms are distorted octahedra consisting of five O and one Cl atoms in the case of Ti(1) and six O atoms in the case of Ti(2). One oxygen atom [O(5)] shows some distortion. The bond lengths reflect the coordination of the methoxy groups. The greater the number of Ti atoms bonded with an oxygen atom, the longer are the bonds: Ti–O(terminal) 1.753(6)–1.799(7) Å [without the disordered O(5) atom], Ti–O( $\mu_2$ ) 1.966(6)–2.053(6) Å, Ti–O( $\mu_3$ ) 2.169(5)–2.204(5) Å. The values are similar to

Table 4. Bond angles (in °) around Ti atoms for  $Ti_4(OCH_3)_{14}Cl_2$ .

O(1)–Ti(1)–O(2)	100.6(3)	O(6) <sup>i</sup> –Ti(1)–Cl(1)	167.2(2)	O(4)–Ti(2)–O(6)	159.6(2)
O(1)–Ti(1)–O(6) <sup>i</sup>	94.9(3)	O(4)–Ti(1)–Cl(1)	88.4(2)	O(5B)–Ti(2)–O(3)	170(2)
O(2)–Ti(1)–O(6) <sup>i</sup>	92.7(3)	O(3)–Ti(1)–Cl(1)	93.9(2)	O(7)–Ti(2)–O(3)	96.4(3)
O(1)–Ti(1)–O(4)	92.3(3)	O(5B)–Ti(2)–O(7)	91(2)	O(5A)–Ti(2)–O(3)	156.8(12)
O(2)–Ti(1)–O(4)	167.1(3)	O(7)–Ti(2)–O(5A)	105.3(13)	O(4)–Ti(2)–O(3)	74.9(2)
O(6) <sup>i</sup> –Ti(1)–O(4)	85.6(2)	O(3)–Ti(2)–O(3) <sup>i</sup>	74.5(2)	O(6)–Ti(2)–O(3)	87.2(2)
O(1)–Ti(1)–O(3)	161.2(3)	O(5B)–Ti(2)–O(4)	97.7(8)	O(5B)–Ti(2)–O(3) <sup>i</sup>	100(2)
O(2)–Ti(1)–O(3)	94.8(3)	O(7)–Ti(2)–O(4)	98.3(3)	O(7)–Ti(2)–O(3) <sup>i</sup>	165.0(3)
O(6) <sup>i</sup> –Ti(1)–O(3)	73.6(2)	O(5A)–Ti(2)–O(4)	93.6(5)	O(5A)–Ti(2)–O(3) <sup>i</sup>	85.8(12)
O(4)–Ti(1)–O(3)	72.5(2)	O(5B)–Ti(2)–O(6)	99.0(6)	O(4)–Ti(2)–O(3) <sup>i</sup>	90.8(2)
O(1)–Ti(1)–C(1)	96.6(2)	O(7)–Ti(2)–O(6)	93.2(3)	O(6)–Ti(2)–O(3) <sup>i</sup>	74.8(2)
O(2)–Ti(1)–Cl(1)	90.7(2)	O(5A)–Ti(2)–O(6)	99.6(4)		

Symmetry transformations used to generate equivalent atoms:  $1-x, -y+1, -z+1$ .

those found in the literature.<sup>5-7</sup> The closest contacts between Ti atoms are Ti(1)–Ti(2) 3.340(2), Ti(1)–Ti(2)<sup>i</sup> 3.308(2) and Ti(2)–Ti(2)<sup>i</sup> 3.458(2) ( $i = -x, -y + 1, -z + 1$ ), indicating no direct interactions between Ti atoms.

The carbon–oxygen bonds also vary depending on the coordination to the methoxy groups. In the terminal groups the distances are 1.351(11)–1.382(9) Å [excluding the disordered O(5) atom]. In the bridging methoxy groups the C–O bond is weaker and the distances are 1.399(9)–1.439(9) Å.

Terminal Ti–O–C angles are significantly larger than Ti–O–C angles in bridging methoxy groups. They vary from 136.4(6) to 159.7(8)°. In bridging methoxy groups the Ti–O–C angles are 116.0(5)–118.4(5)° in the case of the  $\mu_3$ O atom and 120.8(5)–123.4(5)° in the case of  $\mu_2$ O atoms.

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