New Compounds in the Chemistry of Group 4 Transition-metal Alkoxides. Part 4.† Synthesis and Molecular Structures of Two Polymorphs of $[Ti_{16}O_{16}(OEt)_{32}]$ and Refinement of the Structure of $[Ti_7O_4(OEt)_{20}]$‡

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Two polymorphs of the condensed species $[Ti_{16}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_8(\mu\text{-}O)_4(\mu\text{-}OEt)_{16}(OEt)_{16}]$ have been obtained: a monoclinic form prepared in absolute ethanol and a tetragonal one obtained from 5% aqueous ethanol. The monoclinic form (compound **1**) crystallizes in the space group $C2/c$ with a = 23.392(7), b = 19.627(8), c = 24.130(14) Å and β = 96.4(4)°. The tetragonal variety (compound **2**) crystallizes in the space group $P4_2/n$ with a = 14.642(2) and c = 25.972(7) Å. Both structures have been solved by direct methods and refined to R = 0.078 for 5766 independent reflections (compound **1**) and to R = 0.053 for 3130 independent reflections (compound **2**). They are built from different packings of the same hexadecanuclear molecule. Both molecules show slight differences in the titanium–oxygen network and in the orientations of the ethoxy groups. The initial hydrolysis product of tetraethyltitanium(IV), $[Ti_7O_4(OEt)_{20}]$ **3** has been obtained by a new route. Its structure has been solved by direct methods and refined to R = 0.069 for 6293 independent reflections. This redetermination resulted in location of all the ethyl groups.

The use of sol–gel technology to produce advanced materials from chemical precursors is a rapidly growing area.[1,2] The state-of-the-art in sol–gel research has focused on oxide gels. There are two important processes for their formation, namely alkoxide and colloidal methods,[3,4] with alkoxides generally considered as the most suitable precursors. Therefore, the synthesis, properties and structures of alkoxides have stimulated a great deal of interest.[5,6]

However, structural data on homometallic or heterometallic alkoxides as well as oxoalkoxides are still scarce. The early stages of their hydrolysis/condensation have been characterized only through a few X-ray studies of intermediate compounds. Such examples include $[Ti_7O_4(OEt)_{20}]$, $[Nb_8O_{10}(OEt)_{20}]$, $[Zr_{13}O_8(OMe)_{36}]$ and $[Mo_6O_{10}(OEt)_{12}]$.[7–10]

We report here on the synthesis and structural studies of two polymorphs of $[Ti_{16}O_{16}(OEt)_{32}]$, a condensation product of $[Ti(OEt)_4]$. The initial hydrolysis product of titanium tetraethoxide, $[Ti_7O_4(OEt)_{20}]$, has been prepared by a new method and its structure redetermined.

Experimental

Synthesis.—A mixture of titanium tetraethoxide and anhydrous ethanol (1:1 v/v) was placed in a steel bomb at 100 °C during 2 weeks. The bomb was then opened after slow cooling. The yellowish solution contained colourless air-stable single crystals (compound **1**). The same preparation was repeated using 5% aqueous ethanol. This gave colourless crystals which are extremely unstable (compound **2**).

Single crystals of the initial hydrolysis product of $[Ti(OEt)_4]$ were obtained in an unsuccessful attempt to prepare a bimetallic Ti–Cu oxoalkoxide. A solution of $[Ti(OEt)_4]$ in anhydrous ethanol (1:1 v/v) was prepared and basic copper carbonate, $CuCO_3\cdot Cu(OH)_2$, added (molar ratio Ti:Cu = 1:1). This suspension was placed in a steel bomb at 100 °C during 1 month. Tabular colourless single crystals of $[Ti_7O_4(OEt)_{20}]$ **3** were obtained.

Data Collection and Structure Refinements.—Reflection intensities (hkl) were measured on an Enraf-Nonius CAD4 diffractometer. Lattice parameters were refined using least squares for 25 reflections in the range $3 < \theta < 20°$. Table 1 shows crystallographic data and information on data collection and refinement procedures.

In the three studies, the positions of the independent metal atoms as well as those of a part of their oxygen surroundings were derived from direct methods. Remaining atoms were located from successive difference Fourier maps. An empirical absorption correction using the program DIFABS[11] was applied. All refinement calculations were performed with SHELX 76 with a weighting scheme $w = k/[\sigma^2(F) + |k'|F^2]$.[12]

The final positional parameters are given in Tables 2, 3 and 4 for compounds **1**, **2** and **3** respectively. It is noteworthy that some of the carbon atoms show high thermal parameters as a result of minor disorder in ethyl group positions which could not be solved.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Discussion

Description of the Structures.—$[Ti_{16}O_{16}(OEt)_{32}]$. The determination of the crystal structures of compounds **1** and **2** provides evidence that they derive from different packings of the same hexadecanuclear neutral entity $[Ti_{16}O_{16}(OEt)_{32}]$. In the monoclinic form, the 'Ti_{16}' molecules are located on the two-fold axis[13] and the molecular arrangement results in a small tunnel (diameter *ca.* 3.5 Å) along the direction $\frac{1}{4}, y, \frac{1}{2}$ (Fig. 1). In the tetragonal form, the 'Ti_{16}' molecules are located on the $\bar{4}$ axis and a tunnel (diameter *ca.* 2.8 Å), resulting from the packing, expands along the 4_2 screw axis (Fig. 2).

It is noteworthy that the cell volume of the tetragonal form is larger than that of the monoclinic one by 127 Å^3 (calculated for

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† Part 3 is ref. 16.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

$Z = 4$). Although we did not find any solvent molecule in the tetragonal structure, the difference in cell volume may be a clue to the presence of water of crystallization. This may explain the crystal instability of the tetragonal compound.

The geometries of the inorganic $Ti_{16}O_{48}$ cores (ethyl groups omitted for clarity) are shown in Figs. 3 and 4 for compounds **1** and **2** respectively with the same orientation. In both compounds the molecules are built up of two orthogonal blocks of eight TiO_6 octahedra. In each block, six octahedra form a layer with a NiAs-type structure, with the remaining two lying either side of the layer. Fig. 5 shows an idealized view of such a compact block. This structure can be described in terms of triangular M_3O_{13} associations, a structural element which is commonly observed in the building of polyanions, such as $[Nb_6O_{19}]^{6-}$, $[Mo_7O_{24}]^{6-}$ *etc.* and in polycations such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$.[14] The projections shown in Figs. 1 and 2 are equivalent *i.e.* the molecule is projected along the two-fold axis in the monoclinic structure and along the $\bar{4}$ axis in the tetragonal one. Thus, in each case, the central titanium atom hides three other metal atoms. A comparison of both figures shows that the main differences concern the relative orientations of alkoxo groups.

However, careful comparison of the inorganic cores evidences small differences in geometry for the titanium–oxygen networks. The largest deviations are observed for Ti ··· Ti distances through the connection between Ti_8 blocks (Table 5): Ti(1) ··· Ti(2) compared to Ti(3) ··· Ti(3′), Ti(1) ··· Ti(7) compared to Ti(3) ··· Ti(4″) for example. These deviations arise from a slight disorientation of the two blocks in the monoclinic form since there is no crystallographic symmetry to force a regular connection. Moreover, both blocks do not have strictly the same geometry. As examples, the Ti(1) ··· Ti(9) and Ti(2) ··· Ti(8) bond lengths are slightly different as are the distances in the pairs Ti(3) ··· Ti(9) and Ti(4) ··· Ti(8), Ti(5) ··· Ti(9) and Ti(7) ··· Ti(8) (Table 5).

The sixteen titanium atoms are interconnected through four different kinds of oxygen bridges. Four oxygen atoms are bridging (μ), eight others are triply bridging (μ_3) and four atoms are quadruply bridging (μ_4). Finally, sixteen alkoxo groups are μ-co-ordinated. Octahedral surroundings are completed by sixteen terminal alkoxo groups.

The connection of the sixteen TiO_6 octahedra imposes great distortions in the metal environments. For example, the lines Ti(9) ··· Ti(1) ··· Ti(9′) or Ti(8) ··· Ti(2) ··· Ti(8′) in the

Table 1 Crystal data and structure refinement parameters *

Compound	**1**	**2**	**3**
Formula	$C_{64}O_{48}Ti_{16}$	$C_{64}O_{48}Ti_{16}$	$C_{40}O_{24}Ti_7$
M	2 464.4	2 464.4	1 300.5
Crystal system	Monoclinic	Tetragonal	Triclinic
Space group	*C*2/*c*	*P*4₂/*n*	*P*$\bar{1}$
Cell parameters			
a/Å	23.392(7)	14.642(2)	13.91(5)
b/Å	19.627(8)		20.212(9)
c/Å	24.130(14)	25.972(7)	12.162(5)
α/°			90.49(3)°
β/°	96.4(4)°		108.20(4)
γ/°			74.65(2)
Cell volume/Å^3	11 009	5 568	3 124.6
Z	4	2	2
D_c/g cm^{-3}	1.487	1.470	1.382
μ/cm^{-1}	11.46	11.46	9.07
θ/°	2–26	3–25	3–25
Measured reflections	9 418	6 979	11 797
Reflections with $I > 3\sigma(I)$	5 766	3 130	6 293
Refined parameters	579	291	641
R	0.078	0.053	0.069
R′	0.079	0.052	0.068

* Details in common: $T = 20$ °C, scan type ω–θ.

Table 2 Fractional atomic coordinates for compound **1**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti(1)	0.000	0.058 30(4)	0.250	O(24)	0.126 6(4)	0.011 5(3)	0.145 6(2)
Ti(2)	0.000	0.290 17(7)	0.250	C(1)	0.131(1)	0.068(1)	0.406 0(7)
Ti(3)	0.108 24(5)	−0.013 15(6)	0.297 37(8)	C(2)	0.007 5(9)	0.145 0(9)	0.449 6(8)
Ti(4)	0.035 32(7)	0.361 61(8)	0.149 16(9)	C(3)	0.235 8(8)	0.000 3(8)	0.278 9(7)
Ti(5)	0.093 51(8)	0.153 38(7)	0.299 00(9)	C(4)	−0.043(1)	0.150(1)	0.481 4(8)
Ti(6)	0.000	−0.100 06(6)	0.250	C(5)	0.146(1)	0.281(9)	0.136 5(9)
Ti(7)	0.040 78(7)	0.194 99(8)	0.164 25(6)	C(6)	0.196 5(9)	0.068(8)	0.424 6(7)
Ti(8)	0.073 71(6)	0.270 41(7)	0.400 47(5)	C(7)	0.207(1)	0.202(1)	0.264 9(8)
Ti(9)	0.147 70(7)	0.076 11(9)	0.195 69(6)	C(8)	0.158(1)	0.250 6(9)	0.503 9(7)
Ti(10)	0.000	0.448 61(8)	0.250	C(9)	0.080 3(9)	−0.009 2(8)	0.106 3(9)
O(1)	0.027 2(3)	−0.017 3(4)	0.298 9(3)	C(10)	0.246(1)	0.192(1)	0.320 0(7)
O(2)	0.081 3(5)	0.065 3(5)	0.244 3(3)	C(11)	0.118(1)	−0.130 0(8)	0.209 1(7)
O(3)	−0.014 0(3)	0.127 6(4)	0.191 2(3)	C(12)	0.173 0(9)	0.354 9(9)	0.362 2(6)
O(4)	0.058 7(4)	0.220 8(4)	0.242 8(4)	C(13)	0.022 4(8)	0.380 6(9)	0.477 6(7)
O(5)	0.047 1(5)	0.366 0(5)	0.228 6(3)	C(14)	0.156(1)	0.277(1)	0.074 4(8)
O(6)	0.015 4(3)	0.282 9(4)	0.330 2(2)	C(15)	0.248(1)	0.076(1)	0.125 8(8)
O(7)	0.098 3(3)	0.142 0(3)	0.154 5(1)	C(16)	0.073 9(9)	0.462(1)	0.363 2(6)
O(8)	0.163 3(3)	0.149 1(2)	0.260 0(2)	C(17)	0.132 8(9)	0.462(1)	0.104 2(7)
O(9)	0.138 9(3)	−0.068 9(3)	0.351 4(3)	C(18)	0.139(1)	−0.191 2(8)	0.244 4(7)
O(10)	0.015 0(4)	0.342 1(4)	0.420 8(3)	C(19)	0.262 6(8)	−0.056(1)	0.253 9(7)
O(11)	0.007 3(5)	0.197 8(4)	0.408 3(2)	C(20)	−0.003 3(9)	0.341(1)	0.517 3(6)
O(12)	0.020 2(4)	0.434 3(5)	0.333 2(2)	C(21)	0.099 8(8)	0.559 8(9)	0.251 3(7)
O(13)	0.110 5(4)	0.206 2(4)	0.355 5(3)	C(22)	0.219(1)	0.384(1)	0.402 8(7)
O(14)	0.084 1(2)	0.417 2(4)	0.120 9(3)	C(23)	0.176 9(9)	−0.123(1)	0.439 1(8)
O(15)	0.008 8(4)	−0.159 6(5)	0.306 5(3)	C(24)	0.149 8(8)	−0.120 7(8)	0.399 4(6)
O(16)	0.121 8(5)	0.068 3(5)	0.345 8(2)	C(25)	0.103 7(9)	−0.033 3(8)	0.055 1(5)
O(17)	0.175 7(3)	0.005 2(5)	0.255 7(4)	C(26)	0.070 5(8)	0.535(1)	0.391 0(6)
O(18)	0.084 7(4)	0.281 5(4)	0.142 1(2)	C(27)	0.098(1)	0.634 6(8)	0.235 3(6)
O(19)	0.058 3(5)	0.510 1(4)	0.245 4(2)	C(28)	0.284 3(9)	0.126 4(9)	0.103 3(7)
O(20)	0.101 5(4)	0.246 3(4)	0.470 3(2)	C(29)	0.028 1(8)	−0.273 7(9)	0.355 8(6)
O(21)	0.125 4(5)	0.334 4(4)	0.390 1(3)	C(30)	0.149 3(8)	0.254 8(9)	0.567 5(6)
O(22)	0.083 5(3)	−0.085 2(3)	0.240 6(1)	C(31)	0.010 0(9)	−0.198 2(9)	0.356 0(7)
O(23)	0.217 2(4)	0.097 9(5)	0.173 4(2)	C(32)	0.135(1)	0.495 2(8)	0.046 3(6)

Table 3 Fractional atomic coordinates for compound **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti(1)	0.750	0.750	0.042 52(6)	C(11)	0.691(1)	0.628(1)	−0.041 3(7)
Ti(2)	0.568 47(8)	0.750 00(8)	0.108 55(4)	C(12)	0.654(1)	0.618(1)	−0.080 8(5)
Ti(3)	0.750	0.750	0.162 81(6)	C(21)	0.599 3(6)	0.894 7(5)	0.022 0(3)
Ti(4)	0.588 10(7)	0.736 58(7)	0.234 71(4)	C(22)	0.547 1(7)	0.857 2(6)	−0.023 9(3)
Ti(5)	0.563 00(8)	0.934 59(7)	0.176 51(4)	C(31)	0.452(1)	0.629 0(9)	0.036 4(4)
O(1)	0.706 1(4)	0.668 2(4)	−0.003 4(2)	C(32)	0.396(1)	0.643(1)	0.001 1(6)
O(2)	0.634 6(3)	0.822 6(3)	0.054 0(2)	C(41)	0.396 3(7)	0.866 3(8)	0.115 8(4)
O(3)	0.495 3(3)	0.688 9(3)	0.065 8(2)	C(42)	0.352 1(9)	0.905(1)	0.087 5(7)
O(4)	0.490 9(3)	0.859 6(3)	0.123 0(2)	C(51)	0.702 2(7)	1.033 8(7)	0.113 3(3)
O(5)	0.618 5(3)	0.999 4(3)	0.127 2(2)	C(52)	0.701(1)	1.124 5(9)	0.097 1(6)
O(6)	0.473 5(3)	1.014 9(3)	0.192 7(2)	C(61)	0.450 8(8)	1.103 3(6)	0.182 6(4)
O(7)	0.523 7(3)	0.683 7(3)	0.170 2(2)	C(62)	0.399(2)	1.146(1)	0.203 0(9)
O(8)	0.506 5(2)	0.843 9(3)	0.232 2(2)	C(71)	0.476 5(6)	0.599 0(5)	0.170 2(3)
O(9)	0.684 5(3)	0.690 8(2)	0.105 0(1)	C(72)	0.376 6(7)	0.609 1(8)	0.173 2(5)
O(10)	0.635 1(2)	0.814 3(2)	0.168 4(1)	C(81)	0.440 5(6)	0.863 7(6)	0.268 1(4)
O(11)	0.698 2(2)	0.667 7(2)	0.215 0(1)	C(82)	0.358 9(7)	0.824(1)	0.267 9(5)
O(12)	0.534 0(2)	0.658 0(3)	0.274 6(2)				

Table 4 Fractional atomic coordinates for compound **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti(1)	0.701 89(9)	0.294 30(7)	0.204 7(1)	C(32)	0.024 4(8)	0.307 3(6)	0.042 4(9)
Ti(2)	0.813 3(1)	0.294 30(7)	0.468 8(1)	C(41)	−0.020(1)	0.460 6(8)	0.238(1)
Ti(3)	0.910 8(1)	0.186 80(7)	0.223 0(1)	C(42)	−1.022(1)	0.497 9(7)	0.146(1)
Ti(4)	0.594 7(1)	0.259 01(7)	0.374 4(1)	C(51)	0.132(1)	0.104 5(8)	0.340(1)
Ti(5)	0.694 9(1)	0.148 45(7)	0.133 8(1)	C(52)	0.191(1)	0.065(1)	0.424(1)
Ti(6)	0.480 2(1)	0.264 33(8)	0.102 7(1)	C(61)	0.887 6(8)	0.668 4(6)	0.515(1)
Ti(7)	0.915 6(1)	0.337 98(7)	0.287 5(1)	C(62)	0.777 7(8)	0.704 5(8)	0.493(1)
O(1)	0.760 5(4)	0.363 4(3)	0.162 7(4)	C(71)	0.779(1)	0.462(1)	0.410(1)
O(2)	0.834 6(4)	0.123 9(2)	0.261 7(4)	C(72)	0.860(1)	0.458(1)	0.467(1)
O(3)	0.955 0(4)	0.269 4(3)	0.180 7(4)	C(81)	0.965 8(7)	0.805 7(5)	0.411 5(8)
O(4)	0.927 8(4)	0.415 7(3)	0.231 8(5)	C(82)	0.902 6(9)	0.806 7(7)	0.288(1)
O(5)	0.032 2(4)	0.144 8(3)	0.334 8(5)	C(91)	0.177 3(9)	0.645 3(6)	0.303 3(8)
O(6)	0.046 6(4)	0.311 2(3)	0.390 1(5)	C(92)	0.214(1)	0.575 6(7)	0.276(1)
O(7)	0.854 0(4)	0.373 3(2)	0.408 4(4)	C(101)	0.218 5(6)	0.837 1(5)	0.440 8(7)
O(8)	0.059 9(4)	0.754 3(3)	0.440 7(4)	C(102)	0.238(1)	0.817 9(6)	0.330 8(9)
O(9)	0.224 1(4)	0.654 7(3)	0.421 5(4)	C(141)	0.716 6(8)	0.037 7(5)	0.975 6(8)
O(10)	0.254 9(4)	0.780 3(2)	0.524 4(4)	C(142)	0.280 1(9)	0.967 2(6)	0.143 4(8)
O(11)	0.852 6(3)	0.262 4(2)	0.316 0(4)	C(151)	0.505 8(8)	0.411 0(5)	0.079 1(9)
O(12)	0.758 0(3)	0.223 9(2)	0.122 0(4)	C(152)	0.527 9(9)	0.453 4(5)	0.182 3(9)
O(13)	0.624 0(3)	0.225 7(2)	0.224 3(4)	C(161)	0.608 9(7)	0.055 6(5)	0.258 7(8)
O(14)	0.731 4(4)	0.099 0(3)	0.021 1(4)	C(162)	0.603 0(9)	−0.013 2(5)	0.225(1)
O(15)	0.562 7(4)	0.338 9(3)	0.101 2(4)	C(171)	0.447(1)	0.778 2(7)	0.105 7(9)
O(16)	0.646 4(4)	0.087 6(3)	0.187 2(5)	C(172)	0.513(1)	0.802 3(9)	0.189(1)
O(17)	0.559 6(4)	0.205 5(3)	0.012 6(4)	C(181)	0.705(1)	0.654(1)	0.105(1)
O(18)	0.627 1(4)	0.685 6(3)	0.014 9(5)	C(182)	0.747(2)	0.643(1)	0.183(2)
O(19)	0.417 8(4)	0.198 9(3)	0.122 5(6)	C(191)	0.363(1)	0.159 2(9)	0.050(2)
O(20)	0.457 5(4)	0.306 0(3)	0.244 2(4)	C(192)	0.284(1)	0.150 8(9)	0.047(2)
O(21)	0.947 4(4)	0.144 5(3)	0.106 2(4)	C(201)	0.357 8(7)	0.321 9(6)	0.263 6(9)
O(22)	0.675 9(3)	0.322 4(2)	0.343 9(4)	C(202)	0.290 5(9)	0.388 0(7)	0.205(1)
O(23)	0.452 0(4)	0.687 6(3)	0.524 2(4)	C(211)	0.082 4(7)	0.849 2(5)	0.016 2(8)
O(24)	0.556 0(4)	0.185 2(3)	0.408 6(4)	C(212)	0.006 9(9)	0.895 1(7)	0.059 6(9)
C(11)	0.735 3(8)	0.401 5(7)	0.055 6(8)	C(231)	0.478 0(8)	0.619 2(6)	0.498(1)
C(12)	0.294(1)	0.633 7(8)	0.044(1)	C(232)	0.506(1)	0.612 2(9)	0.398(1)
C(21)	0.878 2(7)	0.065 3(5)	0.340 6(7)	C(241)	0.503 8(8)	0.830 8(6)	0.529(1)
C(22)	0.919(1)	0.003 2(5)	0.284(1)	C(242)	0.490(1)	0.114 4(8)	0.492(1)
C(31)	0.046 3(7)	0.262 3(5)	0.146 2(8)				

monoclinic form [Ti(5) • • • Ti(3) • • • Ti(5′) in the tetragonal structure] are folded with Ti • • • Ti • • • Ti angles of 169.6(4) and 168.5(3)° [169.4(5)° in the tetragonal form]. This distortion also appears in Ti(6) and Ti(10) [Ti(1)] surroundings (see Table 5). However, the main deformations are observed for metal atoms directly involved in the connection between 'Ti_8' blocks: Ti(1), Ti(2), Ti(8) and Ti(9) in the monoclinic structure. Table 6 gives, as an example, the deviations from the best equatorial planes in the octahedral environments of these atoms.

The co-ordination geometries of μ_4-oxygen atoms are highly asymmetrical with Ti–O–Ti angles ranging from 94.4 to 149.4° in the monoclinic structure and from 94.6 to 150.3° in the tetragonal one (Table 5). The μ_3-oxygen atoms show two different co-ordination geometries: in the monoclinic variety, O(1) and O(5) [O(9) in the tetragonal form] are tetrahedral whereas O(3) and O(4) [O(11)] are planar.

All terminal alkoxo groups in the tetragonal form have the same co-ordination with a mean Ti–O–C angle equal to 161.2°. This tendency to linearity has already been observed for zirconium oxoalkoxides[15,16] and associated to metal–oxygen π interactions.[17] On the contrary, in the monoclinic form, four groups show similar geometries with a mean Ti–O–C angle equal to 169.3° whereas a mean value of 140.3° is observed for four other groups (Table 5).

[$Ti_7O_4(OEt)_{20}$]. The structure of this compound was first published[7] in 1967 as an extremely short communication. It was refined to $R = 0.13$ in the monoclinic space group $P2_1/a$ with a cell volume of 12 942.8 Å^3. The carbon atoms were not located and the paper did not give atomic coordinates. In the present work, we have refined the structure in the triclinic $P\bar{1}$ space group with a volume, calculated for $Z = 8$, smaller by 444.4 Å^3. So, we can wonder whether both compounds are strictly identical or whether there are any traces of water, or solvent, in the larger cell.

Anyhow, the heptanuclear molecule has the same titanium–

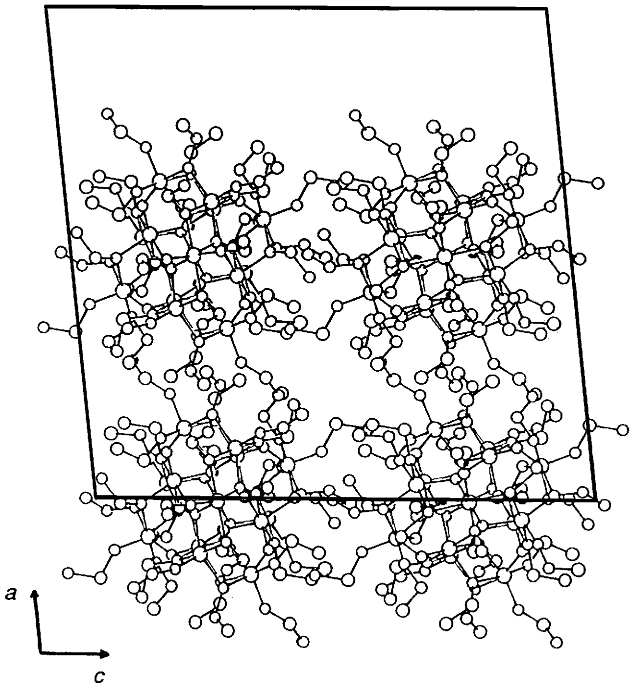

Fig. 1 Projection along the *b* axis of the monoclinic form

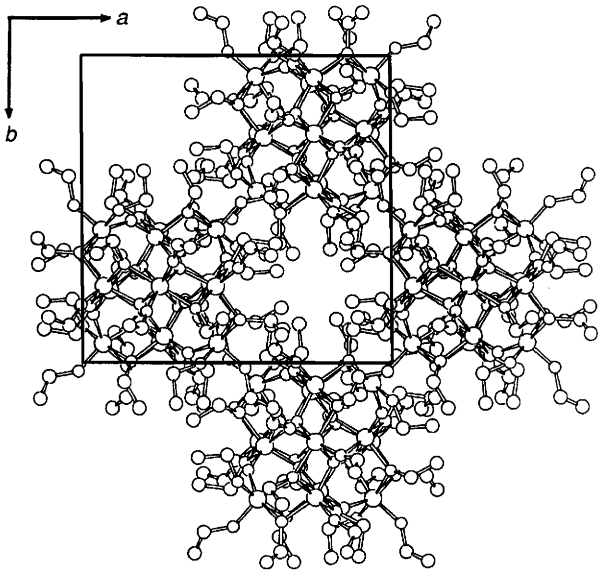

Fig. 2 Projection along the *c* axis of the tetragonal form

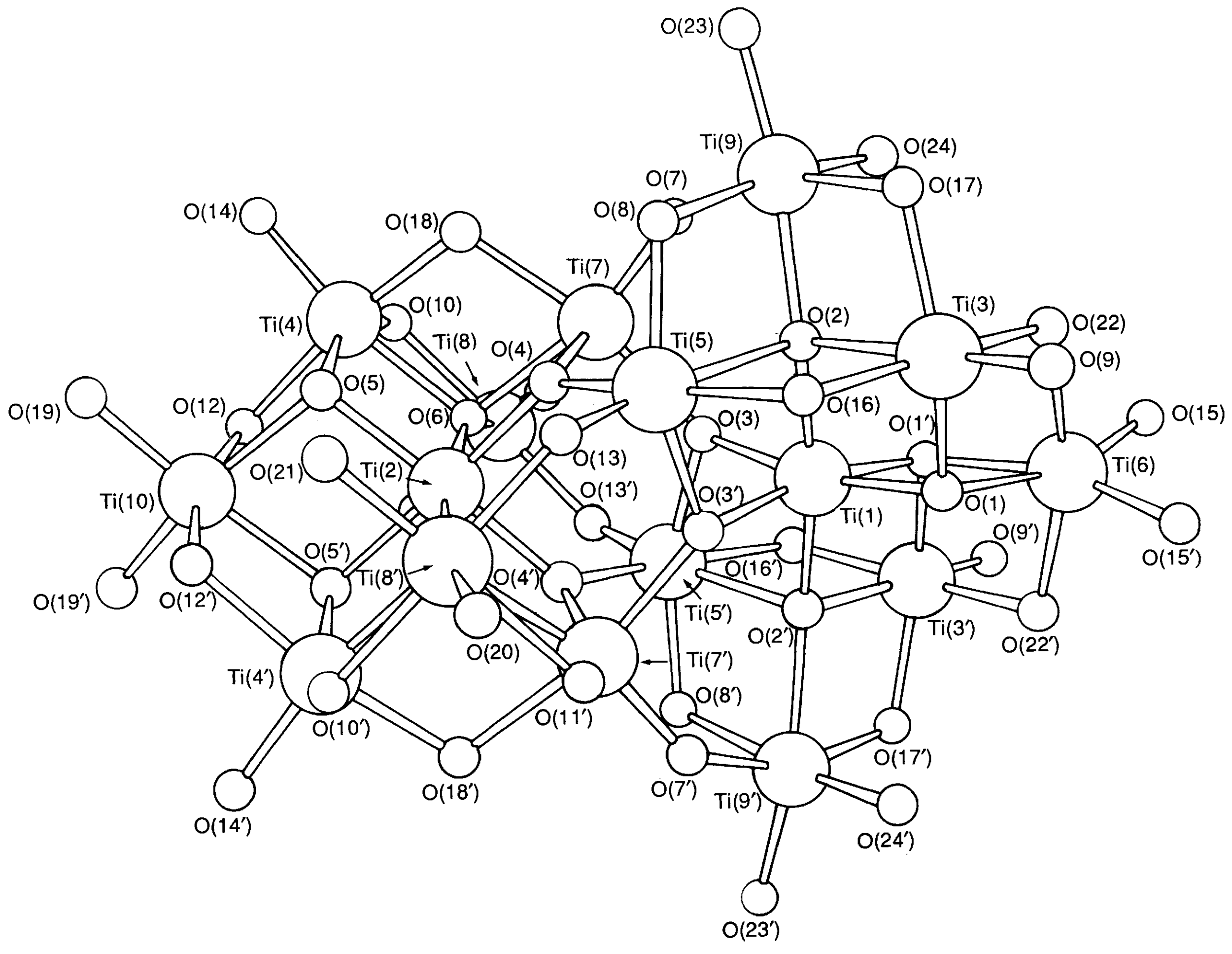

Fig. 3 ORTEP drawing of the $Ti_{16}O_{48}$ core (compound **1**)

Table 5 Selected bond distances (Å) and angles (°) for compounds **1** and **2**

Compound **1** (Monoclinic form)		Compound **2** (Tetragonal form)		Compound **1** (Monoclinic form)		Compound **2** (Tetragonal form)	
Ti(1) ••• Ti(2)	4.551(2)	Ti(3) ••• Ti(3′)	4.524(1)	Ti(1)–O(2)–Ti(9)	149.3(4)	Ti(3)–O(10)–Ti(5)	150.3(2)
Ti(1) ••• Ti(3)	3.005(1)	Ti(3) ••• Ti(2)	3.006(1)	Ti(1)–O(2)–Ti(3)	98.1(3)	Ti(2)–O(10)–Ti(3)	97.6(2)
Ti(1) ••• Ti(5)	3.016(1)	Ti(3) ••• Ti(4)	3.021(1)	Ti(1)–O(2)–Ti(5)	94.4(4)	Ti(3)–O(10)–Ti(4)	94.6(2)
Ti(1) ••• Ti(6)	3.106(2)	Ti(3) ••• Ti(1)	3.121(2)	Ti(2)–O(6)–Ti(8)	149.4(5)		
Ti(1) ••• Ti(7)	3.582(2)	Ti(3) ••• Ti(4″)	3.566(2)	O(12)–Ti(10)–O(12′)	164.7(5)	Ti(3)–O(10)–Ti(5)	163.1(2)
Ti(1) ••• Ti(9)	3.840(2)	Ti(3) ••• Ti(5)	3.861(1)	O(22)–Ti(6)–O(22′)	164.5(5)		
Ti(3) ••• Ti(5)	3.289(2)	Ti(2) ••• Ti(4)	3.292(1)	O(5)–Ti(4)–O(10)	150.0(5)	O(4)–Ti(2)–O(9)	151.4(2)
Ti(4) ••• Ti(8)	3.233(2)	Ti(2) ••• Ti(5)	3.226(1)	O(1)–Ti(3)–O(17)	149.6(6)		
Ti(5) ••• Ti(7)	3.442(2)	Ti(4′) ••• Ti(4″)	3.454(1)	Ti(7)–O(7)–Ti(9)	139.6(5)	Ti(4)–O(12)–Ti(5‴)	139.3(2)
Ti(5) ••• Ti(8)	3.428(1)	Ti(4) ••• Ti(5‴)	3.445(1)	Ti(2)–O(4)–Ti(5)	129.4(4)	Ti(3)–O(11)–Ti(4‴)	128.7(2)
Ti(5) ••• Ti(9)	3.285(1)	Ti(4) ••• Ti(5)	3.287(1)	Ti(1)–O(3)–Ti(7)	128.9(5)		
Ti(7) ••• Ti(8)	3.302(1)			Ti(6)–O(15)–C(31)	168.5(5)	Ti(1)–O(1)–C(11)	163.0(2)
Ti(2) ••• Ti(8)	3.861(2)			Ti(3)–O(9)–C(24)	170.8(4)	Ti(2)–O(3)–C(31)	168.1(2)
Ti(3) ••• Ti(9)	3.222(1)			Ti(9)–O(23)–C(15)	134.8(5)	Ti(5)–O(6)–C(61)	160.5(2)
				Ti(4)–O(14)–C(17)	167.0(6)	Ti(5)–O(5)–C(51)	153.2(2)
				Ti(10)–O(19)–C(21)	170.9(6)		
				Ti(8)–O(20)–C(8)	136.5(5)		
				Ti(8)–O(21)–C(12)	147.3(5)		

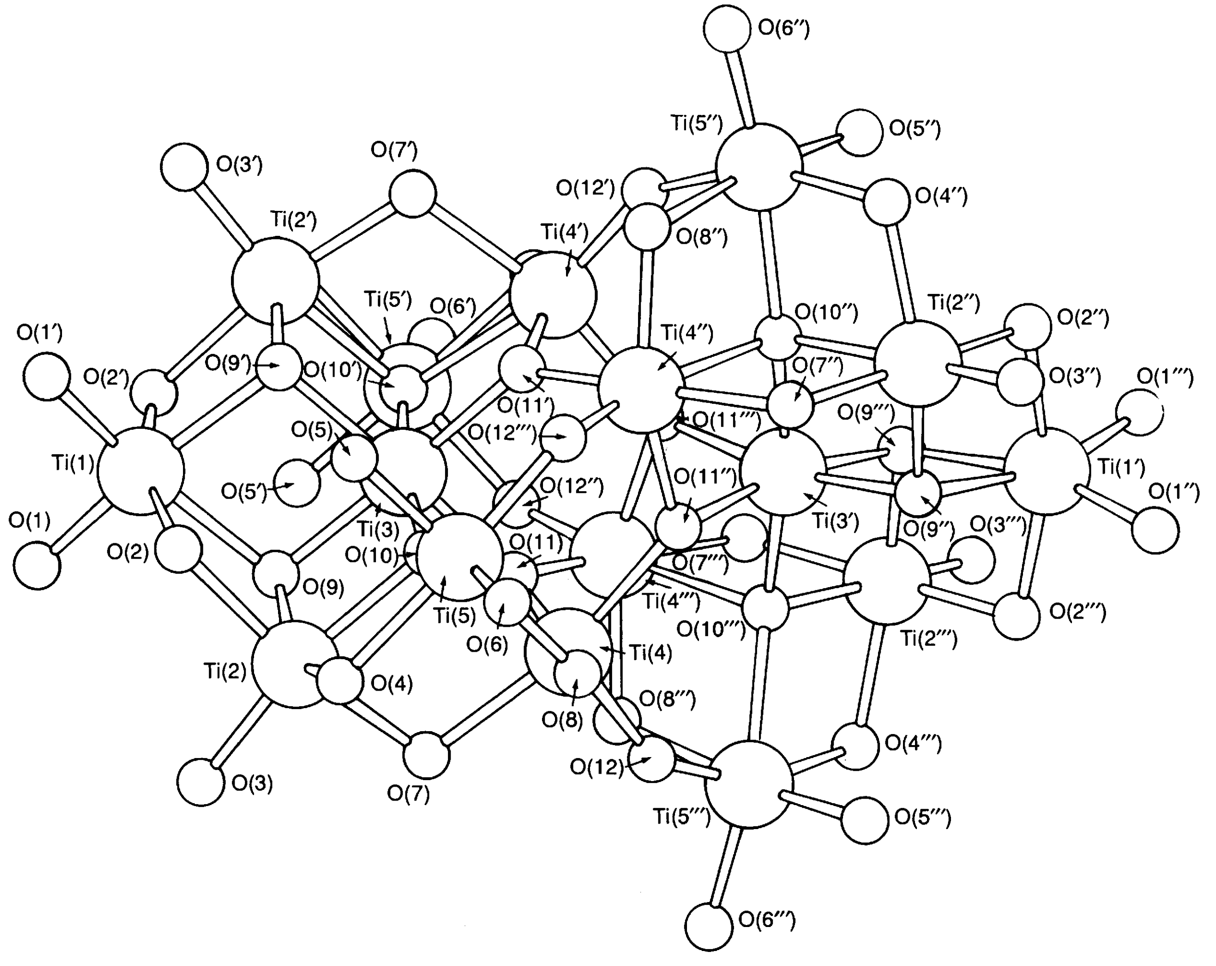

Fig. 4 ORTEP drawing of the $Ti_{16}O_{48}$ core (compound **2**)

oxygen network in both cases (at least qualitatively, as the first paper gave only a schematic illustration of the Ti_7O_{24} core). The molecule consists of seven TiO_6 octahedra, the central octahedron sharing six edges with six surrounding polyhedra (Figs. 6 and 7). An idealized view of the Ti_7O_{24} core shows its structural similarity with the 'Ti_{16}' molecule and the presence of M_3O_{13} associations.

The seven metal atoms are connected through three different kinds of oxygen bridges: two μ_4-O [O(11) and O(13)], two μ_3-O [O(12) and O(22)] and eight μ-alkoxo groups. Titanium surroundings are completed by twelve terminal alkoxo groups which show the shortest Ti–O bond lengths: 1.766(6)–1.810(6) Å (Table 7).

The octahedra are highly distorted, particularly around Ti(1) [O(12)–Ti(1)–O(22) 148.9(2)°], Ti(6) [O(17)–Ti(6)–O(20) 155.8(2)°] and Ti(7) [O(3)–Ti(7)–O(7) 155.1(3)°]. As observed in the 'Ti_{16}' molecule the μ_4-oxygen atoms have an asymmetrical co-ordination with Ti–O–Ti angles ranging from

96.3 to 150.5° (see Table 7). The μ_3-oxygen atoms show a tetrahedral geometry with a slight asymmetry in bond lengths. The co-ordination can be described as a symmetrical μ-O bridge towards Ti(2) and Ti(4) [or Ti(3) and Ti(5)] and a third shorter bond towards Ti(1). Symmetrical bridges are observed for all μ-alkoxo groups except O(1) and O(15) groups which give significantly shorter bonds towards Ti(1).

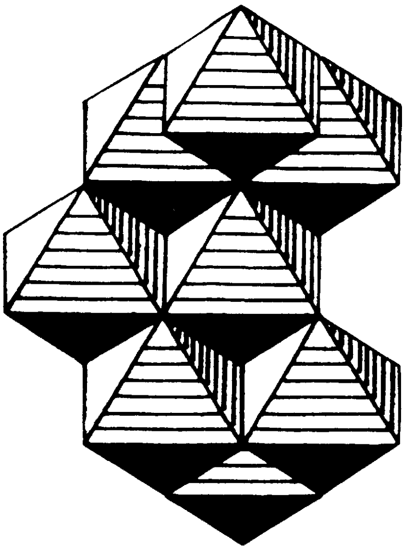

Fig. 5 Idealized view of a 'Ti_8' block

Among the twelve terminal alkoxo groups, ten groups show a 'bent' co-ordination with a mean Ti–O–C angle of 141.3°. The other two groups have a more linear co-ordination [Ti(5)–O(16)–C(161) 160.1(6)°, Ti(6)–O(18)–C(181) 175(2)°].

Table 6 Deviations (Å) from the best equatorial planes in the environments of Ti(1), Ti(2), Ti(8) and Ti(9) for compound **1**

Plane	Distances to the plane
Ti(1)–O(1)–O(1′)	O(3) 0.407
Ti(2)–O(5)–O(5′)	O(4) 0.410
Ti(8)–O(10)–O(21)	O(11) 0.118, O(13) 0.669
Ti(9)–O(17)–O(24)	O(8) 0.230, O(7) 0.662

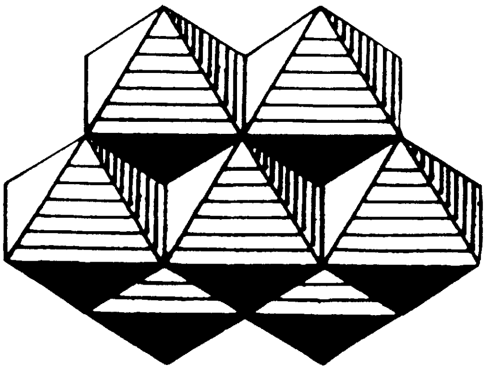

Fig. 7 Idealized view of a 'Ti_7' block

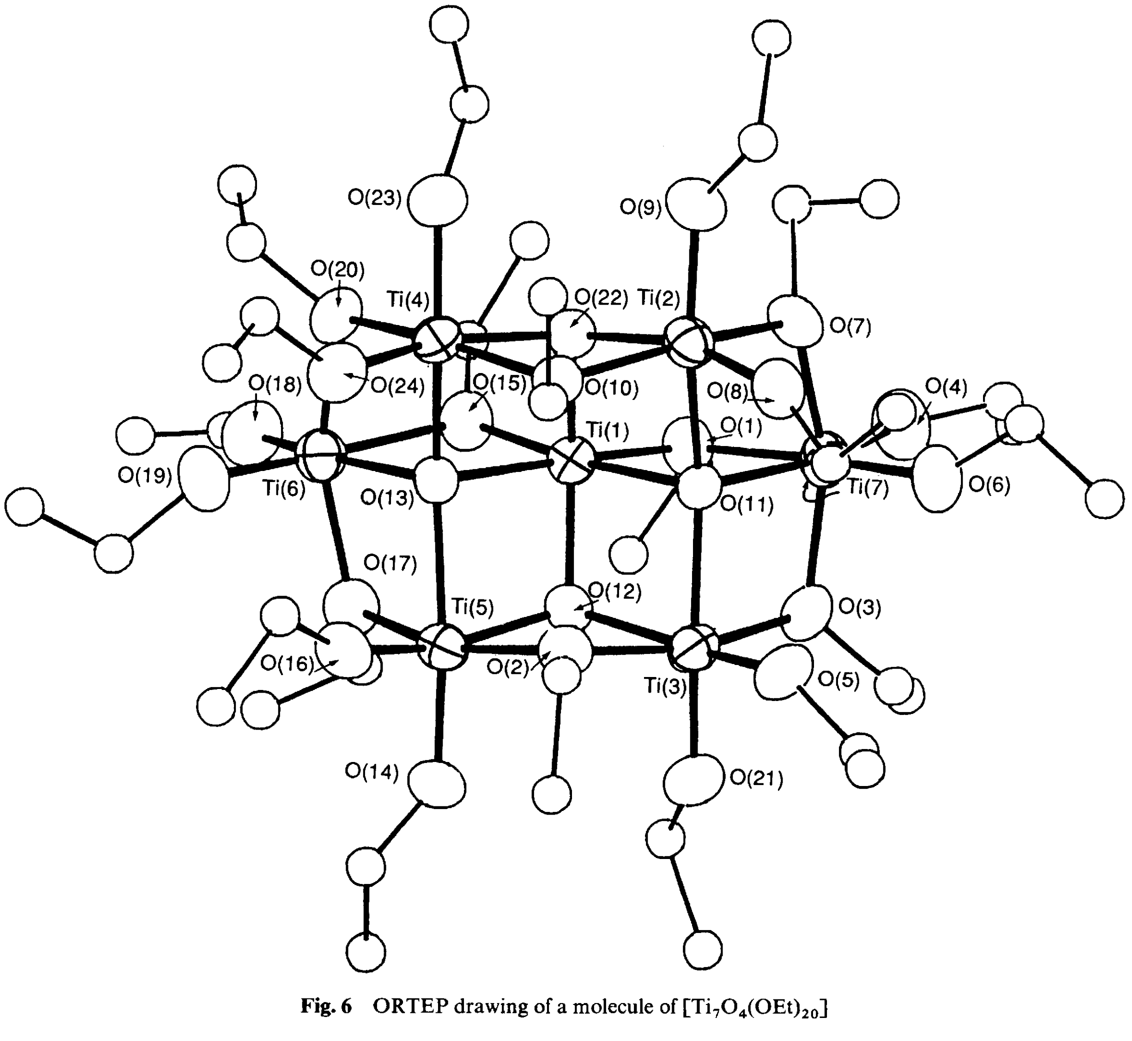

Fig. 6 ORTEP drawing of a molecule of $[Ti_7O_4(OEt)_{20}]$

Table 7 Selected bond distances (pm) and angles (°) for compound **3**

Ti(1)–O(1)	193.9(7)	Ti(2)–O(7)	204.2(6)	Ti(3)–O(2)	200.0(6)	Ti(7)–O(1)	214.6(4)
Ti(1)–O(11)	204.3(4)	Ti(2)–O(8)	178.2(4)	Ti(3)–O(3)	204.6(7)	Ti(7)–O(3)	198.1(5)
Ti(1)–O(12)	187.7(5)	Ti(2)–O(9)	179.9(6)	Ti(3)–O(5)	180.3(4)	Ti(7)–O(4)	178.5(7)
Ti(1)–O(13)	202.9(5)	Ti(2)–O(10)	199.7(6)	Ti(3)–O(11)	203.9(5)	Ti(7)–O(6)	180.0(5)
Ti(1)–O(15)	193.0(5)	Ti(2)–O(11)	214.5(5)	Ti(3)–O(12)	203.4(4)	Ti(7)–O(7)	196.3(6)
Ti(1)–O(22)	189.2(5)	Ti(2)–O(22)	197.8(4)	Ti(3)–O(21)	179.2(6)	Ti(7)–O(11)	203.3(5)
Ti(4)–O(10)	201.4(5)	Ti(5)–O(2)	201.5(4)	Ti(6)–O(13)	203.7(4)		
Ti(4)–O(13)	206.2(5)	Ti(5)–O(13)	197.6(6)	Ti(6)–O(15)	212.5(6)		
Ti(4)–O(20)	205.7(5)	Ti(5)–O(13)	211.2(5)	Ti(6)–O(17)	196.8(6)		
Ti(4)–O(22)	202.4(5)	Ti(5)–O(14)	181.0(6)	Ti(6)–O(18)	178.6(5)		
Ti(4)–O(23)	179.2(6)	Ti(5)–O(16)	176.6(6)	Ti(6)–O(19)	181.9(7)		
Ti(4)–O(24)	180.8(6)	Ti(5)–O(17)	204.8(4)	Ti(6)–O(20)	198.7(6)		
O(12)–Ti(1)–O(22)	148.9(2)	O(9)–Ti(2)–O(11)	163.4(2)	O(13)–Ti(6)–O(18)	163.6(3)	O(13)–Ti(4)–O(23)	161.9(3)
O(1)–Ti(1)–O(13)	171.4(2)	O(7)–Ti(2)–O(10)	161.9(2)	O(15)–Ti(6)–O(19)	173.2(2)	O(10)–Ti(4)–O(20)	166.3(2)
O(11)–Ti(1)–O(15)	170.9(2)	O(8)–Ti(2)–O(22)	162.6(2)	O(17)–Ti(6)–O(20)	155.8(2)	O(22)–Ti(4)–O(24)	164.5(2)
O(2)–Ti(5)–O(17)	160.8(2)	O(2)–Ti(3)–O(3)	165.8(2)	O(4)–Ti(7)–O(11)	161.2(2)	Ti(2)–O(11)–Ti(3)	150.5(2)
O(12)–Ti(5)–O(16)	163.0(2)	O(5)–Ti(3)–O(12)	165.8(3)	O(1)–Ti(7)–O(6)	176.5(3)	Ti(1)–O(11)–Ti(7)	102.8(2)
O(13)–Ti(5)–O(14)	163.7(2)	O(11)–Ti(3)–O(21)	160.8(2)	O(3)–Ti(7)–O(7)	155.1(3)	Ti(1)–O(11)–Ti(3)	98.0(2)
						Ti(3)–O(11)–Ti(7)	101.8(2)
Ti(4)–O(13)–Ti(5)	150.5(2)						
Ti(1)–O(13)–Ti(6)	102.2(2)						
Ti(1)–O(13)–Ti(5)	96.3(2)						
Ti(5)–O(13)–Ti(6)	100.4(2)						

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