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Carboxylic Acid Modified $[Ti(\mu\text{-}ONep)(ONep)_3]_2$ Compounds. Syntheses, Characterizations, X-ray Structures, and Implications for the Thin Film Densification of TiO_2 from $Ti_3(\mu_3\text{-}O)(O_2CH)_2(ONep)_8$, $Ti_3(\mu_3\text{-}O)(O_2CMe)_2(ONep)_8$, $Ti_6(\mu_3\text{-}O)_6(O_2CCHMe_2)_6(ONep)_6$, $[Ti(\mu\text{-}O_2CCMe_3)(ONep)_3]_2$, and $Ti_3(\mu_3\text{-}O)(O_2CCH_2CMe_3)_2(ONep)_8$ ($ONep = OCH_2CMe_3$).[1]

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Abstract. The products isolated from the stoichiometric reactions of $[Ti(\mu\text{-ONep})(ONep)_3]_2$ (**1**, ONep = OCH_2CMe_3) and a variety of sterically hindered carboxylic acids [HORc: HOFc (HO_2CH), HOAc (HO_2CCH_3), HOPc (HO_2CCHMe_2), HOBc (HO_2CCMe_3), or HONc ($HO_2CCH_2CMe_3$)] have been identified as $Ti_3(\mu_3\text{-O})(OFc)_2(ONep)_8$ (**2**), $Ti_3(\mu_3\text{-O})(OAc)_2(ONep)_8$ (**3**), $Ti_6(\mu_3\text{-O})_6(OPc)_6(ONep)_6$ (**4**), $Ti_2(\mu\text{-OBc})_2(ONep)_6$ (**5**), and $Ti_3(\mu_3\text{-O})(ONc)_2(ONep)_8$ (**6**), respectively. Compounds **2**, **3**, and **6** adopt a triangular arrangement of Ti atoms linked by a μ_3-oxide ligand with ORc and ONep ligands supporting the basic framework. For the asymmetric complexes **2** and **6**, the ORc ligands bridge from a single Ti [**2**, Ti(3); **6**, Ti(1)] to each of the other metal centers; in contrast, the OAc ligands of the sy. complex **3** bridge only between Ti(1) and Ti(2). Terminal ONep ligands complete the coordination of Ti (one 5- and two 6-coordinated) metal centers for each complex. Compound **4** adopts a distorted, hexagon-prism geometry of two offset $[\text{-Ti-O-}]_3$ rings with each 6-coordinated metal possessing a terminal ONep and two monodentate OPc ligands. The unique, non-esterified product **5** is dimeric with two μ-ONep, two unidentate bridging OBc, and two terminal ONep ligands which form an octahedral geometry around each of the Ti metal centers. The solution behaviors of **2** - **6** were investigated by molecular weight and/or solution NMR experiments. While each compound was found to undergo some form of dynamic behavior associated with the external ligand set, the trinuclear complexes (**2**, **3**, **6**) appeared to maintain

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the central core integrity. Compound **5** was found to undergo solution rearrangement between the solid state, dinuclear species, and higher order oligomers in solution. Compounds **1 - 6** were used to study the effect of similarly ligated species, with substantially varied structures, on the final densification of the resultant ceramic (in this case TiO_2). The previously characterized HORc modified $Ti(OPr^i)_4$ derivatives were also studied in an analogous manner. The TiO_2 thin films derived from the ONep derivatives were consistently more dense than the OPr^i analogs. Furthermore, the partially hydrolyzed, trinuclear ONep complexes **2**, **3**, **6** were found to yield films with the highest density, as determined from ellipsometric data.

Introduction

Thin films of ceramic materials are often produced through the use of solution route techniques (i.e., dip or spin-coating). In general, these processes involve, (i) dissolution of a precursor in a solvent, (ii) deposition of the precursor solution onto a substrate, and (iii) thermal treatment of the deposited film to convert the metallo-organic species to the ceramic phase. Metal alkoxide precursors are often favored for solution routes due to their high solubility in a variety of solvents, low decomposition/crystallization temperatures, ability to "cross-link" upon exposure to ambient atmosphere, and ease of modification.[2-6] However, alkoxide precursors are often *too* reactive and modifications to their ligand sets are required to tailor hydrolysis and condensation rates to allow for the production of high quality thin films. For example, it has been shown that titanium alkoxides ($Ti(OR)_4$) readily hydrolyze upon exposure to ambient humidity resulting in the formation of complex multi-nuclear species.[7-9]

Multi-dentate ligands are used to modify the reactivity of the $Ti(OR)_4$ precursors by decreasing the number of hydrolyzable (terminal) ligands.[10-16] One modifier that has gained wide-spread use is acetic acid (HOAc = HO_2CMe); however, the reaction of $Ti(OR)_4$ with HOAc does not yield the simple "$Ti(OAc)(OR)_3$" metathesis product. Instead these compounds undergo esterification, forming compounds of the general formula, $Ti_6O_4(OAc)_{16-4n}(OR')_{4n}$ [*n*

= 1, 2: R' = Et, CH_2Me[11]; Pr^i, $(CHMe_2)$[12,13]; *n*-Bu, $(CH_2)_3Me$[14]]. Figure 1a shows the general constructs of these compounds.

Other, more sterically hindered carboxylic acids (HORc) have also been investigated and additional structural types have been isolated (Figure 1 a – c).[1,16-18] Recently, a unique star shaped product, $Ti_9O_8(OMc)_{16}(OPr^i)_4$ (Figure 1d) where OMc = $O_2CC(Me)=CH_2$, was characterized from the reaction of $Ti(OPr^i)_4$ and excess HOMc.[19] Reacting $Ti(OPr^i)_4$ with the sterically, less-demanding formic acid (HOFc - see Table 1), also lead to additional novel structure types (Figure 1 e-f).[20]

HORc modified $Ti(OR)_4$ precursors have been used in the formation of complex ce- thin films (i.e., $Pb(Zr,Ti)O_3$).[21-23] Increasing the density of these ceramic thin films is of interest to improve the quality and reduce the cost of the final devices. Currently, too many variables (both chemically and physically) exist to realistically determine the controlling aspects for the densification of the final films of these complex ceramics. Therefore, we choose to use TiO_2 as a model for more complex ceramics because it is a single component ceramic and a great deal of interest currently exists for dense thin films of TiO_2. For example, recent applications of TiO_2 thin films include catalysts,[24,25] sensors,[26-28] membranes,[29-32] coatings,[33-36] and electrochromic[37-40] devices. A systematic investigation of $Ti(OR)_4$ precursors and their effect on TiO_2, thin films requires a well-characterized family of similarly ligated compounds.

The structurally characterized $Ti(OR)_4$ family, of which there are surprisingly very few members (R = Me[41]; Et[42]; THME[43]), have all been found to adopt a standard M_4O_{16} arrangement. The lack of structural diversity and hyper-reactivity of $Ti(OR)_4$ to ambient humidity made this family of compounds unattractive for probing the densification of TiO_2 thin films. On the other hand, HORc modified $Ti(OPr^i)_4$ compounds are more stable to hydrolysis and possess structurally diverse family members, including $Ti_4(O)(OFc)_2(OPr^i)_{10}$ (Figure 1e),[20] $Ti_6(O)_4(OAc)_8(OPr^i)_{12}$ (Figure 1a),[12] $Ti_2(OBc)_2(OPr^i)_6(HOPr^i)$,[16] $Ti_6(O)_4(ONc)_2(OPr^i)_{12}$ (Figure 1b)[16]. To initiate a valid study on the densification of TiO_2, thin films, the number of well-characterized precursors and the structural types needed to be expanded.

Investigation of the neo-pentoxide (ONep = OCH_2CMe_3) derivative of titanium lead to the crystallographically characterized complex, $[Ti(\mu\text{-}ONep)(ONep)_3]_2$ (**1**),[44] which is half the nuclearity of other crystallographically characterized $Ti(OR)_4$ compounds.[41-43] It was therefore reasoned that additional, reduced nuclearity Ti compounds would be characterized as the chemistry of **1** was studied. Due to the need to develop both the chemistry of **1** and increase the number of HORc modified $Ti(OR)_4$ compounds, a study of the reactivity of **1** with a variety of HORc (see Table 1) was undertaken. A number of novel structural types for HORc modified $Ti(OR)_4$ compounds were identified, including $Ti_3(O)(OFc)_2(ONep)_8$ (**2**),

$Ti_3(O)(OAc)_2(ONep)_8$ (**3**), $Ti_6(O)_6(OPc)_6(ONep)_6$ (**4**), $Ti_2(OBc)_2(ONep)_6$ (**5**), and $Ti_3(O)(ONc)_2(ONep)_8$ (**6**).

With these precursors, and the previously identified OPr^i derivatives, further probing of the subtle changes of nuclearity and structure on the densification of ceramic thin films (i.e., TiO_2) could be undertaken.[1] This paper reports the synthesis, solid state, and solution behavior of **2** - **6**. The crystal structure of the OPr^i derivatives $Ti_2(\mu\text{-}OBc)(OBc)(OPr^i)_6(HOPr^i)$, **5a** and $Ti_6(\mu_3\text{-}O)_4(ONc)_4(OPr^i)_{12}$, **6a** are also presented due to the unreported structural data for these unusual complexes. A structural comparison between the ONep and OPr^i derivatives is presented where appropriate. Thin film characteristics of TiO_2 derived from solution of **2** - **6** and th derivatives were also determined[1] and the various trends presented.

Experimental Section

All compounds described below were handled under dry argon or nitrogen atmospheres with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. FT-IR data were obtained on a Nicolet, Magna System Spectrometer-550 using KBr pellets under an atmosphere of flowing nitrogen. TGA/DTA experiments were performed on a Polymer Laboratories STA 1500 Instrument under an atmosphere of flowing oxygen up to 650 °C and at a ramp rate of 5 °C/ min. Elemental analyses were performed on a Perkin-Elmer 2400 CHN-S/O

Elemental Analyzer. The changes in film thickness and refractive index at room temperature, as a function of drying time were measured by ellipsometry on a Gaertner L116-C Ellipsometer.

All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere. All $^{13}C\{^{1}H\}$ solid state NMR spectra were obtained on a Bruker AMX400 spectrometer, at a frequency of 100.63 MHz using a 4 mm broadband magic angle spinning (MAS) probe, spinning at 4 kHz. For all of the $^{13}C\{^{1}H\}$ cross-polarized (CP) MAS spectra acquired, a standard CP sequence with high power ^{1}H decoupling, and a 1 ms contact time and 64 - 256 scans were utilized. For solution spectra, each sample was redissolved in toluene-d_8 at saturated solution concentrations. All solution spectra were obtained on a Bruker DMX400 spectrometer at 399.87 and 100.54 MHz for ^{1}H and ^{13}C experiments, respectively. A 5 mm broadband probe was used for all experiments. ^{1}H NMR spectra were obtained using a direct single pulse excitation, with a 10 s recycle delay and 8 scan average. The $^{13}C\{^{1}H\}$ NMR spectra were obtained using a WALTZ-16 composite pulse ^{1}H decoupling, a 5 s recycle delay and a $\pi/4$ pulse excitation.

All solvents were freshly distilled from the appropriate drying agent[45] and stored over 4 Å molecular sieves. The following compounds were stored under argon upon receipt (Aldrich) and used without further purification: HONep, HOPc, HOBc, and HONc (see Table 1). HOFc and HOAc were dried over boric anhydride and acetic anhydride/chromium oxide, respectively,

and freshly distilled immediately prior to use. $Ti(OPr^i)_4$ was freshly distilled under vacuum, immediately prior to use. Compound **1**[44] and the HORc modified $Ti(OPr^i)_4$ derivatives were prepared as described in the literature.[1,11-13,16] Crystals of $Ti_2(\mu\text{-OBc})(OBc)(OPr^i)_6(HOPr^i)$, **5a** and $Ti_6(O)_4(ONc)_4(OPr^i)_{12}$, **6a** were isolated by slow evaporation of the reaction mixture of $Ti(OPr^i)_4$ and HOBc or HONc, respectively. Since **2 - 6** were all prepared in an analogous manner, a general synthetic route is described below with any variations noted in the individual sections.

General Synthesis. To a stirring solution of **1** (1.00 g, 2.52 mmol) in toluene (~5 mL), the appropriate HORc (2.52 mmol) in toluene (~1.5 mL) was added via pipette and stirred [illegible] hours. After this time, approximately half of the volatile component of the reaction mixture was removed by rotary evaporation. The solution was allowed to sit at glove box temperatures with slow evaporation of volatile material, until crystals formed. The mother liquor was decanted and the remaining crystals were dried by rotary evaporation. Additional crystalline material was isolated by further slow evaporation of the volatile components.

$Ti_3(O)(OFc)_2(ONep)_8$, 2. HOFc (0.116 g, 2.52 mmol). A white precipitate formed immediately upon addition of HOFc. The reaction was stirred for same amount of time, the insoluble material removed by centrifugation, and the soluble fraction allowed to slowly evaporate (*vide infra*). Crystalline yield 0.291g (36.5%). FT-IR (KBr, cm^{-1}) 2956(s), 2905(m), 2869(m), 2844(m),

2732(w), 2692(w), 1595(s), 1561(m), 1479(m), 1462(m), 1394(m), 1372(m) 1366(m), 1259(w), 1216(w), 1080(s,br), 1038(s), 1023(s), 939(w), 905(w), 801(w)772(w), 753(w), 724(m), 679(m, br), 597(m), 538(m). ^{1}H NMR (tol-d_8, 400.1 MHz) δ 8.48, 8.19 (s, O_2CH), 4.82, 4.51, 4.48, 4.41, 4.40, 4.39, 4.37, 4.36, 4.35, 4.33, 4.29, 4.27, 4.05, 4.02 (s, OCH_2CMe_3) 1.25, 1.09, 1.02, 1.00, 0.79 (s, OCH_2CMe_3). ^{13}C{^{1}H} NMR (tol-d_8, 100.6 MHz) δ 168.3, 167.3 (O_2CH), 88.7, 88.1, 86.7, 86.5, 85.0 ($OCHCMe_3$), 34.1, 33.8, 33.5 (OCH_2CMe_3), 27.1, 27.0, 26.9, 26.4, 25.8 (OCH_2CMe_3). Elem. Anal. Calc'd for $C_{41}H_{89}O_{13}Ti_3$: C, 52.73; H, 9.53. Found: 53.03, C; 9.19, H. TGA/DTA: theoretical weight loss 74.7 %, actual 73.2 %; thermal events (°C): 134 (m, endo), 326 (s, exo, recoalescence), 456 (w, exo).

$Ti_3(O)(OAc)_2(ONep)_8$, 3. HOAc (0.152 g, 2.52 mmol). Crystalline yield 0.700 g (85.1%). FT-IR (KBr, cm^{-1}) 2955(s), 2904(m), 2868(m), 2834(m), 2699(w), 1593(s), 1481(s), 1449(s), 1389(m), 1364(m), 1261(m), 1092(s), 1066(s, sh), 1037(s), 1023(s), 1014(s), 800(m), 751(m), 734(m), 714(m), 694(m, br), 668(m, sh), 631(m), 582(s), 545(w), 502(w). ^{1}H NMR (tol-d_8, 400.1 MHz) δ 4.79, 4.72, 4.49, 4.46, 4.42, 4.40, 4.38, 4.35, 4.34, 4.32, 4.29, 4.27, 4.26, 4.06, 4.03 (s, OCH_2CMe_3), 2.01, 1.98, 1.81 (s, O_2CMe), 1.26, 1.17, 1.09, 1.07, 1.05, 1.03, 1.01, 0.82 (s, OCH_2CMe_3). ^{13}C{^{1}H} NMR (tol-d_8, 100.6 MHz) δ 178.0, 179.9, 177.5 (s, O_2CMe), 90.5, 88.5, 87.8, 86.3, 85.9, 84.6 (OCH_2CMe_3), 35.0, 34.2, 34.0, 33.9, 33.8, 33.5 (OCH_2CMe_3), 27.1, 27.0, 26.9, 26.7, 26.5, 26.5, 25.8, 23.8, 23.5, 22.5 (O_2CMe, OCH_2CMe_3). Elem. Anal. Calc'd for

$C_{44}H_{94}O_{13}Ti_3$: 55.93, C; 9.65, H. Found. 55.72, C; 9.31, H. TGA/DTA: theoretical weight loss 75.4%, actual 70.2 %; thermal events (°C): 128 (w, endo), 154 (w, endo), 317 (s, exo, recoalescence), 456 (w, exo).

$Ti_6(O)_6(OPc)_6(ONep)_6$, 4. HOPc (0.223 g, 2.52 mmol). Crystalline yield 0.270 g (89.9 %). FT-IR (KBr, cm^{-1}) 2954(s), 2905(m), 2867(m), 2837(m), 1570(s), 1540(m), 1473(m), 1428(m), 1393(w), 1363(m), 1263(m), 1095(s, br), 1024(s), 1013(s, sh), 803(m, br), 750(w), 718(m, sh), 698(m, sh), 667(m), 594(w), 526(m). ^1H NMR (tol-d_8, 400.1 MHz) δ 4.80, 4.63, 4.52, 4.49, 4.45, 4.43, 4.40, 4.37, 4.35, 4.32, 4.28, 4.25, 4.31, 4.05 (s, OCH_2CMe_3), 2.52, 2.42 (sept., O_2CCHMe_2, J_{H-H} = 6.8 Hz) 1.26 (mult., O_2CCHMe_2), 1.18, 1.67, 1.16, 1.15, 1.14 (... O_2CCHMe_2) 1.08, 1.03, 1.01, 0.80 (OCH_2CMe_3). $^{13}C\{^1H\}$ NMR (tol-d_8, 100.6 MHz) δ 183.5, 183.4, 183.2, 182.9 (O_2CCHMe_2), 90.1, 88.5, 87.7, 86.1, 85.8, 84.4 (OCH_2CMe_3), 36.4, 36.3 (O_2CCHMe_2), 35.3, 35.0, 34.1, 34.0, 33.9, 33.5 (OCH_2CMe_3), 27.5, 27.1, 26.9, 26.5, 25.8 (OCH_2CMe_3)19.9, 19.5, 19.2, 18.9 (O_2CCHMe_2). Elem. Anal. Calc'd for $C_{54}H_{108}O_{24}Ti_6$: 45.39, C; 7.61, H. Found. 54.27, C; 8.83, H 55.71, 9.70 and 55.02, 9.57. TGA/DTA: theoretical weight loss 32.8 %, actual 78%; thermal events (°C): 122 (w, endo), 168 (w, endo), 327 (s, exo, recoalescence), 458 (w, exo).

$[Ti(OBc)(ONep)_3]_2$, 5. HOBc (0.258 g, 2.52 mmol). Crystalline yield 0.881g (85.0%). FT-IR (KBr, cm^{-1}) 2954(s), 2904(m), 2866(m), 2844(m), 2695(w), 1559(m, sh), 1532(s), 1480(m),

1415(m), 1391(m), 1375(m), 1360(m), 1305 (w), 1288(w), 1255(w), 1223(m), 1111(s), 1080(s), 1039(m), 1016(m), 933(w), 899(w), 789(m), 746(w), 660(m), 617(m), 600(m), 581(m), 476(m), 464(m). ^{1}H NMR (tol-d_8, 400.1 MHz) δ 4.82, 4.78, 4.65, 4.62, 4.58, 4.56, 4.52, 4.49, 4.47, 4.44, 4.38, 4.37, 4.35, 4.32, 4.31, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.11, 4.09 (s, OCH_2CMe_3), 1.38, 1.35, 1.30, 1.26, 1.25, 1.24, 1.23, 1.20, 1.19, 1.18, 1.17, 1.09, 1.08, 1.07, 1.05, 1.04, 1.03, 1.02, 1.00, 0.99, 0.97, 0.94, 0.76 (s, OCH_2CMe_3, O_2CCMe_3). ^{13}C{^{1}H} NMR (tol-d_8, 100.6 MHz, -35 °C) δ 186.8, 185.2, 184.8 (O_2CCMe_3), 88.8, 88.5, 87.5, 87.3, 86.7, 86.1, 85.8, 84.0 (OCH_2CMe_3) 40.1, 39.8, 39.6, 39.3 (OCH_2CMe_3, O_2CCMe_3), 34.5, 34.4, 34.2, 34.0, 33.8 (O_2CCMe_3) 28.2, 28.0, 27.8, 27.6, 27.2, 27.0, 27.0, 26.9, 26.8, 26.7, 25.9 (OCH_2. Elem. Anal. Calc'd. for $C_{20}H_{42}O_5Ti$: 58.53,C; 10.31, H. Found 58.73, C; 10.05, H. TGA/DTA: theoretical weight loss 80.5%, actual 80.7%; thermal events (°C): 93 (w, endo), 111 (w, endo), 199 (w, endo), 255 (w, exo), 373 (s, exo, recoalescence), 431 (w, exo).

$Ti_3(O)(ONc)_2(ONep)_8$, 6. HONc (0.293 g, 5.05 mmol). Crystalline yield 0.832 g (90.9%). FT-IR (KBr, cm^{-1}) 2949(s), 2906(m), 2866(m), 2845(m), 1565(s), 1537(m), 1477(m), 1450(m, br), 1409(m), 1391(m), 1362(m), 1092(s), 1070(s), 1037(m), 1022(m), 1009(m), 934(w), 904(w), 798(w), 721(m), 696(m), 668(s), 640(m), 595(m), 542(m), 499 (m, br). ^{1}H NMR (tol-d_8, 400.1 MHz) δ 4.82, 4.68, 4.59, 4.56,4.51, 4.49, 4.48, 4.46, 4.43, 4.40, 4.34,4.32, 4.20, 4.18 (s, OCH_2CMe_3, $O_2CCH_2CMe_3$), 2.35, 1.28, 1.17, 1.15, 1.12, 1.08, 1.06, 1.03 (OCH_2CMe_3,

$O_2CCH_2CMe_3$). ^{13}C NMR (tol-d_8, 100.6 MHz) δ 179.4, 179.2 ($O_2CCH_2CMe_3$), 86.5, 87.7, 86.5, 86.3, 84.7 (OCH_2CMe_3), 52.0, 51.5 ($O_2CCH_2CMe_3$), 34.2, 34.0, 33.9, 33.6 (OCH_2CMe_3), 30.6, 30.4, 30.2, 29.7 ($O_2CCH_2CMe_3$), 27.2, 27.0, 26.7, 26.6, 26.4, 25.8 (OCH_2CMe_3, $O_2CCH_2CMe_3$). Elem. Anal. Calc'd. for $C_{52}H_{110}O_{13}Ti_3$: 57.46, C; 10.13, H. Found 57.50, C; 9.78, H. TGA/DTA: theoretical weight loss 77.9 %, actual 80.7 %; thermal events (°C): 86 (w, endo), 134 (w, endo), 156 (w, endo), 338 (s, exo, recoalescence), 434 (w, exo).

X-ray Collection, Structure Determination, and Refinement. A crystal was selected from a pool of oil, attached to a glass fiber, and then cooled by a liquid nitrogen vapor stream on the goniometer. The data for **2**, **4**, **5**, and **6** were collected on a Bruker P4/CCD/PC diffractometer with a sealed MoKα X-ray source. Other data were collected on the specific diffractometer listed under their particular compound descriptions. A hemisphere of data was collected using a combination of ϕ and ω scans, with 30 sec. exposures and 0.3 frame widths. The radiation used was graphite monochromatized MoKα radiation (λ = 0.71073). Data collection, indexing, and initial cell refinement were handled using SMART software.[46] Frame integration and final cell refinement were carried out using SAINT software.[47] The final cell parameters were determined from a least-squares refinement. The SADABS program was used to perform any absorption corrections.[48] Structures were solved using Direct Methods and difference Fourier techniques. The final refinement included anisotropic temperature factors on all non-hydrogen atoms.

Structure solution, refinement, graphics, and creation of publication materials were performed using SHEXTL 5.1 software.[49] Additional details of data collection and structure refinement of the various compounds are given in Table 2-4.

Compound **2**. The hydrogen atom positions were fixed in ideal positions, and refined using a riding model. The isotropic temperature factors were fixed to 1.2 (OFc and methylene) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom they were bonded to. The C-H distances were fixed at 0.93 Å (OFc), 0.97 Å (methylene), or 0.96 Å (methyl). Due to disorder, several carbon atom positions, C11, C14, C21, C23, and C25, were refined as two one half occupancy peaks. The final refinement included anisotropic temperature factors on hydrogen atoms.

Compound **3**. The lattice parameters of **3** were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 1.10 ° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software. Data collection parameters are given in Table 3. The data were not corrected for absorption due to the low adsorption coefficient. The structure was solved in space group $P2_1/c$ using Patterson and

difference Fourier techniques. This solution yielded the titanium and the majority of all other non-hydrogen atom positions. Subsequent Fourier synthesis gave all remaining non-hydrogen atom positions. The *tert*-butyl groups of the ONep ligands showed large atomic displacement parameters (ADP's). One atom, C6, had a very large ADP and was modeled as two positions, C6 and C6', with the sum of their site-occupancy-factors fixed to one. All hydrogen atoms were fixed in positions of ideal geometry, with a C-H distance of 0.96 Å for methyl, 0.97 Å for methylene, and 0.98 Å for methine hydrogens. These atoms were refined using the riding model in the HFIX facility in SHELXL 93. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 (methylene and methine) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom they were bonded to. The final refinement[50] included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0756 and R2W= 0.1430.

Compound **4**. The structure was solved using Direct Methods and difference Fourier techniques. The hydrogen atom positions were fixed in ideal positions and refined using a riding model. The isotropic temperature factors were fixed to 1.2 (methine and methylene) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom they were bonded to. The C-H distances were fixed at 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). Due to disorder, several carbon atom positions, C11, C14, C21, C23, and C25, were refined as two one half occupancy peaks.

Compound **5**. Decay of reflection intensity was not observed for **5**. The structure was solved in space P(-1) group using Patterson and difference Fourier techniques. The initial solution

revealed the Ti and the majority of all other non-hydrogen atom positions. The remaining atomic positions were determined from subsequent Fourier synthesis. The hydrogen atom positions were fixed in ideal positions. The C-H distances used for methyl and methylene hydrogen atoms were 0.96 Å and 0.98 Å, respectively. The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.2 (methylene) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom they were bound to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms, and converged to R1= 0.0440 and wR2= 0.1280.

Compound **5a**. A crystal was mounted on a glass fiber and transferred to a Sie- diffractometer. The XSCANS[51] program package was used to determine the Laue symmetry, crystal class, unit-cell parameters and for data collection. Intensity data were collected at 158 K using a $2\theta/\omega$ scan technique with MoKα radiation. The raw data were processed with a local version of CARESS[50] that employs a modified version of the Lehman-Larsen algorithm to obtain intensities and standard deviations from the measured 96-step profiles. Subsequent calculations were carried out using the SHELXTL[52] program. All data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The diffraction symmetry was *mmm* and the systematic absences were consistent with space group *Pnma* that was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[53] for

neutral atoms were used throughout the analysis. There were two independent molecules of the formula unit present. Each molecule was located on a mirror plane. Several carbon atoms were disordered and were included as atom pairs with site-occupancy-factors fixed assuming a 50% disorder model. Hydrogen atoms were not included in the refinement. At convergence, wR2 = 0.3588 and GOF = 1.033 for 319 variables refined against 5608 unique data (As a comparison for refinement on F, R1 = 0.1092 for those 2372 data with $I > 2.0\sigma(I)$).

Compound **6**. A crystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The diffraction symmetry was 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group P21/n that was later determined to bc

At convergence, wR2 = 0.1230 and GOF = 1.107 for 614 variables refined against 15610 unique data (As a comparison for refinement on F, R1 = 0.0545 for those 12092 data with I > 2.0((I)). The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms[53] were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.1230 and GOF = 1.107 for 614 variables refined against 15610 unique data. As a comparison for refinement on F, R1 = 0.0545 for those 12092 data with $I > 2.0\sigma(I)$.

Compound **6a**. A crystal was mounted on a glass fiber and transferred to the cold stream of a Siemens P4 rotating-anode diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard

XSCANS procedures.[51] Intensity data were collected at 158 K using a 2θ-ω scan technique with MoKα radiation. The raw data were processed with a local version of CARESS[50] that employs a modified version of the Lehman-Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 10,660 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. There was no diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P(-1) was determined to be correct. All calculations were carried out using the SHELXL program.[52] The analytical scattering factors for neutral atoms were used throughout the analysis.[53] The structure was solved by direct methods and refined on F2 by full-mat. squares techniques. Hydrogen atoms were included using a riding model. There are two independent molecules of the formal unit present. Each is located about an inversion center which is consistent with Z = 2. Refinement of positional and thermal parameters led to convergence with wR2 = 0.1573 and GOF = 1.089 for 811 variables refined against all 10125 unique data (R1 = 0.679 for those 6235 data with $F > 4.0\sigma(F)$).

Film Precursor Solutions. Each of the above precursors (**2 – 6**) was individually dissolved in toluene (0.2 M solution) and then transferred to a glass syringe (Note: polystyrene syringes yielded inconsistent film thicknesses). Under a nitrogen atmosphere (< 15 % rel. hum.), the

solutions were filter (2 μm) deposited onto cleaned silicon wafers (12 mm^2) and spun at 3000 rpm for 30 secs. Two samples (Film A and B) were generated from each precursor solution.

Film A. Film A was immediately placed on a hot-plate at 100 °C for 60 secs and then transferred to the ellipsometer. Refractive indices were measured using the ellipsometer, the sample transferred to a furnace and fired under ambient atmosphere at 450 °C for 60 min. Refractive indices were again measured to determine the densification of the final film.

Film B. Refractive indices, monitored at regular intervals over a 60 min. period, were recorded for Film B while it air dried (25 °C). After this time the sample was fired under identical conditions noted for Film A and the refractive indices were again obtained.

Results and Discussion.

Schematic representations of the structure types previously reported for HORc modified $Ti(OR)_4$, are shown in Figure 1a-f.[11-14,16-18,20] We were interested in how the steric bulk of the ONep ligands would influence the structure adopted upon modification with a variety of HORc reagents and how these subtle structural changes would affect the densification of TiO_2 thin films. The synthesis, solid state properties, solution behavior, and densification of thin films generated from solutions of these compounds are discussed.[1]

Synthesis.

The products of eqs 1 - 5 were isolated in a similar manner, wherein, compound **1** was dissolved in toluene and the appropriate HORc reagent was added with stirring. For eq 1 where R = Fc, immediately upon addition of the acid, an as of yet unidentified white precipitate formed which did not redissolve over time or with heating. The precipitate was removed by centrifugation and crystals of **2** were isolated by cooling the mother liquor to -35°C or by slow evaporation of the mother liquor (the latter method yielded higher quality crystals). For **3** - **6** (eqs 2 - 5), no precipitate was noted upon mixing of **1** with the HORc. Crystals of **3** - **6** were isolated by slow evaporation of the volatile material from the reaction mixture. Figures
the thermal ellipsoid plots of **2** - **6**, respectively. The generation of the oxo ligand has been attributed to an esterification mechanism for this system, wherein, the free HORc and metathesized generated HOR, esterify, forming H_2O and the appropriate ester. The *in situ* generated H_2O then hydrolyzes the transitory alkoxy acetate to form a hydroxyl intermediate that rapidly forms an oxo ligand.[13]

Table 5 shows the various temperatures of sublimation, crystallization of the ceramic phase (as determined by TGA/DTA), and solubility limit determined for **1** - **6**. The elemental analyses were consistent for the observed solid state structure of each powder except for **4**. Compound **4** was routinely lower in the appropriate percentages for a satisfactory elemental analysis.

Furthermore, the TGA/DTA data indicate substantially higher weight losses than would be consistent with the solid state structure. While this suggests that the bulk of the material is not consistent with the X-ray structure, numerous crystals were solved and all proved to have identical structures. The poor analytical behavior may be a reflection of the volatility and decomposition pathway of this compound.

Each complex was successfully sublimed <175 °C (10^{-3} Torr), however, the FT-IR spectrum recorded for the sublimed material was altered in comparison to the starting spectrum of each precursor. This indicates that further reactivity of **2** - **6** can be expected by either gas phase reactions or heating of the samples. The saturation solubility of these compound from 0.22 to 0.49 M, wherein the larger pendant hydrocarbon chains of the HORc yielded higher molarities. The exception is the unesterified OBc derivative, **5**, which, quite surprisingly, demonstrated the lowest solubility.

Solid State.

X-ray Structure. The skeletal arrangements of known $Ti(O)_w(ORc)_x(OR)_y$ compounds are shown in Figure 1. The basic structural arrangements of this family of compounds are best described as $[Ti\text{-}O]_4$ cubes with different corners removed or reflected. When appropriate, the cube terminology has also been applied to describe the structures of **2** – **6**. The thermal ellipsoid

plots of **2** - **6** are shown in Figure 2 - 6, respectively. Table 2 lists the data collection parameters for **2**, **3**, and **6**. Table 3 lists the collection parameters for **4** and **5**. Table 5 lists the data collection parameters for **5a** and **6a**. Table 6 is a tabulation for the metrical data of **2**, **3**, and **6**. The metrical data for **4** and **5** are presented in Table 7.

Compound **2** is the smallest nuclearity reported for this family of compounds and the first reported dual, corner-missing cube structural arrangement (Figure 1g) observed for HORc modified $Ti(OR)_4$ compounds. Figure 2 is a thermal ellipsoid plot of the structure of **2**, wherein the three Ti metal centers are linked by a μ_3-O ligand. The remainder of the structure is an asymmetric assemblage of bridging and terminal ligands. The Ti(3) and Ti(1) metal ce bridged by one OFc ligand, whereas Ti(3) and Ti(2) are bridged by both OFc and μ-ONep ligands. All three metal centers complete their coordination sphere through the coordination of two terminal ONep ligands. Ti(2) and Ti(3) adopt distorted octahedral (Oh) geometries, whereas Ti(1) adopts a trigonal bipyramidal (tbp) geometry. In comparison to the analogous OPr^i derivative, $Ti_4(O)_2(OFc)_2(OPr^i)_{10}$ (Figure 1e),[20] compound **2** has reduced nuclearity and oxo ligands. This phenomenon can only be attributed to the characteristics of the ONep ligand.

Compound **3** also adopts a dual, corner-missing cube (Figure 1g) structure and the thermal ellipsoid plot of **3** is shown in Figure 3; however, the ligands of **3** are arranged in a more symmetrical manner than was observed for **2**. The basic constructs of **3** consists of three

titanium atoms surrounding a μ_3-O ligand. For Ti(3), two ONep and two μ-ONep ligands form a very distorted tbp geometry around the metal center. Ti(1) and Ti(2) adopt distorted Oh geometries by bridging two OAc ligands and two terminal ONep ligands. Compound **3** is approximately half the size of its OPr^i derivative, $Ti_6(O)_4(OAc)_4(OPr^i)_{12}$ (Figure 1a),[12].

Figure 4 is the thermal ellipsoid plot of **4** and is only the second known modified alkoxide to adopt the hexagonal-prismatic structure (Figure 1f). The hexagon-prism that is formed, consists of two offset $[Ti\text{-}O]_3$ rings stacked on top of each other. The rings are joined by ~100 ° Ti-O-Ti angles and are consistent with the basic constructs reported for $Ti_6(O)_6(OFc)_6(OPr^i)_6$ (Figure 1f).[20] No structure has been reported for the OPr^i/OPc derivative; however, a cubane [illegible] (Figure 1c) has been noted for the OBu^t/OPc derivative, $Ti_4O_4(OBu^t)_4(OPc)_4$.[17] There is some disorder in the crystal structure of **4** that systematically generates a partial atom in a 90 °C rotation to the hexagon-prism. Several crystals were analyzed but all proved to have this disorder. Due to the similarity of the structure with the OFc/OPr^i derivative and the relatively low R value of **4**, it is not unreasonable to assume that the hexagon-prism represents the true structure of **4**.

The OBc derivative, **5** (Figure 5a), represents the first report of a non-condensed, fully exchanged, titanium alkoxy acetate structure. There is *no* oxo ligand present. The two Oh bound metal centers are bridged by two μ-OBc and two μ-ONep ligands. Two terminal ONep

ligands complete the Oh arrangement of each of the metal centers. The acetates are aligned geometrically opposed to each other in the axial positions; however, the ideal 180° angle is distorted due to the bite angle imposed by the acetate ligands. It appears that the OBc ligands metathesize the terminal ligands of **1** and then bridge to fill in the open coordination site of the 5-coordinated metals. In comparison, the only other non-condensed structure was reported for $Ti_2(\mu\text{-OBc})(OBc)(OPr^i)_6(HOPr^i)$, **5a** (Figure 5b).[16] Table 4 details the collection parameters and metrical data for **5a**. Full metrical data can be found in the supplemental information. This unusual compound can be considered an intermediate form of an esterified species. The coordinated acid and alcohol share a proton in what would be the first step toward esterification product. Compounds **5** and **5a** represent a novel set of HORc modified $Ti(OR)_4$ compounds. The large sterically hindering acid, OBc, dictates the formation of simple exchange products, such as **5**. By altering the pendant hydrocarbon chain of the alkoxy ligand, the intermediate **5a** was formed. Thereby, judicious choice of both the acid and alkoxide ligands could lead to a wide range of compounds at various stages of reactivity.

The structure of **6** (Figure 6a) is the third member of the growing family of dual corner-missing (Figure 1g), condensed HORc modified $Ti(OR)_4$ compounds (*vide infra*). The structure of **6** is consistent with the asymmetric structure noted for **2**, wherein there are two Oh coordinated and one tbp coordinated metal centers. These are joined by a μ_3-O ligand, two μ-

ONep and two μ-OFc ligands. The OFc ligands bridge between Ti(3) -Ti(2) and Ti(3)-Ti(1) which results in an identical asymmetric central core as was observed for the structure of **2**. $Ti_6(O)_4(ONc)_4(OPr^i)_{12}$, **6a**[16] adopts an inversion-related, corner-removed, edge-shared cube (Figure 1b). Table 4 details the collection parameters of **6a** and metrical data can be found in the supplemental information. The structure of **6** is approximately half the nuclearity of **6a** and again demonstrates the utility of the ONep ligand in reduction of nuclearity of these compounds. Reducing the steric bulk of the alkoxide, but increasing that of the steric bulk of the acid, leads to $Ti_6O_4(OAcCo_3)_4(OEt)_{12}$[17] where $HOAcCo_3$ = $(HO_2C(\mu_3\text{-}C)[Co_3(CO)_9])$ which also adopts the structure shown in Figure 1b. Again, the ONep ligand appears to be an important str- influence leading to compounds with reduced nuclearities.

Metrical Data. Compounds **2**, **3**, and **6** possess three metal centers, two of which are 6-coordinated and one that is 5-coordinated. The metrical data concerning these trinuclear species are all very similar and therefore, this information will be discussed collectively (tabulated in Table 6). The average Ti---Ti (av. 3.10 Å), and Ti-(μ_3-O) (av. 1.95 Å) distances of **2**, **3**, and **6** are consistent with those values reported for the $Ti_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)(ONep)_8(THF)_4$ (Ti----Ti, av. 3.04 Å and Ti-(μ_3-O), av. 1.93 Å). As is often noted for metal alkoxides,[10] the Ti-O distances of **2**, **3**, and **6** aggrandize with increased binding ($Ti\text{-}O_{term}$ (av. 1.78 Å) < Ti-(μ-OR) (av. 2.02 Å)). The Ti-ORc distances are consistent with the Ti-(μ-OR) distances where the av. Ti-(μ-ORc)

distance is equal to 2.06 Å. The Ti-(μ_3-O) distances are av. 1.95 Å, however, the three distances are not equivalent with an ~0.1 Å range noted for the individual Ti-(μ_3-O) distances of **2**, **3**, and **6**. The angles around the two 6-coordinated Ti atoms adopt a distorted, Oh geometry. The axial ligands typically are the μ-OR and the μ_3-O ligands for **2**, **3**, and **6**. The distortion around the ideal 180 ° O-Ti-O angles of the 6-coordinated Ti atoms for these compounds are clustered around 170 °. Two exceptions are 148 ° for the O(1)-Ti(2)-O(8) angle of **2**, and 148 ° for O(6)-Ti(3)-O(8) for **6**. The 5-coordinated Ti atoms of **2** and **6** adopt a tbp geometry with the μ-OR and one of the oxygens of the ORc ligands adopting the axial positions. The 5-coordinated Ti metal center of **3** is isolated in a distorted square-base geometry. Metrical data of consistent with that reported for **6** and $Ti_6(O)_6(OAc)_{16-4n}(OPr^i)_{4n}$[12,13].

Table 7 is a tabulation of the metrical data for **4** and **5**. Compound **4** has a structure reminiscent of the complex formed by the mixture of the OFc/OPr^i ligand system (Figure 1f). For the OFc/OPr^i derivative, the $[Ti-O]_3$ rings exist at 90° angles to each other with alternating Ti-(μ_3-O)-Ti and (μ_3-O)-Ti- (μ_3-O) angles of ~135 ° and ~100 °, receptively. In comparison, the same angles for the rings of **4** alternate with different internal angles (~137 ° and ~101 °) and rings that are 90 ° to each other but are skewed, with angles approaching 80 ° to 100 °. While the Ti-OR_{term}, Ti-(ORc) and Ti-(μ_3-O) distances of **4** and the OFc/OPr^i derivative are statistically equivalent, the Ti---Ti distances of **4** were found to be consistently shorter by ~ 0.1Å.

For compound **5**, the Ti---Ti distance of 3.10 Å is ~0.1 Å shorter in comparison to the same distance reported for **1**. The bite angle (125.7 °) of the two OBc ligands of **5** force the Ti metals to interact to a greater extent than they would otherwise. For **5a**, the bridging OBc ligand has an even smaller bite angle (123.7 °). Since there is no corresponding ORc ligand, the opposing side of **5a** opens up to relieve strain and this results in a slightly longer Ti--Ti distance for **5a** (3.23 Å). The O(6)-C(13)-O(7) angle of the monodentate OBc ligand is 125.9 °, indicating little change in the bite angle of the OBc ligand as it binds to the Ti metal center. The influence of this confined interaction can be observed from the distortion of the angles away from the idealized 90 ° and 180 ° angles. Again, the higher the degree of binding the ligand und- the longer the Ti-O bond distances that are reported (Ti-OR_{term} (**5**, av. 1.79 Å; **5a**, 1.79 Å) < Ti-μ-OR (**5**, 2.04 Å; **5a**, 2.04 Å). The Ti-OBc distances (**5**, av. 2.06 Å; **5a**, 2.06 Å) are only slightly longer than the Ti-μ-OR distances. This difference is in contrast to the nearly equal distance reported between these two ligand types for the other ORc modified $Ti(OR)_4$ structures. This may be a reflection of the absence of a μ_3-O ligand that reduces the amount of available electron density around the metal center and thus yields shorter Ti-O bond distances.

FT-IR Spectroscopy. Since the basic constructs of the ORc and the ONep pendant hydrocarbon chains are very similar, the FT-IR spectra of **1** - **6** are also very similar. The ONep stretches

obscure a majority of the HORc's stretches. For each compound, the standard ONep aliphatic stretches are present as four sharp stretches around 2900 cm^{-1}, four sharp stretches around 1500 cm^{-1} and a strong broad stretch around 1100 cm^{-1}. The HORc (>1500 cm^{-1}) and M-O (< 700 cm^{-1}) stretching frequency regions[2] are reasonable areas to focus on to discern solid state structural differences.

There are two stretches recorded for the asymmetric compounds **2** and **6** in this region, whereas the symmetric complex **3** displays only a single stretch. Compound **5** has the lowest wave number stretch, possibly a reflection of increased donation by the carboxylate ligand necessitated by the absence of an oxo donating ligand. A stretch around 530 cm^{-1}, present in spectra of **2**, **3**, **4**, **6** and the $Ti(OPr^i)_4$:HOFc product, $Ti_6(O)_6(OFc)_6(OPr^i)_6$[20] but absent in the spectrum of **5**, was assigned as the Ti-(μ_3-O) stretch. For **5**, there is significantly more splitting for each region of the spectrum than was noted for the other samples. This may be due to a solid state asymmetric arrangement of ligands. There are two sharp peaks in the M-O region, significant stretches are present around 700 and 500 cm^{-1} that have been assigned as M-ONep and M-OBc stretches, respectively. The latter stretch was assigned as the M-OBc stretch due to its absence in the other spectra.

FT-IR spectra were obtained on samples of **2** - **6** that had been exposed to room temperature atmospheric conditions (20-25 % relative humidity) for >2 hours. Compounds **2**, **3**, **4** and **6**

showed no change in the resultant FT-IR spectra for each compound; however, **5** demonstrated a slight sensitivity to the ambient atmosphere as evidence by the "doubling" of most of the line present. The relative unstability of **5** to hydrolysis versus the other HORc modified $Ti(OR)_4$ compounds must be a reflection of the reduced oxolation.

TGA/DTA. Thermal analyses of **2** - **6** were conducted under an oxygen atmosphere to insure complete conversion of the precursor to titanium oxide. Each compound undergoes a two step weight loss (except for **5** which has three steps), organic decomposition < 400 °C, crystallization < 475 °C, and has a total weight loss consistent with the expected conversion to TiO_2. T list the various decomposition and crystallization temperatures recorded for these samples. One general trend noted is that as the molecules become more condensed and thus more stable, the decomposition temperature increases. This also raises the crystallization temperatures, since less rearrangement of the final compounds would be necessary.

Solid State NMR. To further characterize the bulk powders of **2** - **6**, solid state NMR experiments were undertaken. Crystalline material of each compound were dried in vacuo and packed into rotors and stored under an argon atmosphere until immediately prior to obtaining a ^{13}C CP-MAS NMR spectrum. A stacked plot of the ^{13}C NMR spectra of the carboxylic carbon

region of **2** - **6** is shown in Figure 7.

For **2**, **3**, and **6**, the number of resonances recorded for the respective CP-MAS spectra are insufficiently resolved to allow for unambiguous determination of the bulk powder structure. The reduction in the number of methylene and methyl resonances observed for the pendant hydrocarbon chains, in comparison with their respective solid state structures, can be accounted for by coincidental overlap of similar ligands. Due to the uniqueness of the carboxylic carbon (O_2C-R) resonances in these compounds, this region was used for structural interpretation (Figure 7). For **2**, the solid state structure is asymmetric yielding two disparate OFc ligands. In the CP-MAS NMR spectrum of **2**, two carboxylate OFc carbon resonances are present at δ and 167.7 ppm. The similarly structured **6** also revealed two carboxylic ONc carbons resonances at δ 178.8 and 178.3 ppm. In contrast, the symmetric **3** revealed only one type of carboxylate carbon resonance at δ 177.9 ppm. The chemical shifts of these O_2C-R resonances are as expected very similar. Due to the change in the number of resonances, it appears the bulk powders of the crystalline materials of **2**, **3**, and **6** are consistent with their respective X-ray structures.

For the symmetrical, hexagon-prism shape of **4**, only a single type of OPc and ONep ligand should be observed; however, with the disorder present in the solid state structure, loss of local symmetry can result. In the CP-MAS NMR spectrum, there is a single carboxylate carbon OPc

resonance at δ 182.8 ppm. Three broad resonances were also observed at δ 87.7, 86.0, 84.1 ppm. The two downfield multiplets were assigned as the ONep methylene shifts. The latter resonance was very broad and much smaller than the ONep resonances and was assigned as the methine resonances of the OPc carboxylate, pendant hydrocarbon chain. Further upfield, the ONep quaternary carbons were recorded at δ 35.8 and 33.8 ppm, followed by two overlapping methyl ONep resonances located at δ 26.8 ppm. A final, very broad peak at 20.2 ppm is consistent with the methyl resonances of the OPc carboxylate hydrocarbon chain. These data indicate that there are two types of ONep ligands and one type of OPc carboxylate ligand present. The extra ONep resonances are not consistent with the idealized hexagon prism structure; however, the di- in the solid state structure may account for this inconsistency.

The dinuclear OBc complex, **5**, has three pseudo-mirror planes and is predicted to display one type of OBc and two types of ONep ligands. The ^{13}C CP-MAS NMR spectrum reveals a single carboxylate OBc carbon present at δ 187.8 ppm. Further upfield there are three peaks (δ 86.0, 85.7, 80.8 ppm) that were assigned as the two ONep methylene and the single OBc quaternary carbon resonances, respectively. The quaternary region was assigned as follows: δ 40.6 as the OBc quaternary carbon; δ 35.2 and 33.6 ppm as the ONep quaternary carbon. The final methyl region consists of 5 peaks. The furthest downfield peak is assigned as the OBc methyl at 28.7 ppm. The remaining resonances, ranging from δ 27.9 to 26.7 ppm, are

representative of the inequivalent ONep methyl resonances. The large number of methyl ONep peaks versus the rest of the ONep resonances can be explained as disorder or "locking out" of the methyl resonances.

Solution state.

One figure of merit that has been postulated to determine the stability of titanium oxo compounds in solution is to calculate the degree of condensation (x/y where x = oxo ligands and y = number of metal cations).[17,20,54] The greater the ratio, the greater the proposed stability of the compound in question. However, this must be tempered with the "amount of o displayed by the various molecules.[17,20,54]

For example, compound **1** was found to possess an x/y = 0 and a relatively "closed" structure. Compound **1** was characterized as a mononuclear complex in toluene.[44] For **2**, **3**, and **6**, x/y = 0.33 and these compounds adopt a somewhat "closed structures". This suggests that these compounds may demonstrate fluxional behavior in solution. For **5**, x/y = 0 and the similarity in structure that of **1**, suggests that dynamic behavior should be observed for this compound. For **4**, the x/y value of 1 coupled with the low degree of "openness" suggests that the structure of **4** should be a stable in solution.

To determine the solution behavior of **2** - **6**, crystalline materials were dried *in vacuo*, redissolved in cold toluene-d_8, and immediately inserted into a cold (-35 °C) probe. This

experimental setup was utilized to minimize the degree of self-esterification that these compounds have been reported to undergo.[20] Samples of **2 - 6** were prepared as concentrated as possible to generate consistent samples and minimize complex solution behavior.

Compound **2**. The $^{13}C\{^{1}H\}$NMR spectrum of the asymmetric molecule **2** at -40 °C reveals two types of carboxylic OFc carbons, four methylene, four quaternary, and two methyl ONep resonances. The solution NMR OFc resonances are slightly shifted in comparison to the CP-MAS resonances. The reduced number of observed ONep resonances in comparison to the solid state structure may be explained by coincidental overlap of the ^{13}C NMR resonances or rapid ligand exchange.

The ^{1}H NMR spectrum at -40 °C reveals two OFc ligands (two minor OFc proton peaks are present as well), more than 16 types of ONep methylene resonances but only three types of ONep methyl ligands. The asymmetric nature of **2**, coupled with rapidly exchanging ONep ligands, complicates this spectrum. The great number of methylene resonances suggests either (a) an equilibrium exists, (b) self-esterification has been initiated, or (c) the asymmetric nature of **2** yields inequivalent methylene protons in solution. In order to elucidate the solution behavior of **2**, higher temperature ^{1}H NMR (VT-NMR) investigations were undertaken.

As the sample was warmed from -35 °C, no change in this spectrum was noted until -10 °C, wherein an additional methyl resonance could be observed. The stability of the compound over this temperature range and the fact that none of the peaks recorded throughout the samples are

consistent with the ester formed by HONep and HOFc eliminates the self-esterification explanation. The ingrowth of a ^{1}H peak at δ 0.96 was coupled with a decrease of the largest multiplet (δ 4.39) in the methylene region. This trend continues until room temperature. At higher temperatures (up to 50 °C) two methyl resonances at δ 1.03 and 0.96 ppm coalesce, as do a majority of the methine resonances. The ^{13}C NMR spectrum at 50 °C again shows two OFc carbon resonances (δ 168.9 and 167.9 ppm); however, at this temperature there are 5 methine, 2 quaternary, and 3 methyl resonances. Upon cooling to room temperature over night, the ^{1}H NMR spectrum of **2** remained identical to the spectrum obtained during the VT-NMR investigation. The coalescence of these peaks suggests that the ligands are in rapid exchange an equilibrium between multi-nuclear species is not occurring. Furthermore, the presence of the two OFc shifts in both the ^{1}H and ^{13}C NMR spectra, independent of temperature or concentration, indicates that the central core of **2** is retained in solution on the NMR time scale. The variability in the ONep region reflects the great deal of dynamic exchange associated with the alkoxide ligands.

Compound **3**. For retention of the solid state structure of **3** in solution, only 1 type of acetate and 5 ONep resonances should be observed. At -40 °C, the ^{13}C{^{1}H} NMR spectrum revealed two carboxylate carbons at δ 178.7 and178.2 ppm and two methyl peaks at δ 24.2 and 23.8 ppm for the OAc ligand. For the ONep ligands, 5 methylene peaks, 3 quaternary carbon, and 3

methyl peaks were recorded. The ^{1}H (-40 °C) NMR spectrum also revealed two acetate ligands with up to 11 methylene and 4 methyl ONep resonances. These low temperature data indicate that an asymmetric structure is adopted in solution. As the solution is warmed (-20 °C) there is a sharpening of the various peaks with a decrease of the major methylene resonance (δ 4.36) and the appearance of a methyl resonance at δ 0.99 ppm. At higher temperatures (+30 °C), the δ 4.30 resonance begins to grow in intensity as it coalesces with the other methylene resonance, as do the methyl resonances. At 50 °C there are only two types of methyl ONep ligands, one acetate and three methylene ONep resonances. The ^{13}C NMR spectrum at 50 °C reveals 5 methylene carbons, one acetate, three ONep methyl resonances (a small signal at δ 178 may repr. quaternary carbons but the low signal to noise ratio makes this difficult to quantify). Upon cooling to room temperature an identical spectrum that was observed in the VT-NMR spectrum was recorded. No peaks associated with the esters formed by the reaction of HOAc and HONep were observed. At high temperature, a symmetric structure of **3** is formed which appears to be consistent with the solid state structure. As the temperature is lowered, an asymmetric geometry is observed in solution that probably resembles the structure observed for **2** and **6**.

Compound **4.** If the solid state structure of **4** is retained in solution, the ^{1}H NMR spectrum should display one set of ONep (methylene and methyl singlets) and one set of OPc (methylene septuplet and methyl doublet) resonances. The -40 °C, $^{13}C\{^{1}H\}$ NMR spectrum revealed two

types of carboxylate OPc carbons, 5 methylene, 5 resonances in the quaternary region, and 3 ONep resonances. The disordered solid state structure of **4** is either disrupted or the solid state disorder was present in solution. The ^{1}H NMR spectrum at this temperature shows more than 13 ONep methylene resonances one methine septuplet and two methyl doublets for the OPc ligand and three ONep methyl singlets. As the sample is warmed to room temperature a coalescence of these resonances can be observed. While this occurs, the doublets of the OPc coalesce under an existing ONep methyl resonance. Further heating yields four types of ONep methylene resonance one type of OPc and two ONep ligands. The high temperature (+50 °C) $^{13}C\{^{1}H\}$ NMR spectrum is greatly simplified by broadening of the carbonyl and methine res-

Upon cooling, the spectra are consistent with the previously obtained room temperature spectra. A number of minor peaks were present which may be correlated with ester generated from the reaction of HOPc and HONep. These VT-NMR investigations suggest that the disruption of the central core of **4** is minimal. The disorder observed in the solid state must carry over to the solution state and does not allow for equalization of the ligands.

Compound **5.** The unique metathesis, non-esterified complex, **5** should display one set of bridging OBc, one set each of terminal and bridging ONep resonances. Complex ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were observed at -40 °C with significantly more and broader resonances (in comparison to **2** - **6**) than can be accounted for by the solid state structure. This implies that **5**

is either undergoing degradation (self-esterification) or that an equilibrium exists. In order to probe the solution behavior, VT-NMR spectra were obtained. As the temperature is increased, the > 15 methine resonances, noted at -40 °C, coalesce into a single resonance; however, several minor peaks are also visible. For the OBc ligand, two methyl resonances could be observed. There is no evidence of any ester formation during the various VT-NMR investigations based upon the NMR of the ester formed from the reaction of HOBc and HONep. This implies that an equilibrium exists for **5**. The disruption of the dinuclear complex to form a mononuclear species was noted for the unmodified complex **1**; however, no equilibrium was observed. Solution molecular weight determinations (Signer Method)[55] studies showed that the nuclearity 1005 or a solution molecular complexity of ~1.23. This indicates that **5** undergoes oligomerization in solution to form larger species; however, the predominant nuclearity is consistent with the solid state structure.

Compound **6**. Both of the ligands of **6** posses the -Nep pendant hydrocarbon chain. For the $^{13}C\{^{1}H\}$ NMR spectrum of the asymmetric complex **6** at -40 °C, two complete sets of ONc ligand resonances (4 types of methyl resonances are noted) and 5 complete sets of ONep resonances are present. If **6** maintains its asymmetric nature, the "missing" ONep resonance can be accounted for by overlapping resonances. The ^{1}H NMR spectrum indicates at least 14 types of methine resonances and 8 types of methyl resonances. The methylene region has significantly more resonances present than can be accounted for by the solid state structure, unless the

methylene protons cannot rotate freely. Upon warming the sample to room temperature, the methyl region deconvolutes whereas the methylene region coalesces into one large peak. The ONc peaks appear to slightly change ratio. Additional warming leads to three types of ONep resonances and one ONc methyl resonance. This is indicative of rapid ligand exchange, consistent with the formation of a highly symmetric complex as noted for **2**. The ^{13}C NMR spectrum of **6** at +50 °C shows similar increases in symmetry. After cooling, the room temperature spectrum reverts back to what had been previously reported for this compound and no resonances, consistent with the formation of the ester from the reaction of HONc and HONep, were observed.

Film Properties

The crystalline materials of **2** - **6** were redissolved to make a precursor solution that could be used for spin-cast deposition of TiO_2 thin films. Under an atmosphere of argon, an ~0.2 M toluene solution was generated for each sample. Immediately upon dissolution, the samples were transferred to a glass syringe. *Note:* Initially standard plastic syringes were used, however, inconsistent, film, thicknesses were recorded. Films were generated under a controlled nitrogen atmosphere (< 15% rel. humidity) to minimize hydrolysis. Two films were generated for each sample and a timer initiated to maintain a systematic investigation. Properties of the final films are listed in Table 8.

The first film was transferred directly to an ellipsometer and a drying pattern was recorded by measuring the index of refraction (η_f) and thickness (Å). For every sample (**1** - **6**) a standard drying curve was noted. For the smaller carboxylate ligated species (**1** - **4**), the thicknesses of the films ranged from 300 to 450 Å. The larger carboxylate ligated species yield significantly thicker films (**5**, 819 Å and **6**, 669 Å). All of the films dried to an average thickness of 223 (46) Å (range 143 - 270 Å) within a 1 h period.

The second film was placed on the stage of an ellipsometer to determine initial film thickness. After this measurement, the film was immediately place into a pre-heated furnace and sintered at 450 °C to form TiO_2. Each sample had similar thickness values as recorded first films. The final η_f and thicknesses were recorded for each film (see Table 8). Normalized density ($\rho_{normalized}$) calculations were determined using the Lorentz-Lorentz equation, eq 6.[56]

As can be discerned there is no trend related to the size of the carboxylic ligand for the ONep family. What was found to be a determining factor in the densification of the TiO_2 thin film was the nuclearity of the precursor material and the degree of condensation (x/y) that had occurred. The samples with ~ 100 % density are the smaller carboxylate corner-missing (Figure 1g) shaped molecules with x/y ratios of 0.3 or lower. The thin film of **1** is dense, possibly due to partial hydrolysis by the remnant humidity in the box (**1** has been reported to adopt a $Ti_{12}(O)_{16}(ONep)_{32}$ structure upon hydrolysis).[16] The lowest density films were formed from

compounds **5** and **6** which have the highest carbon content per molecule. It appears that a fine balance between oxo ligands and carbon content of the HORc must be maintained to optimize densification.

Thin films of the OPr^i derivatives were investigated in a similar manner as presented for the ONep compounds. Table 8 tabulates the final results of the films generated using the OPr^i ligated species. Since these compounds routinely were larger than their ONep counterparts, it was proposed that these films would be thicker and hence less dense than the ONep ligated species. The smaller nuclei ONep compounds were, on average, thicker than the OPr^i films both as the "green" (unfired) and sintered films. The density of the final films, based o. indicate that the ONep ligated species were more dense. Furthermore, higher carbon content appears to decrease the density of the sintered films. The high density of the parent alkoxide films is most likely a result of hydrolysis by residual humidity in the glove box, forming a partially condensed species.

Conclusion

We have synthesized and characterized several new members of the HORc modified $Ti(OR)_4$ family. These compounds were synthesized through the reaction of HORc and **1** and identified by single crystal X-ray diffraction as $Ti_3(O)(OFc)_2(ONep)_8$, $Ti_3(O)(OAc)_2(ONep)_8$,

$Ti_6(O)_6(OPc)_6(ONep)_6$, $[Ti(OBc)(ONep)_3]_2$, $Ti_3(O)(ONc)_2(ONep)_8$. The novel structures identified in this study for HORc modified $Ti(OR)_4$ include: (i) the first example of trinuclear, oxo-, alkoxy, acetate titanium complex, referred to as a dual corner missing complex (**2**, **3**, **6**) and (ii), the first "simple" metathesized acetate-alkoxide isolated product (**5**). The bulk samples of **2** - **6** were found to be consistent with their solid state structures, based on elemental analysis and ^{13}C CP-MAS solid state NMR spectroscopy. In general, each of the ONep derivatives yields a compound that possesses reduced nuclearity (often halved) in comparison to the OPr^i derivatives. While solution NMR spectroscopy studies of **2** - **6** in toluene reveal a great deal of dynamic behavior associated with ligand exchange and multi-nuclear equilibria, the constructs appear to be maintained in solutions.

Films produced from the redissolved crystals of **1** - **6** and the OPr^i analogs indicate several trends that can be exploited for generating higher density films of TiO_2. Thermal decomposition data indicate that lower nuclearity compounds crystallize in the ceramic form at lower temperatures. Complete removal of the oxo ligand, as evidenced for thin films generated using **5**, is not desired for highly dense films. Furthermore, higher, carbon content also leads to less dense films as contrasted by **2** and **6**. Through the introduction of various acids and alkoxy ligands, the nuclearity and shape for HORc modified $Ti(OR)_4$ is beginning to be understood. This ability to tailor the properties of the precursors will ultimately lead to films with controlled

properties.

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Supporting Information Available. A listing of the X-ray crystallographic files in CIF format for the structures of **2** - **6** (**5a** and **6a**) are available (119 pages). This material is available free of charge via the INternet at http://pubs.acs.org.

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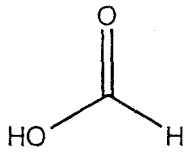
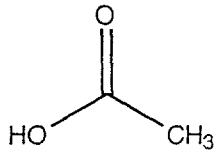
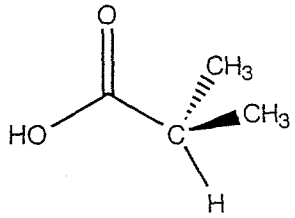
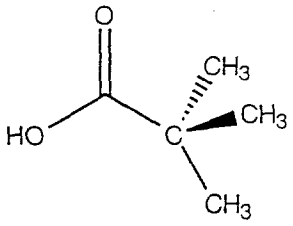
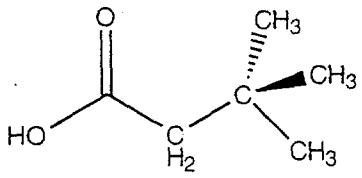
List of Tables

Table 1. Carboxylic acid (HORc) precursor data

Acid (Abbreviation)	Formula (MW) pH[a]	Structure
Formic (HOFc)	CH_2O_2 (46.03) 2.04	
Acetic (HOAc)	$C_2H_4O_2$ (60.05) 2.25	
iso-Butyric (HOPc)	$C_4H_8O_2$ (88.11) 2.57	
Trimethyl Acetic (HOBc)	$C_5H_{10}O_2$ (102.13) 2.90	
tert-Butyl Acetic (HONc)	$C_6H_{12}O_2$ (116.16) 2.93	

[a] Obtained by pH measurement of an ~1.0 M solution of each HORc in deionized water.

Table 2. Data collection parameters for **2**, **3**, and **6**.

Compound	**2**	**3**	**6**
chemical formula	$C_{42}H_{90}O_{13}Ti_3$	$C_{44}H_{94}O_{13}Ti_3$	$C_{52}H_{110}O_{13}Ti_3$
formula weight	946.84	974.89	1087.10
temp (K)	203	198	158
space group	Pbca orthorhombic	$P2_1/c$ monoclinic	$P2_1/n$ monoclinic
a (Å)	23.229 (1)	11.011(1)	15.4865(7)
b (Å)	16.1885 (8)	25.005(3)	20.9548(10)
c (Å)	29.706 (1)	21.342(3)	19.8993(9)
α (deg)			
β (deg)		100.98(1)	91.3170(10)
γ (deg)			
V (Å^3)	11170.6(9)	5768.5(12)	6455.9(5)
Z	8	4	4
λ (Å) (Mo Kα radiation)	0.71073	0.71073	0.71073
D_{calcd}(Mg/m^3)	1.126	1.123	1.118
μ, (mm^{-1}) (Mo Kα radiation)	0.468	0.455	0.413
R1[a] (%)	8.75	7.56	5.45
wR2[b] (%) [I> 2σ(I)]	24.77[c]	14.30[d]	11.27[e]
R1[a] (%, all data)	11.83	14.76	8.04
wR2[b] (%, all data)	26.55[c]	17.21[d]	12.30[e]

[a] **R1** = $\Sigma \; | |F_o|-|F_c| | \; / \; \Sigma \, |F_o| \times 100$

[b] **wR2** = $[\Sigma \; w \, (F_o^2-F_c^2)^2 \; / \; \Sigma \, (w \, |F_o|^2)^2]^{1/2} \times 100$

Final weighting scheme calc:

[c] $w = 1/[\sigma^2(F_o^2) + (0.1339P)^2]$

[d] $w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$

[e] $w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 4.2288P]$

where $P = (Fo^2 + 2\,Fc^2)/3$

Table 3. Data collection parameters for **4** and **5**.

Compound	**4**	**5**
chemical formula	$C_{54}H_{108}O_{24}Ti_6$	$C_{40}H_{84}O_{10}Ti_2$
formula weight	714.40	820.87
temp (K)	203	200
space group	P(-1) triclinic	P(-1) triclinic
a (Å)	11.7931(8)	10.1515(6)
b (Å)	13.431(1)	11.5415(7)
c (Å)	13.9079(9)	11.5495(7)
α (deg)	105.823(1)	75.453(1)
β (deg)	109.011(2)	69.296(1)
γ (deg)	103.632(1)	87.026(1)
V (Å^3)	1872.0(2)	1224.2(1)
Z	1	1
λ (Å) (Mo Kα radiation)	0.71073	0.71073
D_{calcd}(Mg/m^3)	1.267	1.113
μ, (mm^{-1}) (Mo Kα radiation)	0.675	0.372
R1[a] (%)	12.77	4.40
wR2[b] (%) [I>2σ(I)]	26.01[c]	12.80[d]
R1[a] (%, all data)	18.63	5.11
wR2[b] (%, all data)	27.62[c]	13.18[d]

[a] $R1 = \Sigma \; | |F_o|-|F_c| | \; / \; \Sigma \; |F_o| \times 100$

[b] $wR2 = [\Sigma \; w \; (F_o^2-F_c^2)^2 \; / \; \Sigma \; (w \; |F_o|^2)^2]^{1/2} \times 100$

Final weighting scheme calc:

[c] $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$

[d] $w = 1/[\sigma^2(Fo^2) + (0.0635P)^2]$

where $P = (Fo^2 + 2\,Fc^2)/3$

Table 4. Data collection parameters for **5a** and **6a**.

Compound	**5a**	**6a**
chemical formula	$C_{31}H_{68}O_{11}Ti_2$	$C_{60}H_{128}O_{24}Ti_6$
formula weight	712.65	1521.02
temp (K)	158	158
space group	*Pnma* Orthorhombic	P(-1) triclinic
a (Å)	21.443(30	13.033(3)
b (Å)	15.229(2)	15.667(3)
c (Å)	25.168(4)	20.798(4)
α (deg)		69.570(13)
β (deg)		84.748(13)
γ (deg)		83.680(13)
V (Å^3)	8219(2)	3948.9(14)
Z	8	2
λ (Å) (Mo Kα radiation)	0.71073	0.71073
D_{calcd}(Mg/m^3)	1.152	1.279
μ, (mm^{-1}) (Mo Kα radiation)	0.436	0.644
R1[a] (%)	10.92	6.79
wR2[b] (%) [I>2σ(I)]	27.81[c]	12.77[d]
R1[a] (%, all data)	23.64	13.07
wR2[b] (%, all data)	35.88[c]	15.73[d]

[a] $R1 = \Sigma \; | |F_o| - |F_c| | \; / \; \Sigma \; |F_o| \times 100$

[b] $wR2 = [\Sigma \; w \; (F_o^2 - F_c^2)^2 \; / \; \Sigma \; (w \; |F_o|^2)^2]^{1/2} \times 100$

Final weighting scheme calc:

[c] $w = 1/[\sigma^2(F_o^2) + (0.1864P)^2 + 23.6208P]$

[d] $w = 1/[\sigma^2(F_o^2) + (0.02586P)^2 + 22.5336P]$

where $P = (F_o^2 + 2 F_c^2)/3$

Table 5. Properties of compound **1 – 6**: degree of condensation (x/y), maximum Molarity (M_{max}), temperature of sublimation (T_{sub}), temperature of decomposition (T_{dec}), and temperature of crystallization (T_{cry}).

Compound	Mol. Form.	x/y	~M_{max} (g/1 mL)	~T_{sub}[a] (°C)	~T_{dec} (°C)	~T_{cry} (°C)	Ref.
1	$Ti_2(ONep)_4$	0.0	>2.5	90	----	-----	44
2	$Ti_3(O)(OFc)_2(ONep)_8$	0.33	0.36	130	326	456	b
3	$Ti_3(O)(OAc)_2(ONep)_8$	0.33	0.35	130	317	456	b
4	$Ti_6(O)_6(OPc)_6(ONep)_6$	1.0	0.76	155	342	489	b
5	$Ti_2(OBc)_2(ONep)_6$	0.0	0.27	100	328	431	b
6	$Ti_3(O)(ONc)_2(ONep)_8$	0.33	0.49	135	338	434	b

[a]Sublimation performed at 10-4 Torr.
[b]This work

Table 6. Comparison of the Interatomic Distances (Å) and Angles (deg) for **2**, **3**, and **6**.

Distances (Å)	2		3		6	
Ti---Ti	Ti(1)---Ti(2)	3.071(1)	Ti(1)---Ti(3)	3.087(2)	Ti(1)---Ti(3)	3.143(1)
	Ti(2)---Ti(3)	3.160(1)	Ti(2)---Ti(3)	3.091(2)	Ti(2)---Ti(3)	3.074(1)
Ti-OR[a]	Ti(1)-O(2)	1.777(3)	Ti(1)-O(5)	1.774(6)	Ti(1)-O(5)	1.804(2)
	Ti(1)-O(3)	1.775(3)	Ti(1)-O(6)	1.788(6)	Ti(1)-O(7)	1.802(2)
	Ti(2)-O(5)	1.785(3)	Ti(2)-O(7)	1.793(6)	Ti(2)-O(9)	1.791(2)
	Ti(2)-O(6)	1.806(3)	Ti(2)-O(8)	1.762(6)	Ti(2)-O(10)	1.782(2)
	Ti(3)-O(10)	1.789(3)	Ti(3)-O(9)	1.801(5)	Ti(3)-O(11	1.797(2)
	Ti(3)-O(11)	1.791(3)	Ti(3)-O(10)	1.780(5)	Ti(3)-O(12)	1.807(2)
Ti-(μ-OR)	Ti(1)-O(1)	1.995(3)	Ti(1)-O(11)	2.029(5)	Ti(1)-O(6)	2.024(1)
	Ti(2)-O(1)	2.043(3)	Ti(3)-O(11)	1.986(5)	Ti(2)-O(8)	1.987(2)
	Ti(2)-O(8)	2.010(3)	Ti(2)-O(12)	2.036(5)	Ti(3)-O(6)	2.013(2)
	Ti(3)-O(8)	2.020(3)	Ti(3)-O(12)	1.990(5)	Ti(3)-O(8)	2.038(2)
Ti-(μ-ORc)[b]	Ti(1)-O(4)	2.053(3)	Ti(1)-O(1)	2.024(6)	Ti(1)-O(1)	2.038(2)
	Ti(2)-O(7)	2.153(3)	Ti(2)-O(2)	2.036(6)	Ti(1)-O(3)	2.161(2)
	Ti(3)-O(12)	2.135(3)	Ti(2)-O(3)	2.114(6)	Ti(2)-O(2)	2.039(2)
	Ti(3)-O(13)	2.059(3)	Ti(1)-O(4)	2.147(6)	Ti(3)-O(4)	2.132(2)
	Ti(1)-O(9)	1.849(3)	Ti(1)-O(13)	1.989(5)	Ti(1)-O(13)	1.980(2)
Ti-(μ_3-O)	Ti(2)-O(9)	2.013(3)	Ti(2)-O(13)	1.975(5)	Ti(2)-O(13)	1.854(2)
	Ti(3)-O(9)	1.993(3)	Ti(3)-O(13)	1.874(5)	Ti(3)-O(13)	2.042(2)

Angles (deg)	2	3	6
(RO)-Ti-(OR)	O(2)-Ti(1)-O(3)	O(5)-Ti(1)-O(6)	O(5)-Ti(1)-O(7)
	116.10(18)	98.0(3)	96.08(7)
	O(5)-Ti(2)-O(6)	O(7)-Ti(2)-O(8)	O(9)-Ti(2)-O(10)
	96.37(14)	97.5(3)	114.93(8)
	O(10)-Ti(3)-O(11)	O(9)-Ti(3)-O(10)	O(11)-Ti(3)-O(12)
	98.84(15)	110.6(3)	96.72(7)

(μ-OR)-Ti-(OR)	O(1)-Ti(1)-O(2) 97.58(14)	O(5)-Ti(1)-O(11) 97.1(2)	O(5)-Ti(1)-O(6) 99.10(6)
	O(1)-Ti(1)-O(3) 98.60(15)	O(6)-Ti(1)-O(11) 100.0(2)	O(7)-Ti(1)-O(6) 99.01(7)
	O(1)-Ti(2)-O(5) 104.00(13)	O(7)-Ti(2)-O(12) 96.6(2)	O(8)-Ti(2)-O(9) 93.79(7)
	O(1)-Ti(2)-O(6) 94.23(13)	O(8)-Ti(2)-O(12) 100.4(2)	O(8)-Ti(2)-O(10) 102.31(7)
	O(6)-Ti(2)-O(8) 100.66(13)	O(9)-Ti(3)-O(11) 93.3(2)	O(6)-Ti(3)-O(11) 106.57(6)
	O(5)-Ti(2)-O(8) 101.69(13)	O(9)-Ti(3)-O(12) 93.0(2)	O(8)-Ti(3)-O(11) 100.34(6)
	O(8)-Ti(3)-O(10) 99.81(14)	O(10)-Ti(3)-O(11) 102.8(2)	O(6)-Ti(3)-O(12) 95.61(7)
	O(8)-Ti(3)-O(11) 97.40(14)	O(10)-Ti(3)-O(12) 103.3(2)	O(8)-Ti(3)-O(12) 96.37(6)
(μ-OR)-Ti-(μ-OR)	O(1)-Ti(2)-O(8) 148.56(12)	O(11)-Ti(3)-O(12) 148.9(2)	O(6)-Ti(3)-O(8) 148.94(6)
(μ-OR)-Ti-(μ_3-O)	O(1)-Ti(1)-O(9) 80.06(12)	O(11)-Ti(1)-O(13) 74.7(2)	O(6)-Ti(1)-O(13) 77.53(6)
	O(1)-Ti(2)-O(9) 75.19(11)	O(12)-Ti(2)-O(13) 74.2(2)	O(8)-Ti(2)-O(13) 80.13(6)
	O(8)-Ti(2)-O(9) 75.48(11)	O(11)-Ti(3)-O(13) 78.2(2)	O(6)-Ti(3)-O(13) 76.36(5)
	O(8)-Ti(3)-O(9) 75.71(11)	O(12)-Ti(3)-O(13) 77.5(2)	O(8)-Ti(3)-O(13) 74.65(5)
(RO)-Ti-(μ_3-O)	O(2)-Ti(1)-O(9) 120.24(15)	O(5)-Ti(1)-O(13) 168.1(2)	O(5)-Ti(1)-O(13) 166.57(7)
	O(3)-Ti(1)-O(9) 123.33(16)	O(6)-Ti(1)-O(13) 91.9(3)	O(7)-Ti(1)-O(13) 97.29(7)
	O(5)-Ti(2)-O(9) 165.99(12)	O(7)-Ti(2)-O(13) 165.6(2)	O(9)-Ti(2)-O(13) 130.92(8)
	O(6)-Ti(2)-O(9) 97.64(13)	O(8)-Ti(2)-O(13) 95.2(2)	O(10)-Ti(2)-O(13) 113.94(7)
	O(10)-Ti(3)-O(9) 167.25(14)	O(9)-Ti(3)-O(13) 140.3(2)	O(11)-Ti(3)-O(13) 170.30(7)
	O(11)-Ti(3)-O(9) 93.61(3)	O(10)-Ti(3)-O(13) 109.0(2)	O(12)-Ti(3)-O(13) 92.14(6)

(RO)-Ti-O(Rc)	O(2)-Ti(1)-O(4) 90.24(15)	O(5)-Ti(1)-O(1) 96.1(3)	O(1)-Ti(1)-O(5) 93.54(7)
	O(3)-Ti(1)-O4) 88.35(17)	O(6)-Ti(1)-O(1) 91.9(3)	O(1)-Ti(1)-O(7) 93.10(7)
	O(5)-Ti(2)-O(7) 82.22(12)	O(7)-Ti(2)-O(2) 91.0(3)	O(3)-Ti(1)-O(5) 82.71(6)
	O(6)-Ti(2)-O(7) 174.90(13)	O(8)-Ti(2)-O(2) 97.0(2)	O(3)-Ti(1)-O(7) 176.11(6)
	O(10)-Ti(3)-O(12) 84.09(14)	O(7)-Ti(2)-O(3) 104.7(2)	O(2)-Ti(2)-O(9) 93.79(7)
	O(11)-Ti(3)-O(12) 174.81(14)	O(8)-Ti(2)-O(3) 133.1(2)	O(2)-Ti(2)-O(10) 91.62(7)
	O(10)-Ti(3)-O(13) 94.97(15)	O(5)-Ti(1)-O(4) 86.2(3)	O(4)-Ti(3)-O(11) 86.44(7)
	O(11)-Ti(3)-O(13) 92.82 (15)	O(6)-Ti(1)-O(4) 172.7(3)	O(4)-Ti(3)-O(12) 176.84(6)
(μ-OR)-Ti-O(Rc)	O(1)-Ti(1)-O(4) 165.91(2)	O(11)-Ti(1)-O(1) 160.8(2)	O(1)-Ti(1)-O(6) 161.41(6)
	O(1)-Ti(2)-O(7) 81.40(11)	O(12)-Ti(2)-O(2) 160.9(2)	O(3)-Ti(1)-O(6) 84.84(6)
	O(8)-Ti(2)-O(7) 84.43(11)	O(12)-Ti(2)-O(3) 85.1(2)	O(2)-Ti(2)-O(8) 164.29(6)
	O(8)-Ti(3)-O(12) 86.26(12)	O(11)-Ti(1)-O(4) 85.3(2)	O(4)-Ti(3)-O(6 83.59(6)
	O(8)-Ti(3)-O(13) 160.49(12)		O(4)-Ti(3)-O(8) 82.89(6)
(μ_3-O)-Ti-O(Rc)	O(9)-Ti(1)-O(4) 85.87(12)	O(13)-Ti(1)-O(1) 90.0(2)	O(13)-Ti(1)-O(1) 87.03(6)
	O(9)-Ti(2)-O(7) 83.84(11)	O(13)-Ti(2)-O(2) 89.7(2)	O(13)-Ti(2)-O(2) 87.66(6)
	O(9)-Ti(3)-O(12) 83.70(12)	O(13)-Ti(2)-O(3) 83.9(2)	O(13)-Ti(1)-O(3) 84.03(6)
	O(9)-Ti(3)-O(13) 87.13(11)	O(13)-Ti(1)-O(4) 84.6 (2)	O(13)-Ti(3)-O(4) 84.70(6)
Ti-(μ_3-O)-Ti	Ti(1)-O(9)-Ti(2) 105.23(13)	Ti(1)-O(13)-Ti(2) 132.9(3)	Ti(1)-O(13)-Ti(2) 140.73(8)
	Ti(1)-O(9)-Ti(3) 140.86(15)	Ti(1)-O(13)-Ti(3) 106.0(2)	Ti(1)-O(13)-Ti(3) 102.80(6)
	Ti(2)-O(9)-Ti(3) 104.16(12)	Ti(2)-O(13)-Ti(3) 106.8(2)	Ti(2)-O(13)-Ti(3) 104.11(6)

(Rc)O-C-O(Rc)	O(4)-C(41)-O(13) 128.2(4)	O(1)-C(1)-O(2) 123.5(9)	O(1)-C(1)-O(2) 117.57(19)
	O(7)-C(42)-O(12) 127.5(4)	O(3)-C(3)-O(4) 125.6(8)	O(2)-C(7)-O(4) 124.59(19)

[a]OR = OCH_2CMe_3

[b]ORc = O_2CR [R = H, **2**; CH_3, **3**; $CH_2C(CH_3)_3$, **6**]

Table 7. Comparison of the Interatomic Distances (Å) and Angles (deg) for **4** and **5**.

Distances (Å)	4		5	
Ti---Ti	Ti(1)---Ti(2)	3.068(2)	Ti(1)---Ti(1')	3.1026
	Ti(1)---Ti(3)	3.052(2)		
	Ti(2)---Ti(3')	3.052(2)		
	Ti(3)---Ti(2')	3.052(2)		
Ti-OR[a]	Ti(1)-O(5)	1.786(6)	Ti(1)-O(1)	1.792(1)
	Ti(2)-O(9)	1.797(6)	Ti(1)-O(2)	1.790(1)
	Ti(3)-O(12)	1.781(5)		
Ti-(μ-OR)		------	Ti(1)-O(5)	2.039(1)
Ti-(μ-ORc)[b]	Ti(1)-O(1)	2.025(6)		
	Ti(1)-O(2)	2.053(6)	Ti(1)-O(3)	2.054(1)
	Ti(2)-O(7)	2.053(6)	Ti(1)-O(4)	2.061(1)
	Ti(2)-O(8)	2.009(6)		
	Ti(3)-o(10)	2.075(6)		
	Ti(3)-O(11)	2.043(6)		
Ti-(μ_3-O)	Ti(1)-O(3)	1.870(5)		------
	Ti(1)-O(4)	1.786(6)		
	Ti(1)-O(6)	2.138(5)		
	Ti(2)-O(3')	1.853(5)		
	Ti(2)-O(4)	2.145(5)		
	Ti(2)-O(6)	1.911(5)		
	Ti(3)-O(3)	2.149(5)		
	Ti(3)-O(4')	1.895(5)		
	Ti(3)-O(6)	1.863(5)		

Angles (deg)			
(RO)-Ti-(OR)	-----	O(1)-Ti(1)-O(2)	95.76(7)
(μ-OR)-Ti-(OR)	-----	O(1)-Ti(1)-O(5)	91.73
		O(1)-Ti(1)-O(5')	169.93(6)
		O(2)-Ti(1)-O(5)	92.34
		O(2)-Ti(1)-O(5')	170.24(6)
(μ-OR)-Ti-(μ-OR)	-----	O(5)-Ti(1)-O(5')	80.93(5)

(μ-OR)-Ti-(μ_3-O)	-----		-----	
(μ_3-O)-Ti-(μ_3-O)	O(3)-Ti(1)-O(4)	101.3(2)	-----	
	O(3')-Ti(2)-O(4)	79.26(19)		
	O(3)-Ti(3)-O(4')	78.26(18)		
	O(3)-Ti(1)-O(6)	78.73(19)		
	O(3')-Ti(2)-O(6)	101.4(2)		
	O(3)-Ti(3)-O(6)	78.58(19)		
	O(4)-Ti(1)-O(6)	79.26(19)		
	O(4)-Ti(2)-O(6)	77.98(19)		
	O(4')-Ti(3)-O(6)	100.8(2)		
(RO)-Ti-(μ_3-O)	O(5)-Ti(1)-O(3)	97.5(2)	-----	
	O(5)-Ti(1)-O(4)	97.9(3)		
	O(5)-Ti(1)-O(6)	174.6(2)		
	O(9)-Ti(2)-O(3')	99.5(2)		
	O(9)-Ti(2)-O(4)	173.7(3)		
	O(9)-Ti(2)-O(6)	95.3(3)		
	O(12)-Ti(3)-O(3)	175.6(2)		
	O(12)-Ti(3)-O(4')	98.1(2)		
	O(12)-Ti(3)-O(6)	99.9(2)		
(RO)-Ti-O(Rc)	O(5)-Ti(1)-O(1)	95.4(3)	O(1)-Ti(1)-O(3)	92.82(6)
	O(5)-Ti(1)-O(2)	94.9(3)	O(1)-Ti(1)-O(4)	103.04(6)
	O(9)-Ti(2)-O(7)	94.3(3)	O(2)-Ti(1)-O(3)	103.42(6)
	O(9)-Ti(2)-O(8)	97.6(3)	O(2)-Ti(1)-O(4)	92.66(6)
	O(12)-Ti(3)-O(10)	93.5(3)		
	O(12)-Ti(3)-O(11)	95.2(2)		
(μ-OR)-Ti-O(Rc)	-----		O(5)-Ti(1)-O(3)	79.45(5)
			O(5')-Ti(1)-O(3)	82.40(5)
			O(5)-Ti(1)-O(4)	82.51(5)
			O(5')-Ti(1)-O(4)	79.52(5)
(cRO)-Ti-(ORc)	O(1)-Ti(1)-O(2)	77.4(3)	O(3)-Ti(1)-O(4)	156.19(6)
	O(7)-Ti(2)-O(8)	78.0(3)		
	O(10)-Ti(3)-O(11)	79.1(3)		

(μ_3-O)-Ti-O(Rc)	O(1)-Ti(1)-O(6)	89.1(2)	-----	
	O(2)-Ti(1)-O(6)	88.9(2)		
	O(1)-Ti(1)-O(3)	162.1(2)		
	O(2)-Ti(1)-O(3)	89.1(2)		
	O(1)-Ti(1)-O(4)	89.2(2)		
	O(2)-Ti(1)-O(4)	162.3(2)		
	O(7)-Ti(2)-O(3')	163.0(2)		
	O(8)-Ti(2)-O(3')	90.3(2)		
	O(7)-Ti(2)-O(6)	87.1(2)		
	O(8)-Ti(2)-O(6)	161.0(2)		
	O(7)-Ti(2)-O(4)	88.2(2)		
	O(8)-Ti(2)-O(4)	89.7(2)		
	O(10)-Ti(3)-O(3)	88.8(2)		
	O(11)-Ti(3)-O(3)	88.9(2)		
	O(10)-Ti(3)-O(4')	87.1(2)		
	O(11)-Ti(3)-O(4')	161.4(2)		
	O(10)-Ti(3)-O(6)	163.3(2)		
	O(11)-Ti(3)-O(6)	89.7(2)		
Ti-(μ_3-O)-Ti	Ti(1)-O(3)-Ti(2')	137.1(3)	-----	
	Ti(1)-O(3)-Ti(3)	98.6(2)		
	Ti(2')-O(3)-Ti(3)	99.1(2)		
	Ti(1)-O(4)-Ti(2)	99.7(2)		
	Ti(1)-O(4)-Ti(3')	137.1(3)		
	Ti(2)-O(4)-Ti(3')	97.9(2)		
	Ti(1)-O(6)-Ti(2)	98.4(2)		
	Ti(1)-O(6)-Ti(3)	99.2(2)		
	Ti(2)-O(6)-Ti(3)	136.0(3)		
(Rc)O-C-O(Rc)	O(1)-C(1)-O(7)	124.0(8)	O(3)-C(11)-O(4')	125.7(2)
	O(2)-C(5)-O911)	127.0(9)		
	O(8')-C(24)-O(10)	128.0(11)		

[a]OR = OCH_2CMe_3

[b]ORc = O_2CR [R = $CH(CH_3)_2$, 4; $C(CH_3)_3$, 5]

Table 8. Film properties of 0.2 M solutions of **1** - **6** for sintered films.

compound	green thick. (av. Å)	sintered thick. (av. Å)	η_f (av.)[a]	$\rho_{normalized}$ (av.)[b]	Ref
1	388	212	2.13	99.0	c
2	344	199	2.19	102	c
3	435	232	2.17	101	c
4	330	151	2.10	97.0	c
5	819	273	1.92	86.5	c
6	793	281	1.94	87.5	c
$Ti(OPr^i)_4$	361	218	2.113	97.95	1, 16, c
$Ti_4(O)_2(OFc)_2(OPr^i)_8$	345	186	2.170	100.7	1, 16, c
$Ti_6(O)_4(OAc)_4(OPr^i)_{12}$	312	101	2.038	93.65	1, 16, c
$Ti(OPr^i)_4$/HOPc	400	183	2.082	96.20	1, 16, c
$Ti_2(OBc)_2(OPr^i)_6(HOPr^i)$	1028	316	1.802	78.26	1, 16, c
$Ti_6(O)_4(ONc)_4(OPr^i)_{12}$	556	222	1.9660	89.24	1, 16, c

[a]Index of refraction. Average determined by a point-to-point sampling of at least two thin films.
[b]Normalized density. Average determined by a point-to-point sampling of at least two thin films.
[c]This work

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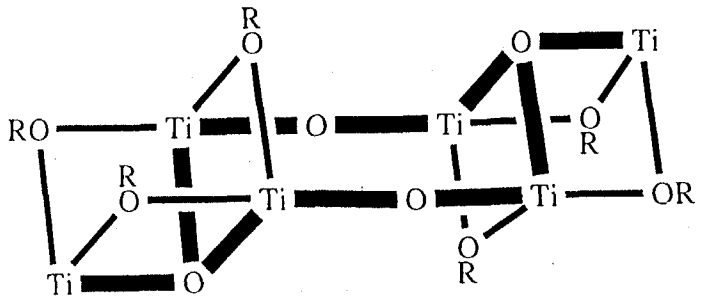
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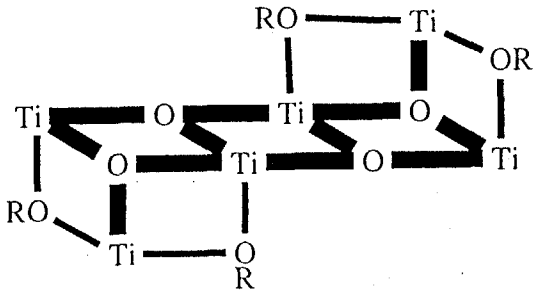
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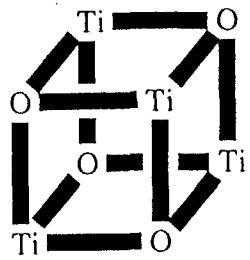
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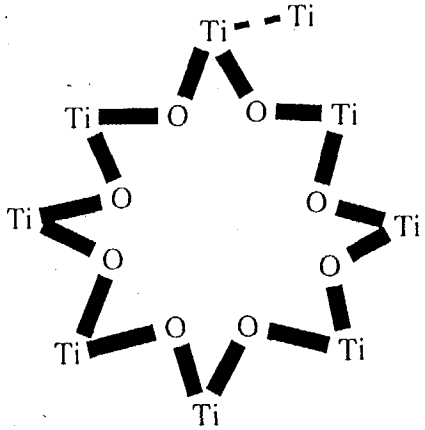
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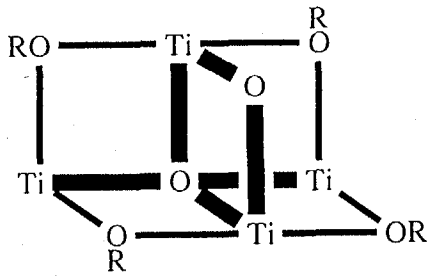
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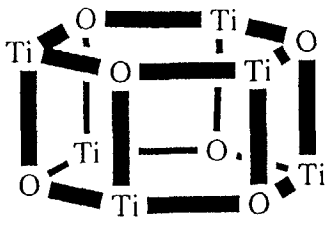
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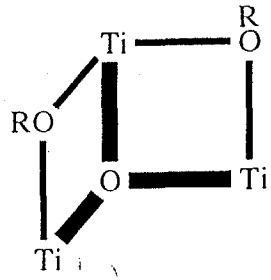
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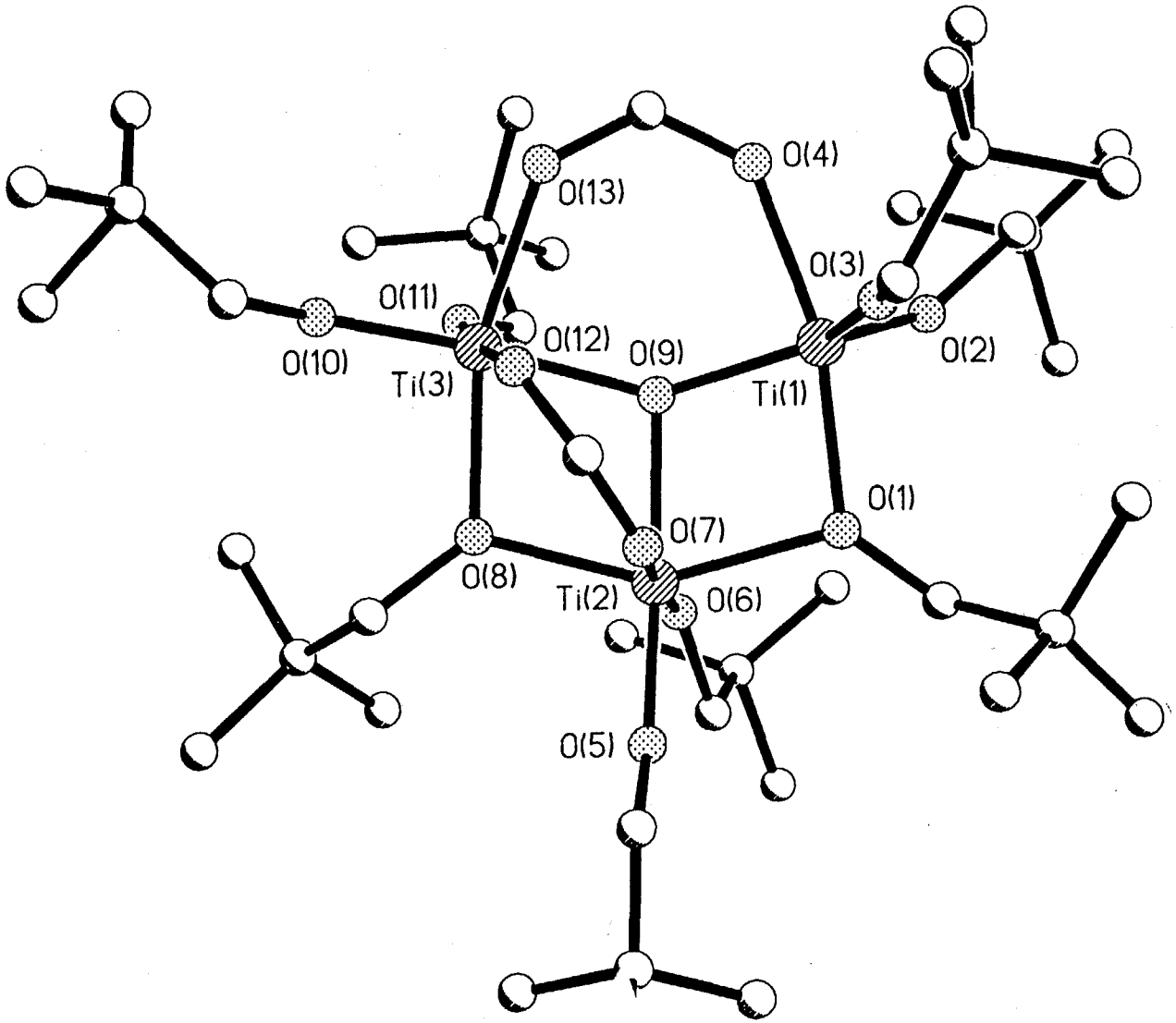
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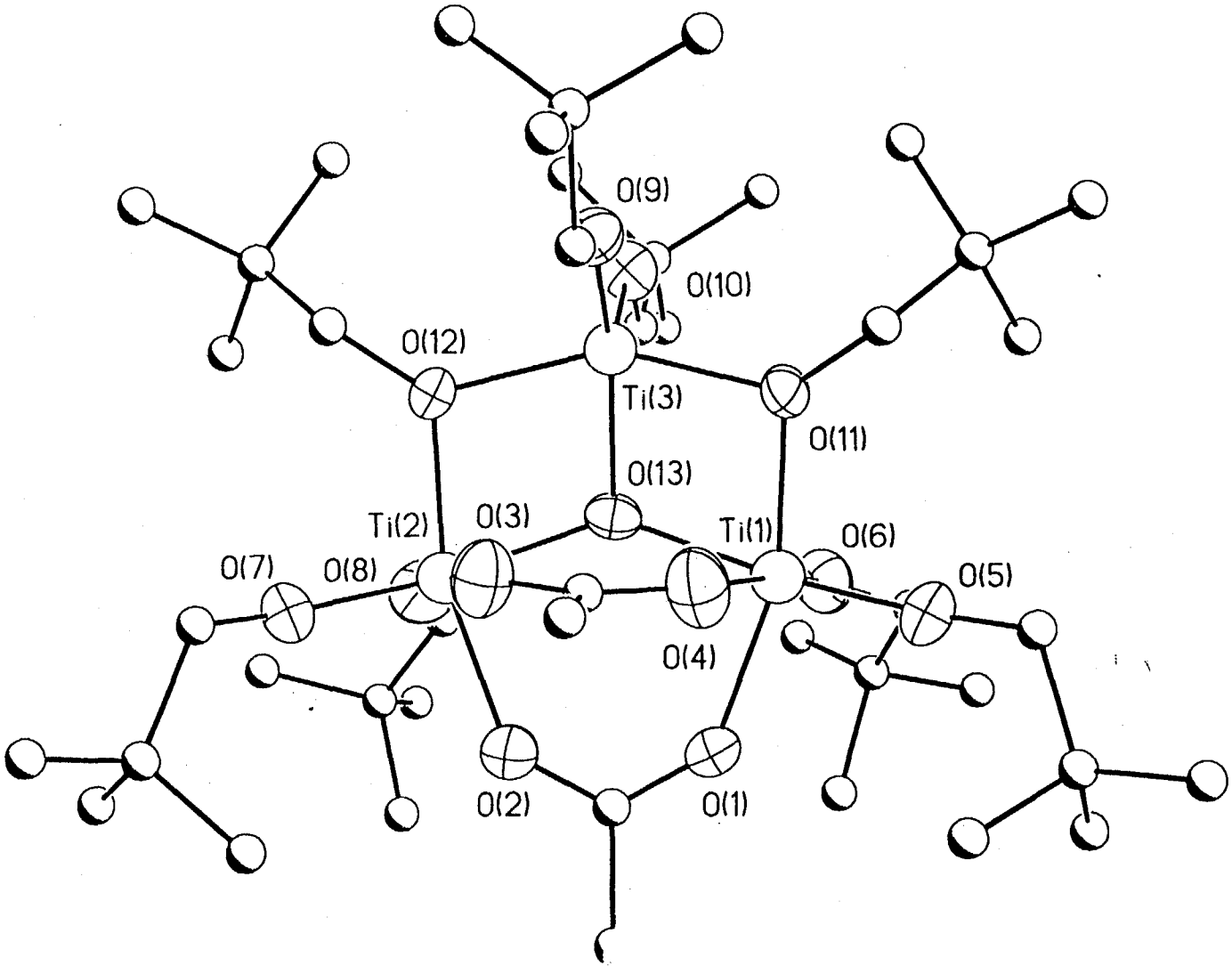
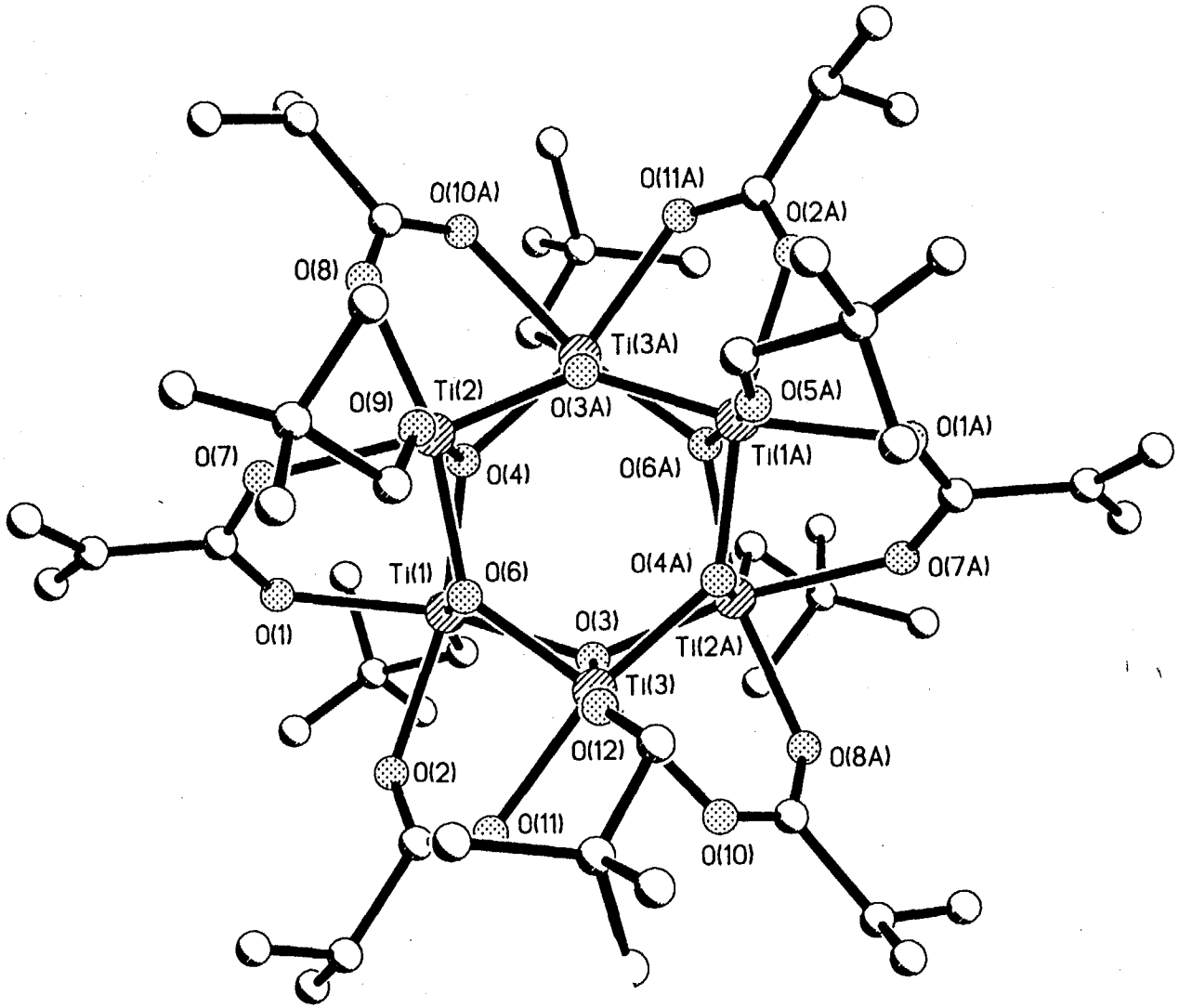
O(6)
O(5)


O(9)
O(10)
O(12)
Ti(3)
O(11)
O(13)
Ti(2)
O(3)
Ti(1)
O(6)
O(7)
O(8)
O(5)
O(4)
O(2)
O(1)


O(10A)
O(11A)
O(2A)
O(8)
Ti(3A)
O(9)
Ti(2)
O(3A)
O(5A)
O(1A)
O(7)
O(4)
O(6A)
Ti(1A)
Ti(1)
O(6)
O(4A)
O(7A)
O(1)
O(3)
Ti(2A)
Ti(3)
O(12)
O(8A)
O(2)
O(11)
O(10)

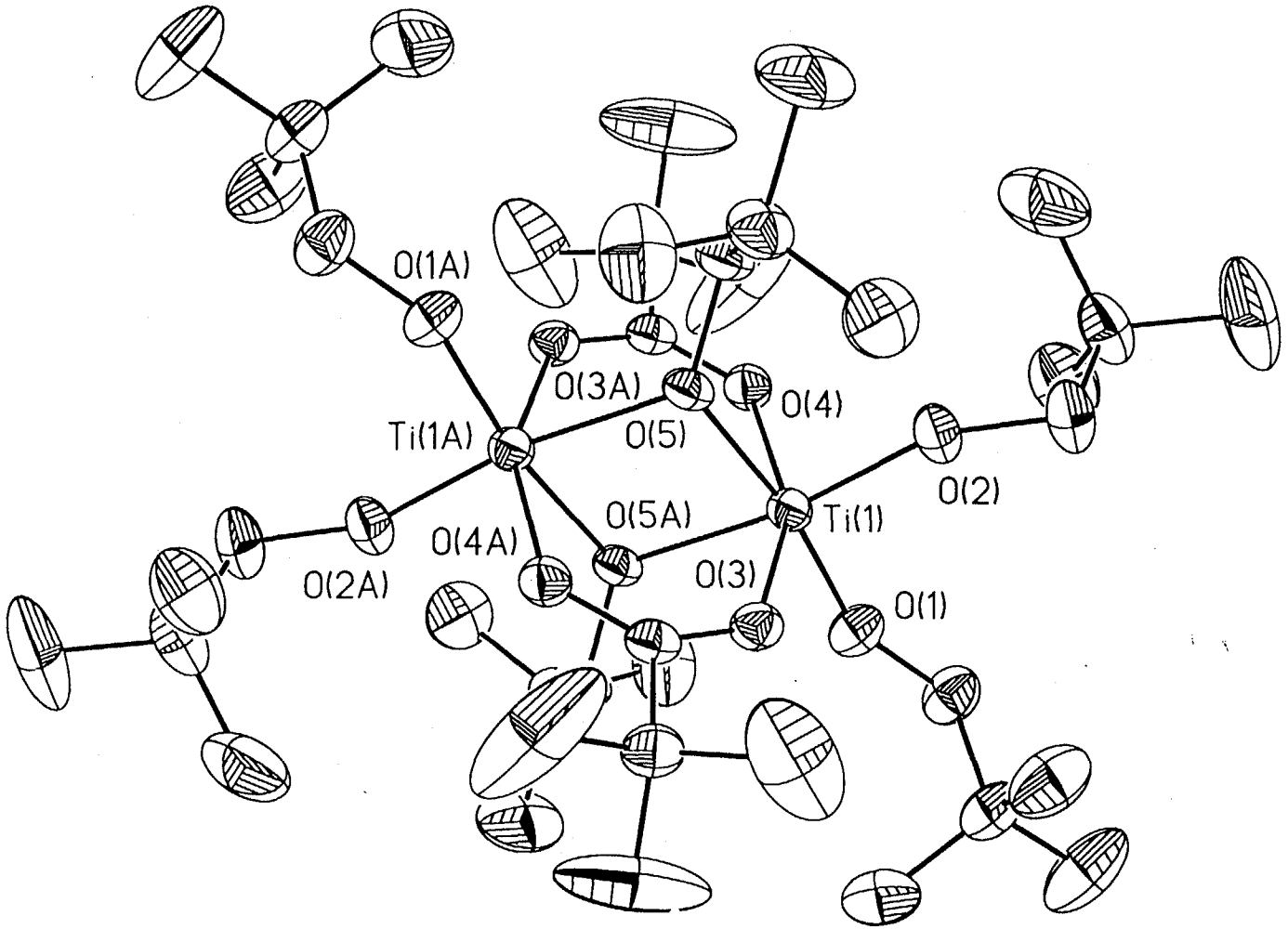
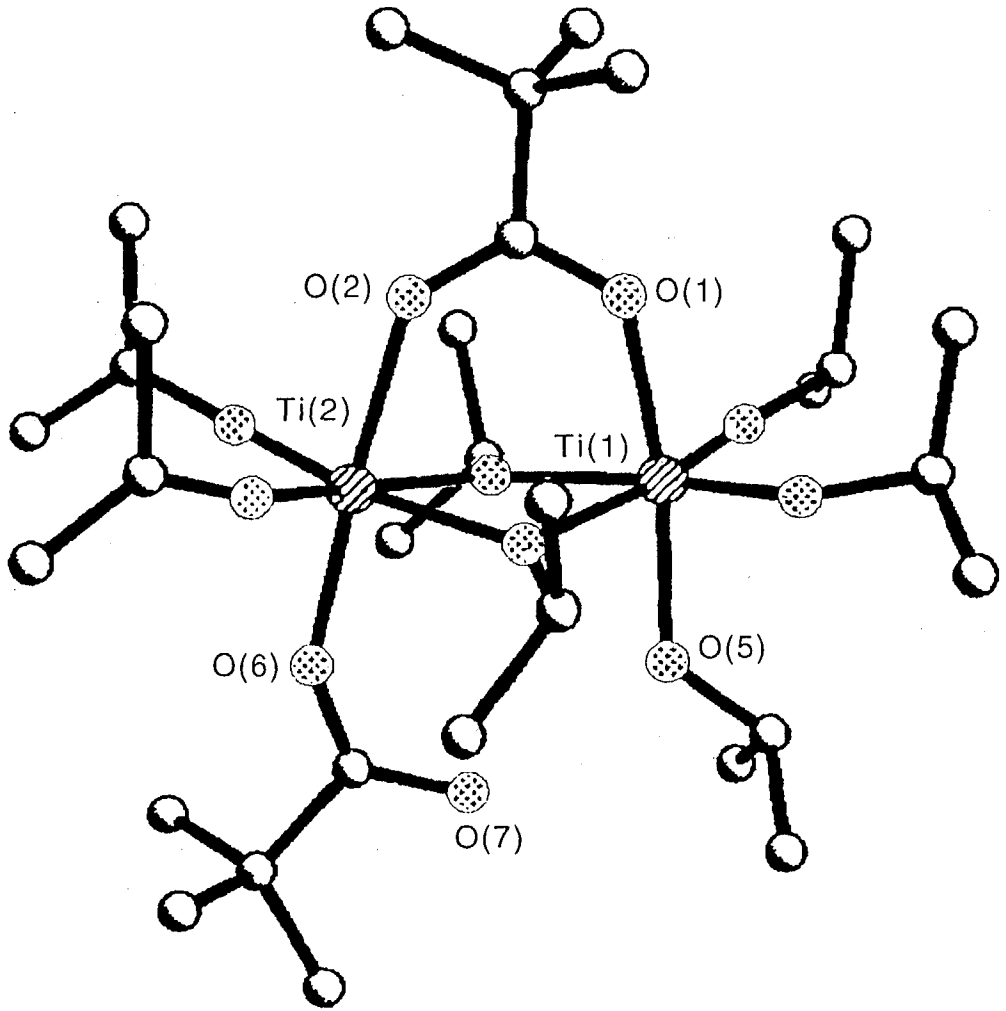
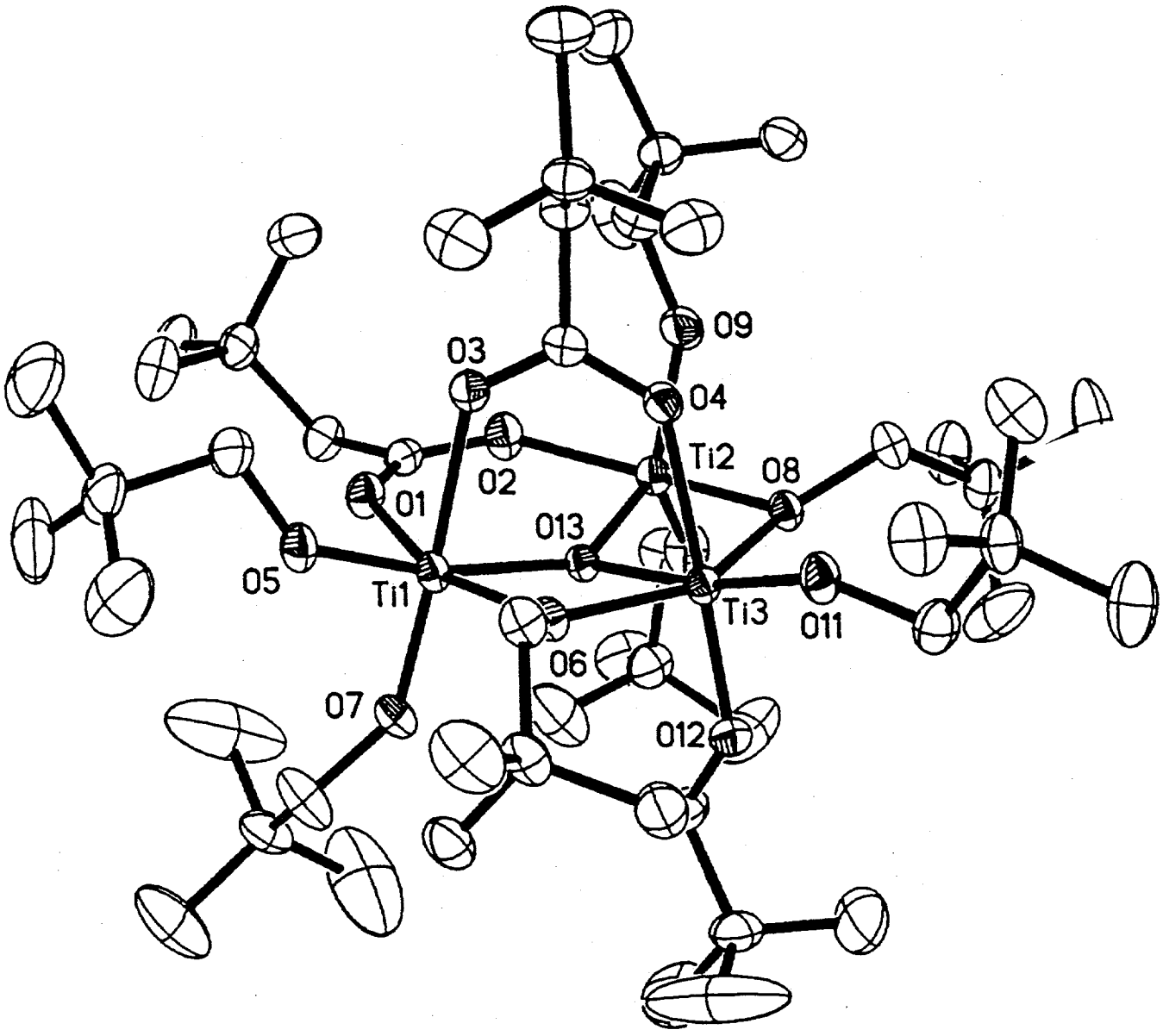
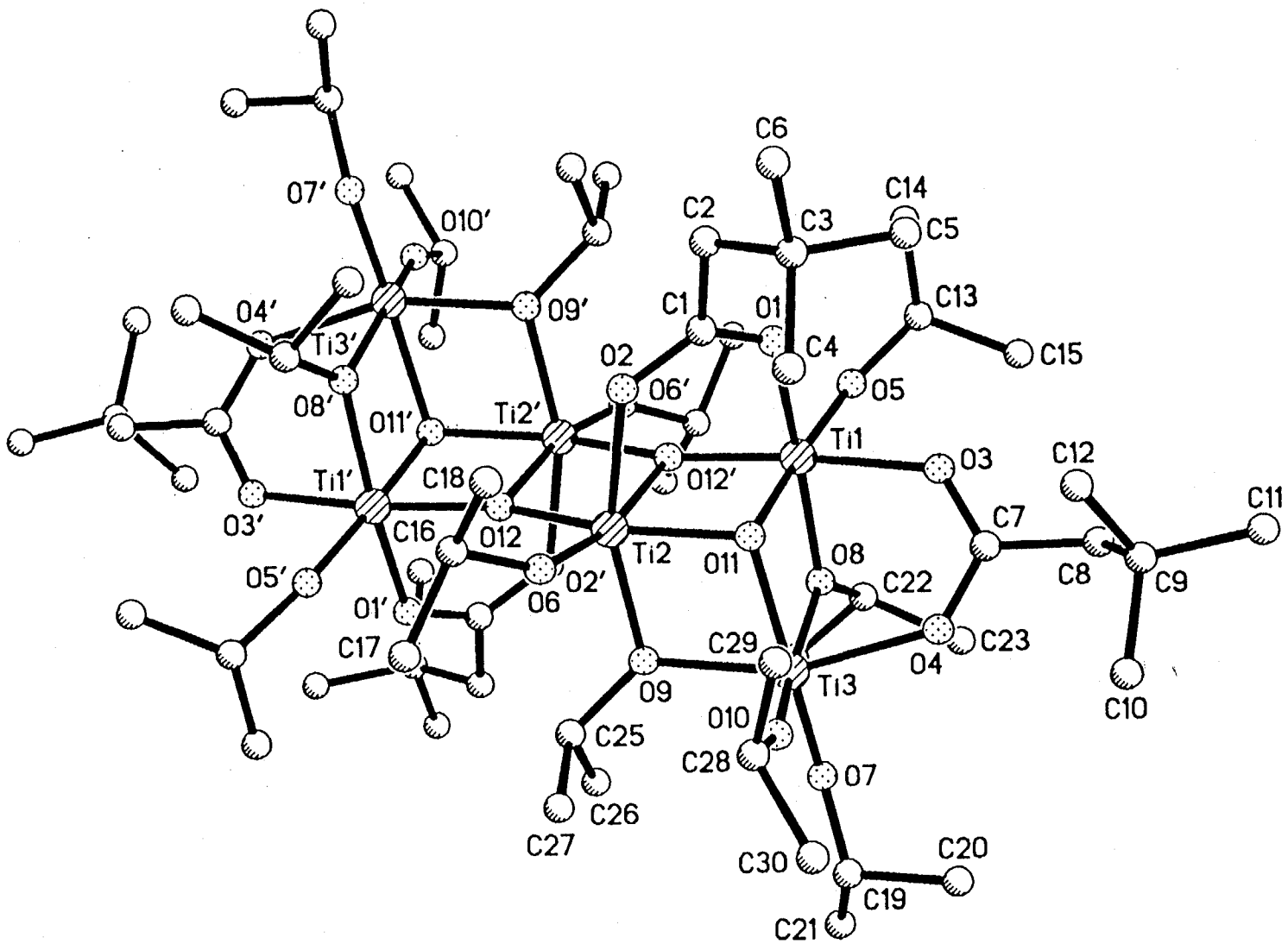
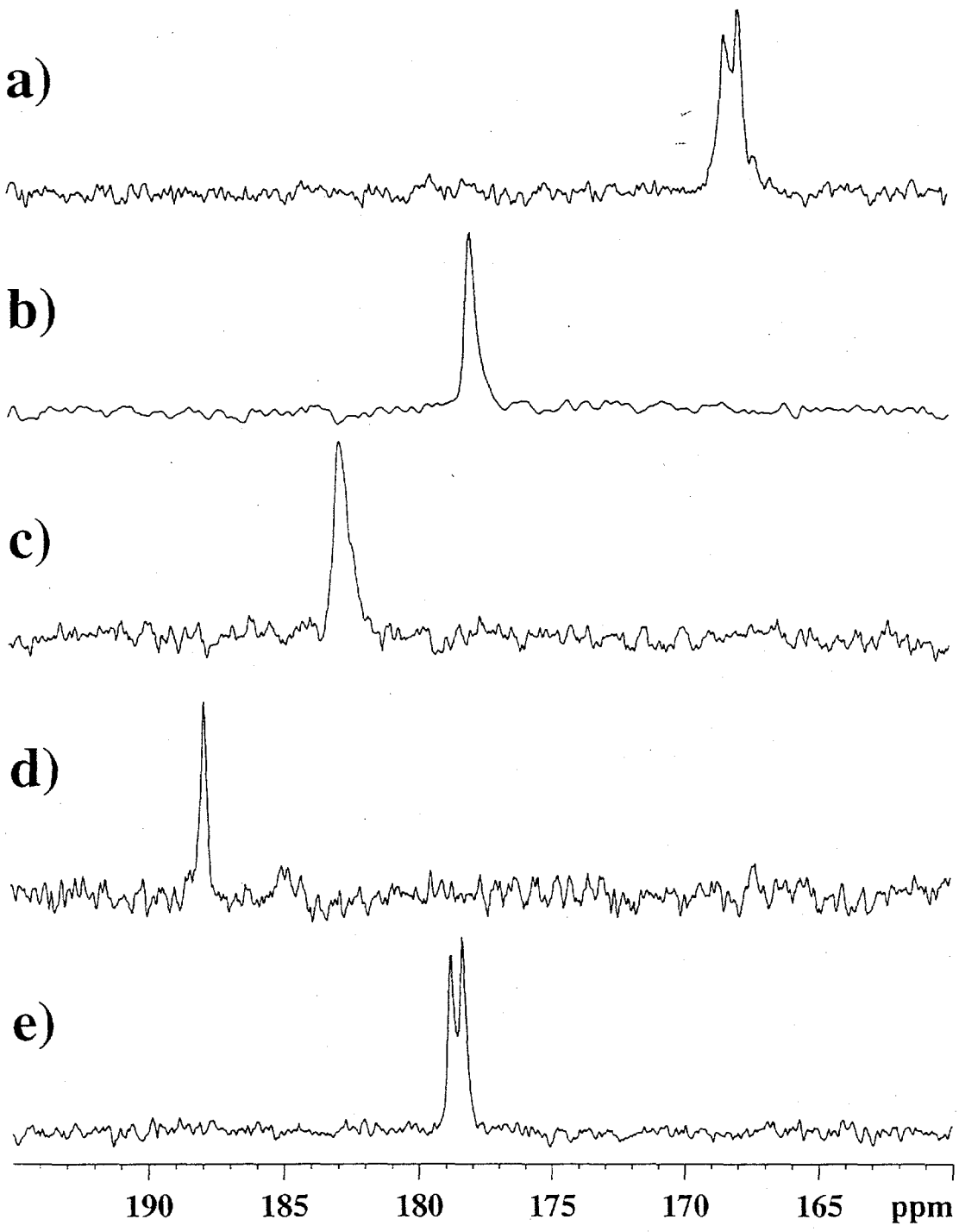


Table 5a


O(2)
O(1)
Ti(2)
Ti(1)
O(6)
O(5)
O(7)


09
03
04
Ti2
08
02
01
013
05
Ti1
Ti3
011
06
07
012


C6
C14
C2
C3
C5
O7′
O10′
C1
O1
C13
O4′
O9′
Ti3′
O2
C4
C15
O8′
O6′
O5
O11′
Ti2′
Ti1
O3
C12
Ti1′
C18
O12′
C11
O3′
C16
O12
C7
Ti2
O11
O8
C8
C9
O5′
O2′
C22
O1′
O6
C23
C17
C29
O4
O9
Ti3
C10
O10
C25
C28
O7
C26
C27
C30
C20
C19
C21


a)
b)
c)
d)
e)
190
185
180
175
170
165
ppm

$$[Ti(\mu\text{-}ONp)(ONp)_3]_2 + 2\ HOFc \xrightarrow{\text{toluene}} 2/3\ Ti_3(O)(OFc)_2(ONp) \quad (1)$$

$$[Ti(\mu\text{-}ONp)(ONp)_3]_2 + 2\ HOAc \xrightarrow{\text{toluene}} 2/3\ Ti_3(O)(OAc)_2(ONp)_8 \quad (2)$$

$$[Ti(\mu\text{-}ONp)(ONp)_3]_2 + 2\ HOPc \xrightarrow{\text{toluene}} 1/3\ Ti_6(O)_6(OPc)_6(ONp)_6 \quad (3)$$

$$[Ti(\mu\text{-}ONp)(ONp)_3]_2 + 2\ HOBc \xrightarrow{\text{toluene}} Ti_2(OBc)_2(ONp)_6 \quad (4)$$

$$[Ti(\mu\text{-}ONp)(ONp)_3]_2 + 2\ HONc \xrightarrow{\text{toluene}} 2/3\ Ti_3(O)(ONc)_2(ONp)_8 \quad (5)$$

$$\rho_{normalized} = \frac{[(n_f^2 - 1)(n_a^2 + 2)]}{[(n_f^2 + 2)(n_a^2 - 1)]} \quad (6)$$

n_f = Film index of refraction.
n_a = Anatase index of refraction.

Supplemental Material for:

Carboxylic Acid Modified $[Ti(\mu\text{-}ONep)(ONep)_3]_2$ Compounds: Syntheses, Characterizations, X-ray Structures, and Implications for the Thin Film Densification of TiO_2 from $Ti_3(\mu_3\text{-}O)(O_2CH)_2(ONep)_8$, $Ti_3(\mu_3\text{-}O)(O_2CMe)_2(ONep)_8$, $Ti_6(\mu_3\text{-}O)_6(O_2CCHMe_2)_6(ONep)_6$, $[Ti(O_2CCMe_3)(ONep)_3]_2$, and $Ti_3(\mu_3\text{-}O)(O_2CCH_2CMe_3)_2(ONep)_8$ ($ONep = OCH_2CMe_3$).[1]

by:

Timothy J. Boyle, Ryan P. Tyner, Todd M. Alam,
Brian L. Scott, Joseph W. Ziller, B. G. Potter, Jr.

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Table S2.1. Crystal data and structure refinement for **2**.

Empirical formula	$C_{42} H_{90} O_{13} Ti_3$
Formula weight	946.84
Temperature	203 K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 23.229(1) Å
	b = 16.1885(8) Å
	c = 29.706(1) Å
Volume	11170.6(9) $Å^3$
Z	8
Density (calculated)	1.126 Mg/m^3
Absorption coefficient	0.468 mm^{-1}
F(000)	4096
Crystal size	0.10 x 0.10 x 0.25 mm^3
Theta range for data collection	1.4 to 26.7°.
Index ranges	0<=h<=29, 0<=k<=20, 0<=l<=37
Reflections collected	55820
Independent reflections	11499 [R(int) = 0.0495]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11499 / 0 / 577
Goodness-of-fit on F^2	1.384
Final R indices [I>2sigma(I)]	R1 = 0.0875, wR2 = 0.2477
R indices (all data)	R1 = 0.1183, wR2 = 0.2655
Largest diff. peak and hole	1.677 and -0.623 $e.Å^{-3}$

Table S2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	4391(1)	1982(1)	1161(1)	39(1)
Ti(2)	5370(1)	2107(1)	1852(1)	36(1)
Ti(3)	5738(1)	864(1)	1084(1)	42(1)
O(1)	4538(1)	2482(2)	1764(1)	39(1)
O(2)	4168(2)	2898(2)	881(1)	60(1)
O(3)	3836(2)	1284(2)	1315(1)	68(1)
O(4)	4448(1)	1380(2)	554(1)	59(1)
O(5)	5482(1)	2188(2)	2452(1)	47(1)
O(6)	5669(1)	3090(2)	1711(1)	48(1)
O(7)	4944(1)	980(2)	2046(1)	43(1)
O(8)	6017(1)	1355(2)	1669(1)	40(1)
O(9)	5166(1)	1746(2)	1224(1)	37(1)
O(10)	6178(2)	-42(2)	1062(1)	60(1)
O(11)	6146(1)	1511(2)	713(1)	53(1)
O(12)	5185(1)	113(2)	1487(1)	50(1)
O(13)	5190(1)	493(2)	578(1)	54(1)
C(1)	4323(3)	3217(5)	1948(3)	99(2)
C(2)	3773(2)	3199(4)	2192(2)	63(1)
C(3)	3274(3)	2965(6)	1860(3)	124(3)
C(4)	3590(5)	3846(12)	2451(5)	316(13)
C(5)	3814(5)	2453(8)	2561(4)	165(4)
C(6)	3768(2)	3203(3)	560(2)	61(1)
C(7)	3982(2)	3965(3)	328(2)	63(1)
C(8)	3547(4)	4229(5)	-13(3)	124(3)
C(9)	4081(4)	4669(4)	673(3)	101(2)
C(10)	4546(4)	3782(6)	82(3)	124(3)
C(11)	3505(8)	636(14)	1499(7)	106(7)
C(11')	3640(9)	461(15)	1167(13)	167(13)
C(12)	3035(3)	362(5)	1206(2)	92(2)
C(13)	2611(5)	1077(10)	1251(7)	226(8)
C(14)	3059(16)	560(30)	671(10)	230(20)
C(14')	3274(19)	90(30)	790(12)	300(30)

C(15)	2814(8)	-500(11)	1223(9)	357(15)
C(16)	5377(2)	1772(3)	2861(2)	58(1)
C(17)	5612(3)	2217(3)	3266(2)	63(1)
C(18)	5457(4)	1712(5)	3678(2)	116(3)
C(19)	5343(4)	3069(4)	3300(3)	116(3)
C(20)	6261(4)	2263(7)	3229(3)	133(4)
C(21)	5810(5)	3821(6)	1965(4)	68(3)
C(21')	5708(6)	3723(6)	1399(3)	67(3)
C(22)	5955(3)	4534(3)	1623(2)	71(2)
C(23')	6557(12)	4325(13)	1864(14)	233(18)
C(23)	6538(6)	4317(7)	1380(5)	79(4)
C(24')	5943(13)	5188(9)	1230(8)	187(13)
C(24)	5448(8)	4704(11)	1335(7)	126(7)
C(25)	6067(7)	5318(9)	1953(6)	101(5)
C(25')	5475(8)	4826(8)	1941(6)	112(6)
C(26)	6426(2)	984(3)	1970(2)	50(1)
C(27)	7030(2)	1353(3)	1928(2)	61(1)
C(28)	7296(2)	1135(4)	1470(2)	83(2)
C(29)	7396(3)	958(5)	2295(3)	95(2)
C(30)	7010(3)	2267(4)	1978(3)	92(2)
C(31)	6224(5)	-874(4)	1181(3)	155(5)
C(32)	6500(3)	-1416(4)	860(2)	78(2)
C(33)	6510(6)	-2298(5)	1021(3)	159(5)
C(34)	6590(8)	-1248(8)	409(4)	238(9)
C(35)	7126(6)	-1199(12)	1024(9)	362(16)
C(36)	6179(3)	2284(3)	540(2)	69(2)
C(37)	6385(3)	2296(4)	51(2)	68(1)
C(38)	5951(3)	1831(5)	-237(2)	100(2)
C(39)	6969(3)	1938(5)	19(3)	101(2)
C(40)	6392(4)	3212(5)	-91(3)	128(3)
C(41)	4749(2)	800(3)	408(2)	55(1)
C(42)	4933(2)	304(3)	1847(2)	48(1)

Table S2.3. Bond lengths [Å] and angles [°] for **2**.

Ti(1)-O(3)	1.775(3)
Ti(1)-O(2)	1.777(3)
Ti(1)-O(9)	1.849(3)
Ti(1)-O(1)	1.995(3)
Ti(1)-O(4)	2.053(3)
Ti(1)-Ti(2)	3.0707(10)
Ti(2)-O(6)	1.785(3)
Ti(2)-O(5)	1.806(3)
Ti(2)-O(8)	2.010(3)
Ti(2)-O(9)	2.013(3)
Ti(2)-O(1)	2.043(3)
Ti(2)-O(7)	2.153(3)
Ti(2)-Ti(3)	3.1602(10)
Ti(3)-O(10)	1.789(3)
Ti(3)-O(11)	1.791(3)
Ti(3)-O(9)	1.993(3)
Ti(3)-O(8)	2.020(3)
Ti(3)-O(13)	2.059(3)
Ti(3)-O(12)	2.135(3)
O(1)-C(1)	1.402(7)
O(2)-C(6)	1.421(6)
O(3)-C(11)	1.410(17)
O(3)-C(11')	1.48(2)
O(4)-C(41)	1.250(5)
O(5)-C(16)	1.410(6)
O(6)-C(21')	1.386(10)
O(6)-C(21)	1.440(11)
O(7)-C(42)	1.244(5)
O(8)-C(26)	1.436(5)
O(10)-C(31)	1.397(7)
O(11)-C(36)	1.355(6)
O(12)-C(42)	1.259(5)
O(13)-C(41)	1.245(5)
C(1)-C(2)	1.467(9)
C(2)-C(4)	1.368(11)

C(2)-C(3)	1.569(8)
C(2)-C(5)	1.632(11)
C(6)-C(7)	1.497(7)
C(7)-C(8)	1.494(8)
C(7)-C(10)	1.531(10)
C(7)-C(9)	1.549(8)
C(11)-C(12)	1.466(19)
C(11')-C(12)	1.42(2)
C(11')-C(14')	1.53(4)
C(12)-C(15)	1.486(14)
C(12)-C(13)	1.524(15)
C(12)-C(14)	1.62(3)
C(16)-C(17)	1.506(7)
C(17)-C(18)	1.513(8)
C(17)-C(19)	1.518(8)
C(17)-C(20)	1.514(10)
C(21)-C(22)	1.574(12)
C(22)-C(24)	1.482(17)
C(22)-C(23)	1.573(14)
C(22)-C(25)	1.625(16)
C(22)-C(21')	1.581(11)
C(22)-C(23')	1.606(22)
C(22)-C(24')	1.577(19)
C(22)-C(25')	1.537(16)
C(26)-C(27)	1.530(6)
C(27)-C(30)	1.487(7)
C(27)-C(29)	1.523(8)
C(27)-C(28)	1.535(8)
C(31)-C(32)	1.446(9)
C(32)-C(34)	1.383(11)
C(32)-C(33)	1.505(10)
C(32)-C(35)	1.574(17)
C(36)-C(37)	1.529(8)
C(37)-C(39)	1.480(9)
C(37)-C(38)	1.523(9)
C(37)-C(40)	1.540(9)

O(3)-Ti(1)-O(2)	116.10(18)
O(3)-Ti(1)-O(9)	123.33(16)
O(2)-Ti(1)-O(9)	120.24(15)
O(3)-Ti(1)-O(1)	98.60(15)
O(2)-Ti(1)-O(1)	97.58(14)
O(9)-Ti(1)-O(1)	80.06(12)
O(3)-Ti(1)-O(4)	88.35(17)
O(2)-Ti(1)-O(4)	90.24(15)
O(9)-Ti(1)-O(4)	85.87(12)
O(1)-Ti(1)-O(4)	165.91(12)
O(3)-Ti(1)-Ti(2)	114.03(13)
O(2)-Ti(1)-Ti(2)	118.29(12)
O(9)-Ti(1)-Ti(2)	39.25(8)
O(1)-Ti(1)-Ti(2)	41.10(8)
O(4)-Ti(1)-Ti(2)	124.82(9)
O(6)-Ti(2)-O(5)	96.37(14)
O(6)-Ti(2)-O(8)	100.66(13)
O(5)-Ti(2)-O(8)	101.69(13)
O(6)-Ti(2)-O(9)	97.64(13)
O(5)-Ti(2)-O(9)	165.99(12)
O(8)-Ti(2)-O(9)	75.48(11)
O(6)-Ti(2)-O(1)	94.23(13)
O(5)-Ti(2)-O(1)	104.00(13)
O(8)-Ti(2)-O(1)	148.56(12)
O(9)-Ti(2)-O(1)	75.19(11)
O(6)-Ti(2)-O(7)	174.90(13)
O(5)-Ti(2)-O(7)	82.22(12)
O(8)-Ti(2)-O(7)	84.43(11)
O(9)-Ti(2)-O(7)	83.84(11)
O(1)-Ti(2)-O(7)	81.40(11)
O(6)-Ti(2)-Ti(1)	100.93(10)
O(5)-Ti(2)-Ti(1)	140.52(11)
O(8)-Ti(2)-Ti(1)	109.47(9)
O(9)-Ti(2)-Ti(1)	35.53(8)
O(1)-Ti(2)-Ti(1)	39.92(8)
O(7)-Ti(2)-Ti(1)	77.42(8)
O(6)-Ti(2)-Ti(3)	107.01(11)

O(5)-Ti(2)-Ti(3)	136.04(10)
O(8)-Ti(2)-Ti(3)	38.45(8)
O(9)-Ti(2)-Ti(3)	37.69(8)
O(1)-Ti(2)-Ti(3)	110.60(8)
O(7)-Ti(2)-Ti(3)	77.14(8)
Ti(1)-Ti(2)-Ti(3)	71.03(2)
O(10)-Ti(3)-O(11)	98.84(15)
O(10)-Ti(3)-O(9)	167.25(14)
O(11)-Ti(3)-O(9)	93.61(13)
O(10)-Ti(3)-O(8)	99.81(14)
O(11)-Ti(3)-O(8)	97.40(14)
O(9)-Ti(3)-O(8)	75.71(11)
O(10)-Ti(3)-O(13)	94.97(15)
O(11)-Ti(3)-O(13)	92.82(15)
O(9)-Ti(3)-O(13)	87.13(11)
O(8)-Ti(3)-O(13)	160.49(12)
O(10)-Ti(3)-O(12)	84.09(14)
O(11)-Ti(3)-O(12)	174.81(14)
O(9)-Ti(3)-O(12)	83.70(12)
O(8)-Ti(3)-O(12)	86.26(12)
O(13)-Ti(3)-O(12)	82.63(13)
O(10)-Ti(3)-Ti(2)	134.66(12)
O(11)-Ti(3)-Ti(2)	102.42(11)
O(9)-Ti(3)-Ti(2)	38.15(8)
O(8)-Ti(3)-Ti(2)	38.23(8)
O(13)-Ti(3)-Ti(2)	123.13(9)
O(12)-Ti(3)-Ti(2)	78.19(8)
C(1)-O(1)-Ti(1)	129.4(4)
C(1)-O(1)-Ti(2)	122.6(4)
Ti(1)-O(1)-Ti(2)	98.99(11)
C(6)-O(2)-Ti(1)	142.7(3)
C(11)-O(3)-C(11')	43.6(12)
C(11)-O(3)-Ti(1)	165.8(8)
C(11')-O(3)-Ti(1)	136.1(11)
C(41)-O(4)-Ti(1)	134.3(3)
C(16)-O(5)-Ti(2)	142.2(3)
C(21')-O(6)-C(21)	74.2(6)

C(21')-O(6)-Ti(2)	147.3(5)
C(21)-O(6)-Ti(2)	134.2(5)
C(42)-O(7)-Ti(2)	129.0(3)
C(26)-O(8)-Ti(2)	125.5(3)
C(26)-O(8)-Ti(3)	125.7(3)
Ti(2)-O(8)-Ti(3)	103.32(12)
Ti(1)-O(9)-Ti(3)	140.86(15)
Ti(1)-O(9)-Ti(2)	105.23(13)
Ti(3)-O(9)-Ti(2)	104.16(12)
C(31)-O(10)-Ti(3)	145.6(5)
C(36)-O(11)-Ti(3)	143.4(3)
C(42)-O(12)-Ti(3)	128.1(3)
C(41)-O(13)-Ti(3)	133.5(3)
O(1)-C(1)-C(2)	119.0(6)
C(4)-C(2)-C(1)	122.2(10)
C(4)-C(2)-C(3)	108.0(6)
C(1)-C(2)-C(3)	109.7(5)
C(4)-C(2)-C(5)	101.9(10)
C(1)-C(2)-C(5)	107.2(6)
C(3)-C(2)-C(5)	106.6(7)
O(2)-C(6)-C(7)	112.2(4)
C(8)-C(7)-C(6)	108.8(5)
C(8)-C(7)-C(10)	108.1(7)
C(6)-C(7)-C(10)	110.1(5)
C(8)-C(7)-C(9)	109.8(5)
C(6)-C(7)-C(9)	110.6(5)
C(10)-C(7)-C(9)	109.4(6)
O(3)-C(11)-C(12)	113.7(12)
O(3)-C(11')-C(14)	111(2)
C(14')-C(12)-C(11)	108.5(19)
C(11)-C(12)-C(13)	101.4(12)
C(15)-C(12)-C(13)	119.1(12)
C(11)-C(12)-C(14)	119.7(14)
C(15)-C(12)-C(14)	103.4(19)
C(13)-C(12)-C(14)	87.5(19)
O(5)-C(16)-C(17)	113.4(4)
C(16)-C(17)-C(18)	107.6(5)

C(16)-C(17)-C(19)	109.7(5)
C(18)-C(17)-C(19)	109.9(6)
C(16)-C(17)-C(20)	109.1(5)
C(18)-C(17)-C(20)	108.8(6)
C(19)-C(17)-C(20)	111.7(7)
O(6)-C(21)-C(22)	108.3(8)
O(6)-C(21')-C(22)	110.8(7)
C(24)-C(22)-C(21)	109.7(9)
C(24)-C(22)-C(23)	117.5(12)
C(21)-C(22)-C(23)	108.5(7)
C(25')-C(22)-C(21')	104.5(8)
C(25')-C(22)-C(24')	103.6(11)
C(21')-C(22)-C(24')	103.8(10)
C(21')-C(22)-C(23')	109.3(10)
C(24')-C(22)-C(23')	119.2(17)
C(24)-C(22)-C(25)	109.3(10)
C(21)-C(22)-C(25)	102.6(8)
C(23)-C(22)-C(25)	108.3(8)
O(8)-C(26)-C(27)	113.0(4)
C(30)-C(27)-C(26)	110.6(4)
C(30)-C(27)-C(29)	111.3(5)
C(26)-C(27)-C(29)	106.7(5)
C(30)-C(27)-C(28)	109.3(5)
C(26)-C(27)-C(28)	110.6(5)
C(29)-C(27)-C(28)	108.3(5)
O(10)-C(31)-C(32)	116.9(6)
C(34)-C(32)-C(31)	125.8(7)
C(34)-C(32)-C(33)	119.5(7)
C(31)-C(32)-C(33)	112.0(7)
C(34)-C(32)-C(35)	96.6(13)
C(31)-C(32)-C(35)	94.1(9)
C(33)-C(32)-C(35)	95.7(10)
O(11)-C(36)-C(37)	113.0(5)
C(39)-C(37)-C(38)	112.1(6)
C(39)-C(37)-C(36)	110.1(5)
C(38)-C(37)-C(36)	108.7(5)
C(39)-C(37)-C(40)	110.5(6)

C(38)-C(37)-C(40)	109.3(6)
C(36)-C(37)-C(40)	106.0(6)
O(13)-C(41)-O(4)	128.2(4)
O(7)-C(42)-O(12)	127.5(4)

Table S2.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Ti(1)	38(1)	37(1)	43(1)	-4(1)	-5(1)	6(1)
Ti(2)	38(1)	31(1)	40(1)	0(1)	-4(1)	-1(1)
Ti(3)	43(1)	42(1)	41(1)	2(1)	2(1)	11(1)
O(1)	40(2)	35(1)	43(2)	-6(1)	2(1)	2(1)
O(2)	72(2)	50(2)	58(2)	1(2)	-18(2)	18(2)
O(3)	53(2)	79(2)	73(2)	-9(2)	-8(2)	-25(2)
O(4)	56(2)	70(2)	52(2)	-20(2)	-18(2)	18(2)
O(5)	56(2)	43(2)	43(2)	0(1)	-12(1)	-3(1)
O(6)	48(2)	37(2)	59(2)	6(1)	-6(1)	-4(1)
O(7)	52(2)	36(2)	40(2)	0(1)	4(1)	-7(1)
O(8)	38(2)	41(2)	42(2)	7(1)	-3(1)	4(1)
O(9)	39(2)	37(1)	36(1)	1(1)	-2(1)	4(1)
O(10)	66(2)	51(2)	62(2)	6(2)	8(2)	25(2)
O(11)	54(2)	60(2)	45(2)	10(2)	8(1)	12(2)
O(12)	60(2)	35(2)	56(2)	-2(1)	8(2)	-1(1)
O(13)	63(2)	50(2)	49(2)	-10(1)	-6(2)	17(2)
C(1)	101(6)	86(5)	111(6)	-23(4)	-5(4)	8(4)
C(2)	51(3)	81(4)	58(3)	-13(3)	6(2)	17(3)
C(3)	67(4)	193(9)	112(6)	-59(6)	-16(4)	49(5)
C(4)	186(12)	530(30)	236(15)	-281(19)	-99(11)	222(16)
C(5)	152(10)	194(11)	150(10)	51(9)	-7(7)	-27(9)
C(6)	62(3)	54(3)	68(3)	1(2)	-23(3)	9(2)
C(7)	78(4)	45(3)	67(3)	7(2)	-14(3)	5(2)
C(8)	172(8)	89(5)	111(6)	28(4)	-78(6)	4(5)
C(9)	148(7)	57(4)	98(5)	-4(3)	-33(5)	0(4)
C(10)	122(7)	125(7)	126(7)	36(6)	25(5)	-1(6)
C(11)	78(12)	110(15)	130(15)	49(12)	-31(10)	-47(10)
C(11')	68(11)	97(13)	330(40)	-20(20)	9(19)	-41(10)
C(12)	69(4)	105(5)	101(5)	-29(4)	18(3)	-41(4)
C(13)	74(7)	222(15)	380(20)	-62(15)	-51(10)	-9(8)
C(14)	160(20)	440(60)	99(17)	110(30)	-70(18)	-100(30)
C(14')	340(50)	400(50)	170(30)	-200(30)	150(30)	-310(40)

C(15)	247(18)	223(17)	600(40)	150(20)	-170(20)	-196(16)
C(16)	80(4)	48(3)	46(3)	-1(2)	-9(2)	-9(2)
C(17)	92(4)	51(3)	46(3)	-2(2)	-19(3)	-5(3)
C(18)	210(9)	86(5)	53(4)	11(3)	-22(5)	-30(6)
C(19)	208(10)	68(4)	71(4)	-21(3)	-9(5)	21(5)
C(20)	103(6)	204(10)	94(6)	-39(6)	-52(5)	6(6)
C(21)	81(8)	46(5)	78(8)	-3(5)	0(6)	-15(5)
C(21')	127(10)	33(4)	42(5)	-4(4)	20(6)	-21(5)
C(22)	68(3)	36(3)	109(5)	10(3)	5(3)	-11(2)
C(23')	200(30)	96(14)	400(50)	40(20)	-190(30)	-72(16)
C(23)	78(8)	55(6)	105(10)	-4(7)	32(7)	-26(6)
C(24')	350(30)	46(8)	162(18)	20(9)	130(20)	-48(13)
C(24)	140(15)	93(11)	147(16)	46(11)	-57(13)	-16(10)
C(25)	109(11)	79(9)	116(12)	-18(8)	3(9)	-5(8)
C(25')	167(16)	49(7)	120(13)	-31(7)	49(11)	-6(8)
C(26)	40(2)	59(3)	50(3)	12(2)	-7(2)	7(2)
C(27)	37(2)	62(3)	83(4)	5(3)	-9(2)	7(2)
C(28)	50(3)	88(4)	110(5)	12(4)	9(3)	-2(3)
C(29)	53(3)	117(6)	114(5)	11(4)	-29(3)	16(3)
C(30)	52(3)	67(4)	158(7)	-7(4)	-20(4)	-6(3)
C(31)	248(12)	71(5)	144(8)	38(5)	107(8)	89(6)
C(32)	107(5)	72(4)	55(3)	-16(3)	-13(3)	32(3)
C(33)	266(14)	81(5)	130(8)	-17(5)	-24(8)	90(7)
C(34)	390(20)	201(12)	122(9)	24(8)	77(12)	176(15)
C(35)	128(12)	260(20)	700(50)	-170(30)	-108(18)	95(13)
C(36)	82(4)	59(3)	66(3)	7(3)	12(3)	14(3)
C(37)	78(4)	71(3)	55(3)	12(3)	9(3)	0(3)
C(38)	120(6)	121(6)	58(4)	15(4)	-7(4)	-24(5)
C(39)	85(5)	116(6)	103(6)	1(4)	23(4)	7(4)
C(40)	145(8)	96(5)	143(8)	60(5)	14(6)	7(5)
C(41)	60(3)	59(3)	46(3)	-14(2)	-7(2)	11(2)
C(42)	54(3)	37(2)	51(3)	5(2)	3(2)	-6(2)

Table S2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	4285	3613	1705	119
H(1B)	4612	3432	2152	119
H(3A)	3386	2495	1684	185
H(3B)	3197	3423	1664	185
H(3C)	2934	2834	2029	185
H(4A)	3223	3714	2582	474
H(4B)	3554	4331	2268	474
H(4C)	3865	3947	2687	474
H(5A)	3934	1955	2413	248
H(5B)	3443	2370	2696	248
H(5C)	4088	2597	2789	248
H(6A)	3407	3326	709	73
H(6B)	3695	2779	336	73
H(8A)	3681	4717	-164	186
H(8B)	3188	4346	135	186
H(8C)	3492	3795	-229	186
H(9A)	4223	5150	519	151
H(9B)	4358	4495	893	151
H(9C)	3724	4800	819	151
H(10A)	4682	4275	-63	187
H(10B)	4482	3362	-141	187
H(10C)	4829	3594	294	187
H(16A)	5548	1226	2846	69
H(16B)	4965	1703	2897	69
H(18A)	5629	1175	3655	174
H(18B)	5047	1657	3697	174
H(18C)	5598	1985	3943	174
H(19A)	4932	3016	3325	174
H(19B)	5436	3382	3035	174
H(19C)	5490	3348	3561	174
H(20A)	6417	1715	3209	200

H(20B)	6415	2534	3491	200
H(20C)	6364	2570	2965	200
H(26A)	6446	396	1908	60
H(26B)	6293	1053	2277	60
H(28A)	7307	546	1435	124
H(28B)	7680	1352	1454	124
H(28C)	7067	1371	1233	124
H(29A)	7406	371	2251	142
H(29B)	7232	1080	2584	142
H(29C)	7780	1174	2280	142
H(30A)	6783	2499	1740	138
H(30B)	7394	2486	1964	138
H(30C)	6841	2405	2263	138
H(31A)	5840	-1083	1238	185
H(31B)	6436	-906	1462	185
H(33A)	6443	-2313	1340	238
H(33B)	6879	-2538	956	238
H(33C)	6215	-2606	870	238
H(34A)	6783	-1706	271	357
H(34B)	6822	-760	381	357
H(34C)	6226	-1160	264	357
H(35A)	7157	-1299	1341	542
H(35B)	7205	-627	963	542
H(35C)	7400	-1537	866	542
H(36A)	6441	2609	722	83
H(36B)	5802	2541	557	83
H(38A)	5579	2084	-208	150
H(38B)	5929	1267	-139	150
H(38C)	6070	1847	-547	150
H(39A)	7095	1947	-289	152
H(39B)	6962	1377	125	152
H(39C)	7230	2255	200	152
H(40A)	6011	3436	-67	192
H(40B)	6522	3256	-396	192
H(40C)	6647	3514	103	192
H(41)	4629	568	137	66
H(42)	4713	-109	1981	57

Table 1. Crystal data and structure refinement for 3

Empirical formula	$C_{44}\ H_{94}\ O_{13}\ Ti_3$
Formula weight	974.89
Temperature	198 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.011(1) Å b = 25.005(3) Å β = 100.98(1)° c = 21.342(3) Å
Volume, Z	5768.5(12) $Å^3$, 4
Density (calculated)	1.123 Mg/m^3
Absorption coefficient	0.455 mm^{-1}
Absorption correction	none applied
F(000)	2112
Crystal size	0.21 x 0.29 x 0.37 mm
Theta range for data collection	2.54° to 22.49°
Limiting indices	-1<=h<=10, -1<=k<=26, -22<=l<=22
Reflections collected	7739
Independent reflections	5668 [R(int) = 0.0727]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5660 / 1 / 554
Goodness-of-fit on F^2	1.229
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1430
R indices (all data)	R1 = 0.1476, wR2 = 0.1721
Largest diff. peak and hole	0.456 and -0.290 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 3
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	2024(2)	1937(1)	2906(1)	46(1)
Ti(2)	1905(2)	502(1)	2626(1)	43(1)
Ti(3)	-277(1)	1217(1)	2829(1)	36(1)
O(1)	3706(5)	1664(3)	2804(3)	63(2)
O(2)	3644(5)	790(2)	2654(3)	53(2)
O(3)	2338(6)	648(2)	3619(3)	55(2)
O(4)	2512(6)	1525(2)	3801(3)	59(2)
O(5)	2571(5)	2523(2)	3335(3)	59(2)
O(6)	1739(6)	2219(2)	2122(3)	60(2)
O(7)	2340(5)	-173(2)	2847(3)	48(2)
O(8)	1689(6)	417(2)	1792(3)	54(2)
O(9)	-943(5)	1109(2)	3527(2)	40(2)
O(10)	-1456(5)	1333(2)	2147(2)	43(2)
O(11)	286(5)	1951(2)	3094(2)	38(2)
O(12)	124(5)	446(2)	2755(2)	39(2)
O(13)	1268(4)	1243(2)	2585(2)	35(1)
C(1)	4210(9)	1230(4)	2719(4)	46(2)
C(2)	5551(7)	1239(4)	2683(4)	65(3)
C(3)	2635(8)	1047(4)	3973(4)	46(3)
C(4)	3143(10)	943(4)	4660(4)	85(4)
C(5)	2913(11)	2913(5)	3792(6)	123(5)
C(5A)	4255(9)	3056(4)	3925(5)	64(3)
C(5B)	4648(13)	3201(6)	3342(6)	171(7)
C(5C)	4951(14)	2571(6)	4181(7)	182(8)
C(5D)	4513(13)	3491(6)	4385(7)	192(9)
C(6)	1843(18)	2656(9)	1728(9)	119(9)
C(6')	1800(30)	2086(14)	1504(9)	61(14)
C(6A)	2310(12)	2544(4)	1155(5)	75(3)
C(6B)	2425(18)	3069(7)	942(11)	258(12)
C(6C)	1713(22)	2248(7)	615(8)	279(14)
C(6D)	3659(16)	2366(8)	1359(8)	221(10)
C(7)	2655(9)	-544(4)	3334(5)	64(3)
C(7A)	3957(9)	-762(4)	3425(5)	57(3)
C(7B)	4098(9)	-1193(4)	3935(5)	89(4)
C(7C)	4885(10)	-317(4)	3638(5)	99(4)
C(7D)	4178(11)	-989(5)	2813(5)	109(4)
C(8)	1736(16)	515(7)	1185(7)	176(7)
C(8A)	2468(15)	218(6)	826(6)	109(5)
C(8B)	2132(22)	-340(7)	818(11)	278(14)
C(8C)	2257(22)	396(10)	180(8)	305(16)
C(8D)	3781(14)	325(9)	1128(8)	253(13)
C(9)	-452(8)	1003(3)	4179(4)	51(3)
C(9A)	-1407(9)	960(4)	4599(4)	59(3)
C(9B)	-741(10)	847(5)	5276(4)	96(4)
C(9C)	-2310(9)	517(4)	4368(5)	82(3)
C(9D)	-2091(10)	1487(4)	4588(4)	82(3)

C(10)	-1235(10)	1425(5)	1523(5)	100(4)
C(10A)	-2264(10)	1523(5)	1016(5)	72(3)
C(10B)	-3216(14)	1096(6)	976(5)	163(8)
C(10C)	-1876(11)	1613(6)	391(5)	147(6)
C(10D)	-2892(18)	2026(7)	1187(6)	215(10)
C(11)	-103(9)	2312(3)	3536(4)	55(3)
C(11A)	-1006(9)	2742(4)	3221(5)	55(3)
C(11B)	-2247(9)	2486(4)	2942(5)	74(3)
C(11C)	-1175(10)	3142(4)	3744(5)	91(4)
C(11D)	-475(10)	3027(4)	2706(4)	74(3)
C(12)	-399(8)	-4(3)	3006(4)	50(3)
C(12A)	-1300(9)	-325(3)	2520(5)	55(3)
C(12B)	-2481(10)	-2(4)	2298(5)	99(4)
C(12C)	-1656(9)	-832(3)	2860(5)	76(3)
C(12D)	-725(11)	-479(4)	1956(5)	85(4)

Table 3. Bond lengths [A] and angles [°]

Ti(1)-O(5)	1.774(6)
Ti(1)-O(6)	1.788(6)
Ti(1)-O(13)	1.989(5)
Ti(1)-O(1)	2.024(6)
Ti(1)-O(11)	2.029(5)
Ti(1)-O(4)	2.147(6)
Ti(1)-Ti(3)	3.087(2)
Ti(2)-O(8)	1.762(6)
Ti(2)-O(7)	1.793(6)
Ti(2)-O(13)	1.975(5)
Ti(2)-O(2)	2.036(6)
Ti(2)-O(12)	2.036(5)
Ti(2)-O(3)	2.114(6)
Ti(2)-Ti(3)	3.091(2)
Ti(3)-O(10)	1.780(5)
Ti(3)-O(9)	1.801(5)
Ti(3)-O(13)	1.874(5)
Ti(3)-O(11)	1.986(5)
Ti(3)-O(12)	1.990(5)
O(1)-C(1)	1.247(10)
O(2)-C(1)	1.258(10)
O(3)-C(3)	1.256(10)
O(4)-C(3)	1.250(10)
O(5)-C(5)	1.378(11)
O(6)-C(6')	1.37(2)
O(6)-C(6)	1.40(2)
O(7)-C(7)	1.388(9)
O(8)-C(8)	1.328(14)
O(9)-C(9)	1.418(8)
O(10)-C(10)	1.418(10)
O(11)-C(11)	1.429(9)
O(12)-C(12)	1.415(9)
C(1)-C(2)	1.494(11)
C(3)-C(4)	1.490(11)
C(5)-C(5A)	1.494(14)
C(5A)-C(5B)	1.439(13)
C(5A)-C(5D)	1.456(14)
C(5A)-C(5C)	1.48(2)
C(6)-C(6A)	1.44(2)
C(6')-C(6A)	1.53(3)
C(6A)-C(6B)	1.40(2)
C(6A)-C(6C)	1.42(2)
C(6A)-C(6D)	1.53(2)
C(7)-C(7A)	1.512(12)
C(7A)-C(7D)	1.486(12)
C(7A)-C(7B)	1.520(12)
C(7A)-C(7C)	1.520(13)
C(8)-C(8A)	1.42(2)
C(8A)-C(8C)	1.43(2)
C(8A)-C(8B)	1.44(2)
C(8A)-C(8D)	1.49(2)
C(9)-C(9A)	1.511(11)
C(9A)-C(9C)	1.507(12)

C(9A)-C(9B)	1.517(11)
C(9A)-C(9D)	1.516(12)
C(10)-C(10A)	1.431(12)
C(10A)-C(10B)	1.487(14)
C(10A)-C(10C)	1.493(13)
C(10A)-C(10D)	1.51(2)
C(11)-C(11A)	1.531(11)
C(11A)-C(11D)	1.516(11)
C(11A)-C(11B)	1.525(12)
C(11A)-C(11C)	1.536(11)
C(12)-C(12A)	1.520(11)
C(12A)-C(12D)	1.514(12)
C(12A)-C(12B)	1.527(12)
C(12A)-C(12C)	1.547(11)

O(5)-Ti(1)-O(6)	98.0(3)
O(5)-Ti(1)-O(13)	168.1(2)
O(6)-Ti(1)-O(13)	91.9(3)
O(5)-Ti(1)-O(1)	96.1(3)
O(6)-Ti(1)-O(1)	91.9(3)
O(13)-Ti(1)-O(1)	90.0(2)
O(5)-Ti(1)-O(11)	97.1(2)
O(6)-Ti(1)-O(11)	100.0(2)
O(13)-Ti(1)-O(11)	74.7(2)
O(1)-Ti(1)-O(11)	160.8(2)
O(5)-Ti(1)-O(4)	86.2(3)
O(6)-Ti(1)-O(4)	172.7(3)
O(13)-Ti(1)-O(4)	84.6(2)
O(1)-Ti(1)-O(4)	81.7(3)
O(11)-Ti(1)-O(4)	85.3(2)
O(5)-Ti(1)-Ti(3)	134.8(2)
O(6)-Ti(1)-Ti(3)	100.6(2)
O(13)-Ti(1)-Ti(3)	35.68(14)
O(1)-Ti(1)-Ti(3)	123.8(2)
O(11)-Ti(1)-Ti(3)	39.25(14)
O(4)-Ti(1)-Ti(3)	80.3(2)
O(8)-Ti(2)-O(7)	97.5(3)
O(8)-Ti(2)-O(13)	95.2(2)
O(7)-Ti(2)-O(13)	165.6(2)
O(8)-Ti(2)-O(2)	91.0(3)
O(7)-Ti(2)-O(2)	97.0(2)
O(13)-Ti(2)-O(2)	89.7(2)
O(8)-Ti(2)-O(12)	100.4(2)
O(7)-Ti(2)-O(12)	96.6(2)
O(13)-Ti(2)-O(12)	74.2(2)
O(2)-Ti(2)-O(12)	160.9(2)
O(8)-Ti(2)-O(3)	173.9(3)
O(7)-Ti(2)-O(3)	84.3(2)
O(13)-Ti(2)-O(3)	83.9(2)
O(2)-Ti(2)-O(3)	83.0(2)
O(12)-Ti(2)-O(3)	85.1(2)
O(8)-Ti(2)-Ti(3)	104.7(2)
O(7)-Ti(2)-Ti(3)	133.1(2)
O(13)-Ti(2)-Ti(3)	35.48(14)
O(2)-Ti(2)-Ti(3)	122.9(2)
O(12)-Ti(2)-Ti(3)	39.3(2)
O(3)-Ti(2)-Ti(3)	78.0(2)

O(10)-Ti(3)-O(9)	110.6(3)
O(10)-Ti(3)-O(13)	109.0(2)
O(9)-Ti(3)-O(13)	140.3(2)
O(10)-Ti(3)-O(11)	102.8(2)
O(9)-Ti(3)-O(11)	93.3(2)
O(13)-Ti(3)-O(11)	78.2(2)
O(10)-Ti(3)-O(12)	103.3(2)
O(9)-Ti(3)-O(12)	93.0(2)
O(13)-Ti(3)-O(12)	77.5(2)
O(11)-Ti(3)-O(12)	148.9(2)
O(10)-Ti(3)-Ti(1)	114.3(2)
O(9)-Ti(3)-Ti(1)	120.2(2)
O(13)-Ti(3)-Ti(1)	38.3(2)
O(11)-Ti(3)-Ti(1)	40.3(2)
O(12)-Ti(3)-Ti(1)	112.1(2)
O(10)-Ti(3)-Ti(2)	116.4(2)
O(9)-Ti(3)-Ti(2)	118.7(2)
O(13)-Ti(3)-Ti(2)	37.7(2)
O(11)-Ti(3)-Ti(2)	111.4(2)
O(12)-Ti(3)-Ti(2)	40.4(2)
Ti(1)-Ti(3)-Ti(2)	72.08(5)
C(1)-O(1)-Ti(1)	138.6(6)
C(1)-O(2)-Ti(2)	139.0(6)
C(3)-O(3)-Ti(2)	136.3(6)
C(3)-O(4)-Ti(1)	135.6(6)
C(5)-O(5)-Ti(1)	165.9(7)
C(6')-O(6)-C(6)	65.6(14)
C(6')-O(6)-Ti(1)	141(2)
C(6)-O(6)-Ti(1)	148.4(10)
C(7)-O(7)-Ti(2)	147.4(6)
C(8)-O(8)-Ti(2)	159.9(9)
C(9)-O(9)-Ti(3)	134.4(5)
C(10)-O(10)-Ti(3)	124.5(6)
C(11)-O(11)-Ti(3)	130.9(5)
C(11)-O(11)-Ti(1)	123.7(5)
Ti(3)-O(11)-Ti(1)	100.5(2)
C(12)-O(12)-Ti(3)	128.9(5)
C(12)-O(12)-Ti(2)	125.3(5)
Ti(3)-O(12)-Ti(2)	100.3(2)
Ti(3)-O(13)-Ti(2)	106.8(2)
Ti(3)-O(13)-Ti(1)	106.0(2)
Ti(2)-O(13)-Ti(1)	132.9(3)
O(1)-C(1)-O(2)	123.5(9)
O(1)-C(1)-C(2)	117.7(9)
O(2)-C(1)-C(2)	118.8(9)
O(4)-C(3)-O(3)	125.6(8)
O(4)-C(3)-C(4)	117.0(9)
O(3)-C(3)-C(4)	117.4(9)
O(5)-C(5)-C(5A)	115.5(10)
C(5B)-C(5A)-C(5D)	110.0(12)
C(5B)-C(5A)-C(5C)	107.8(12)
C(5D)-C(5A)-C(5C)	110.0(11)
C(5B)-C(5A)-C(5)	110.2(10)
C(5D)-C(5A)-C(5)	111.5(10)
C(5C)-C(5A)-C(5)	107.3(10)
O(6)-C(6)-C(6A)	116(2)
O(6)-C(6')-C(6A)	112(2)

C(6B)-C(6A)-C(6C)	106.3(14)
C(6B)-C(6A)-C(6)	99.2(14)
C(6C)-C(6A)-C(6)	127(2)
C(6B)-C(6A)-C(6')	157(2)
C(6C)-C(6A)-C(6')	81.4(13)
C(6)-C(6A)-C(6')	60.6(12)
C(6B)-C(6A)-C(6D)	102.8(13)
C(6C)-C(6A)-C(6D)	110.7(14)
C(6)-C(6A)-C(6D)	107.4(13)
C(6')-C(6A)-C(6D)	94(2)
O(7)-C(7)-C(7A)	115.6(8)
C(7D)-C(7A)-C(7)	109.6(8)
C(7D)-C(7A)-C(7B)	110.3(9)
C(7)-C(7A)-C(7B)	108.2(8)
C(7D)-C(7A)-C(7C)	109.3(9)
C(7)-C(7A)-C(7C)	110.0(8)
C(7B)-C(7A)-C(7C)	109.5(8)
O(8)-C(8)-C(8A)	124(2)
C(8)-C(8A)-C(8C)	111(2)
C(8)-C(8A)-C(8B)	110(2)
C(8C)-C(8A)-C(8B)	107(2)
C(8)-C(8A)-C(8D)	106.0(12)
C(8C)-C(8A)-C(8D)	109.1(14)
C(8B)-C(8A)-C(8D)	114(2)
O(9)-C(9)-C(9A)	114.6(7)
C(9C)-C(9A)-C(9B)	110.2(8)
C(9C)-C(9A)-C(9)	110.4(8)
C(9B)-C(9A)-C(9)	108.3(8)
C(9C)-C(9A)-C(9D)	109.8(9)
C(9B)-C(9A)-C(9D)	109.0(8)
C(9)-C(9A)-C(9D)	109.2(8)
O(10)-C(10)-C(10A)	119.0(9)
C(10)-C(10A)-C(10B)	111.6(10)
C(10)-C(10A)-C(10C)	112.4(10)
C(10B)-C(10A)-C(10C)	112.1(10)
C(10)-C(10A)-C(10D)	107.0(11)
C(10B)-C(10A)-C(10D)	105.2(13)
C(10C)-C(10A)-C(10D)	108.2(11)
O(11)-C(11)-C(11A)	113.8(7)
C(11D)-C(11A)-C(11)	109.9(8)
C(11D)-C(11A)-C(11B)	110.8(8)
C(11)-C(11A)-C(11B)	109.5(8)
C(11D)-C(11A)-C(11C)	109.8(8)
C(11)-C(11A)-C(11C)	107.2(8)
C(11B)-C(11A)-C(11C)	109.4(8)
O(12)-C(12)-C(12A)	115.0(7)
C(12D)-C(12A)-C(12)	111.0(8)
C(12D)-C(12A)-C(12B)	110.4(9)
C(12)-C(12A)-C(12B)	109.8(8)
C(12D)-C(12A)-C(12C)	110.3(8)
C(12)-C(12A)-C(12C)	107.7(8)
C(12B)-C(12A)-C(12C)	107.6(8)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 3

	U11	U22	U33	U23	U13	U12
Ti(1)	40(1)	36(1)	65(1)	3(1)	19(1)	-1(1)
Ti(2)	36(1)	37(1)	56(1)	-4(1)	13(1)	1(1)
Ti(3)	36(1)	34(1)	39(1)	2(1)	11(1)	0(1)
O(1)	36(4)	39(4)	121(6)	-11(4)	30(4)	-8(4)
O(2)	41(4)	41(4)	81(5)	-7(3)	23(3)	-2(3)
O(3)	69(5)	43(4)	50(4)	5(3)	4(4)	-3(4)
O(4)	67(5)	46(4)	57(4)	-6(3)	-4(4)	7(4)
O(5)	48(4)	37(4)	92(5)	-14(4)	14(4)	-12(3)
O(6)	73(5)	35(4)	85(5)	28(4)	49(4)	6(3)
O(7)	44(4)	35(3)	67(4)	1(3)	10(3)	6(3)
O(8)	66(5)	63(4)	40(4)	-14(3)	26(3)	-8(4)
O(9)	45(4)	39(3)	41(4)	7(3)	16(3)	-2(3)
O(10)	47(4)	46(4)	35(3)	3(3)	7(3)	4(3)
O(11)	43(4)	30(3)	47(3)	-6(3)	22(3)	0(3)
O(12)	37(4)	27(3)	54(4)	1(3)	14(3)	-4(3)
O(13)	32(3)	42(3)	34(3)	-1(3)	15(3)	1(3)
C(1)	53(7)	43(7)	43(6)	-2(5)	12(5)	-3(7)
C(2)	30(6)	57(7)	111(9)	6(6)	27(6)	-5(6)
C(3)	37(6)	59(8)	43(7)	6(6)	14(5)	15(6)
C(4)	91(9)	101(9)	51(7)	3(6)	-17(6)	15(7)
C(5)	77(11)	138(12)	158(13)	-64(10)	30(9)	-27(9)
C(5A)	40(7)	68(7)	81(8)	10(6)	0(6)	-14(6)
C(5B)	142(15)	238(19)	148(14)	30(13)	67(12)	-88(13)
C(5C)	127(15)	147(15)	232(19)	32(13)	-70(13)	-5(12)
C(5D)	112(13)	214(18)	231(17)	-168(16)	-12(12)	-18(12)
C(6)	124(18)	146(23)	110(16)	-30(15)	80(14)	-33(15)
C(6')	70(26)	82(31)	36(22)	-8(18)	24(18)	-44(21)
C(6A)	106(11)	54(7)	82(8)	0(6)	62(8)	-10(7)
C(6B)	199(23)	109(15)	462(36)	53(19)	57(22)	8(14)
C(6C)	447(40)	200(20)	145(16)	-95(15)	-59(20)	-39(22)
C(6D)	160(19)	341(28)	202(18)	99(18)	134(16)	94(19)
C(7)	52(8)	52(7)	88(8)	11(6)	17(6)	5(6)
C(7A)	46(7)	52(7)	74(7)	-2(6)	10(6)	16(6)
C(7B)	59(8)	84(8)	121(9)	33(8)	12(7)	21(7)
C(7C)	55(8)	101(10)	134(11)	3(8)	5(8)	-10(7)
C(7D)	104(11)	120(11)	105(10)	-15(8)	22(8)	53(8)
C(8)	158(17)	259(22)	127(14)	-13(15)	63(13)	-12(15)
C(8A)	133(14)	144(13)	72(9)	-43(9)	74(10)	-34(11)
C(8B)	312(33)	115(16)	412(36)	-99(19)	81(25)	-50(18)
C(8C)	391(38)	434(39)	102(15)	10(18)	74(18)	-162(29)
C(8D)	80(13)	507(39)	193(18)	-156(21)	80(12)	-85(18)
C(9)	50(7)	54(6)	52(6)	3(5)	14(6)	-5(5)
C(9A)	63(8)	72(7)	50(7)	4(6)	34(6)	-12(7)
C(9B)	97(10)	145(11)	51(7)	31(7)	26(7)	-22(8)
C(9C)	66(8)	85(8)	106(9)	27(7)	45(7)	-7(7)
C(9D)	94(9)	88(9)	80(8)	4(6)	59(7)	4(8)
C(10)	66(9)	155(12)	74(9)	35(8)	-1(8)	-15(8)
C(10A)	61(8)	108(10)	45(7)	17(6)	3(7)	-11(8)
C(10B)	172(16)	219(18)	85(10)	33(10)	-12(10)	-124(15)

C(10C)	96(11)	268(19)	71(9)	46(10)	6(8)	-40(12)
C(10D)	285(25)	247(22)	106(12)	7(13)	21(13)	171(20)
C(11)	59(7)	58(6)	51(6)	-2(5)	18(6)	-10(6)
C(11A)	41(7)	48(6)	80(7)	-9(6)	18(6)	-1(6)
C(11B)	56(8)	63(7)	107(9)	-6(6)	23(7)	12(6)
C(11C)	82(9)	72(8)	127(10)	-32(7)	42(8)	6(7)
C(11D)	83(9)	55(7)	92(8)	23(6)	34(7)	27(6)
C(12)	45(7)	33(5)	74(7)	6(5)	16(6)	0(5)
C(12A)	49(7)	29(6)	83(8)	3(5)	3(6)	-6(5)
C(12B)	65(9)	66(8)	150(11)	25(7)	-20(8)	-15(7)
C(12C)	64(8)	45(6)	119(9)	-2(6)	16(7)	-13(6)
C(12D)	112(10)	59(7)	90(8)	-29(6)	37(8)	-33(7)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U11 + \ldots + 2hka^*b^*U12]$

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 3

	x	y	z	U(eq)
H(2A)	5824(7)	882(4)	2618(4)	97
H(2B)	6019(7)	1379(4)	3074(4)	97
H(2C)	5671(7)	1462(4)	2334(4)	97
H(4A)	3193(10)	565(4)	4735(4)	127
H(4B)	2609(10)	1101(4)	4916(4)	127
H(4C)	3954(10)	1097(4)	4773(4)	127
H(5A)	2688(11)	2794(5)	4187(6)	148
H(5B)	2439(11)	3234(5)	3657(6)	148
H(5B1)	4469(13)	2914(6)	3041(6)	256
H(5B2)	5521(13)	3270(6)	3429(6)	256
H(5B3)	4215(13)	3517(6)	3168(6)	256
H(5C1)	4706(14)	2465(6)	4571(7)	273
H(5C2)	5821(14)	2647(6)	4262(7)	273
H(5C3)	4776(14)	2287(6)	3875(7)	273
H(5D1)	4244(13)	3391(6)	4771(7)	287
H(5D2)	4080(13)	3806(6)	4211(7)	287
H(5D3)	5386(13)	3561(6)	4477(7)	287
H(6A)	2383(18)	2918(9)	1975(9)	143
H(6B)	1033(18)	2820(9)	1606(9)	143
H(6'1)	979(30)	1993(14)	1276(9)	73
H(6'2)	2325(30)	1775(14)	1506(9)	73
H(6B1)	2824(18)	3286(7)	1292(11)	386
H(6B2)	1619(18)	3211(7)	775(11)	386
H(6B3)	2911(18)	3069(7)	613(11)	386
H(6C1)	1611(22)	1884(7)	737(8)	419
H(6C2)	2208(22)	2258(7)	290(8)	419
H(6C3)	917(22)	2402(7)	452(8)	419
H(6D1)	3684(16)	2006(8)	1517(8)	332
H(6D2)	4075(16)	2599(8)	1690(8)	332
H(6D3)	4065(16)	2382(8)	999(8)	332
H(7A)	2081(9)	-841(4)	3252(5)	76
H(7B)	2544(9)	-379(4)	3731(5)	76
H(7B1)	3955(9)	-1041(4)	4328(5)	134
H(7B2)	4920(9)	-1338(4)	3999(5)	134
H(7B3)	3508(9)	-1473(4)	3802(5)	134
H(7C1)	4747(10)	-170(4)	4035(5)	148
H(7C2)	4785(10)	-41(4)	3320(5)	148
H(7C3)	5709(10)	-459(4)	3696(5)	148
H(7D1)	5005(11)	-1128(5)	2872(5)	164
H(7D2)	4073(11)	-714(5)	2493(5)	164
H(7D3)	3597(11)	-1272(5)	2679(5)	164
H(8A)	1987(16)	885(7)	1167(7)	212
H(8B)	891(16)	494(7)	951(7)	212
H(8B1)	2629(22)	-538(7)	574(11)	417
H(8B2)	1274(22)	-379(7)	627(11)	417
H(8B3)	2271(22)	-475(7)	1247(11)	417
H(8C1)	2758(22)	192(10)	-54(8)	458
H(8C2)	2470(22)	768(10)	168(8)	458

H(8C3)	1400(22)	349(10)	-8(8)	458
H(8D1)	4319(14)	134(9)	902(8)	379
H(8D2)	3926(14)	209(9)	1565(8)	379
H(8D3)	3944(14)	702(9)	1112(8)	379
H(9A)	124(8)	1286(3)	4343(4)	62
H(9B)	11(8)	671(3)	4207(4)	62
H(9B1)	-168(10)	1131(5)	5418(4)	144
H(9B2)	-300(10)	515(5)	5287(4)	144
H(9B3)	-1333(10)	824(5)	5552(4)	144
H(9C1)	-2727(9)	593(4)	3940(5)	123
H(9C2)	-2907(9)	493(4)	4641(5)	123
H(9C3)	-1873(9)	185(4)	4376(5)	123
H(9D1)	-1512(10)	1768(4)	4736(4)	123
H(9D2)	-2688(10)	1464(4)	4861(4)	123
H(9D3)	-2506(10)	1563(4)	4160(4)	123
H(10A)	-794(10)	1117(5)	1404(5)	120
H(10B)	-681(10)	1729(5)	1544(5)	120
H(10C)	-3893(14)	1174(6)	633(5)	245
H(10D)	-3512(14)	1079(6)	1370(5)	245
H(10E)	-2857(14)	758(6)	898(5)	245
H(10F)	-2593(11)	1677(6)	66(5)	220
H(10G)	-1447(11)	1303(6)	281(5)	220
H(10H)	-1336(11)	1918(6)	424(5)	220
H(10I)	-3592(18)	2105(7)	857(6)	322
H(10J)	-2318(18)	2319(7)	1228(6)	322
H(10K)	-3163(18)	1974(7)	1584(6)	322
H(11A)	621(9)	2485(3)	3784(4)	66
H(11B)	-495(9)	2108(3)	3830(4)	66
H(11C)	-2565(9)	2307(4)	3275(5)	111
H(11D)	-2138(9)	2231(4)	2621(5)	111
H(11E)	-2820(9)	2757(4)	2755(5)	111
H(11F)	-1507(10)	2959(4)	4070(5)	136
H(11G)	-1736(10)	3419(4)	3562(5)	136
H(11H)	-390(10)	3296(4)	3928(5)	136
H(11I)	-1046(10)	3295(4)	2510(4)	112
H(11J)	-339(10)	2773(4)	2389(4)	112
H(11K)	296(10)	3192(4)	2893(4)	112
H(12A)	-825(8)	117(3)	3338(4)	60
H(12B)	267(8)	-239(3)	3203(4)	60
H(12C)	-2835(10)	93(4)	2661(5)	148
H(12D)	-3063(10)	-213(4)	2008(5)	148
H(12E)	-2287(10)	317(4)	2087(5)	148
H(12F)	-2018(9)	-729(3)	3217(5)	114
H(12G)	-928(9)	-1043(3)	3008(5)	114
H(12H)	-2241(9)	-1039(3)	2567(5)	114
H(12I)	-1310(11)	-681(4)	1657(5)	128
H(12J)	0(11)	-692(4)	2101(5)	128
H(12K)	-499(11)	-162(4)	1753(5)	128

Table S4.1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{54}H_{108}O_{24}Ti_6$	
Formula weight	714.40	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P(-1)	
Unit cell dimensions	a = 11.7931(8) Å	α= 105.823(1)°.
	b = 13.431(1) Å	β= 109.011(2)°.
	c = 13.9079(9) Å	γ = 103.632(1)°.
Volume	1872.0(2) $Å^3$	
Z	1	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.675 mm^{-1}	
F(000)	756	
Crystal size	0.12 x 0.16 x 0.23 mm^3	
Theta range for data collection	1.7 to 26.8°.	
Index ranges	-14<=h<=13, -16<=k<=16, 0<=l<=17	
Reflections collected	9235	
Independent reflections	6747 [R(int) = 0.032]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6747 / 0 / 379	
Goodness-of-fit on F^2	1.962	
Final R indices [I>2sigma(I)]	R1* = 0.1277, wR2 = 0.2601	
R indices (all data)	R1 = 0.1863, wR2 = 0.2762	
Largest diff. peak and hole	2.621 and -0.532 $e.Å^{-3}$	

Table S4.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å2x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	1683(1)	1068(1)	4789(1)	62(1)
Ti(2)	-1235(1)	297(1)	3504(1)	61(1)
Ti(3)	475(2)	-1440(1)	4042(1)	61(1)
O(1)	1549(6)	1776(5)	3664(5)	74(2)
O(2)	2797(5)	514(5)	4063(5)	76(2)
O(3)	1748(4)	39(4)	5461(4)	48(1)
O(4)	352(4)	1473(3)	4999(4)	48(1)
O(5)	2992(5)	2225(5)	5900(5)	73(2)
O(6)	57(4)	-348(4)	3572(3)	46(1)
O(7)	-524(6)	1138(5)	2672(5)	72(2)
O(8)	-2113(6)	1410(5)	3515(5)	78(2)
O(9)	-2467(5)	-816(5)	2276(5)	73(2)
O(10)	1476(6)	-2323(5)	4748(6)	81(2)
O(11)	1865(6)	-1300(5)	3463(5)	75(2)
O(12)	-679(5)	-2646(4)	2888(4)	57(1)
C(1)	589(11)	1661(8)	2865(8)	70(2)
C(2)	794(12)	2227(12)	2095(11)	121(5)
C(3)	1880(30)	3094(19)	2484(17)	310(16)
C(4)	-180(20)	1850(20)	1088(16)	380(20)
C(5)	2638(9)	-464(8)	3546(8)	69(2)
C(6)	3488(10)	-619(9)	2931(9)	88(3)
C(7)	4748(15)	230(16)	3479(16)	252(13)
C(8)	2775(18)	-800(20)	1830(13)	307(18)
C(9)	4017(16)	2695(13)	6652(16)	191(8)
C(10)	4986(10)	3697(8)	6658(10)	89(3)
C(11)	5140(20)	3473(19)	5716(19)	370(20)
C(12)	4445(19)	4513(14)	6860(30)	310(18)
C(13)	6190(30)	4120(20)	7730(20)	360(20)
C(14)	-2747(13)	-1609(13)	1418(13)	164(7)
C(15)	-3775(11)	-1660(10)	343(8)	96(3)
C(16)	-4982(14)	-1950(18)	532(12)	228(11)
C(17)	-3451(18)	-627(18)	180(13)	267(14)

C(18)	-4020(20)	-2708(18)	-587(14)	262(13)
C(19)	-1353(11)	-3780(8)	2331(9)	102(4)
C(20)	-1031(10)	-4329(7)	1450(9)	85(3)
C(21)	-1093(14)	-3766(10)	642(10)	125(5)
C(22)	397(15)	-4295(11)	2082(12)	161(6)
C(23)	-1884(15)	-5509(9)	817(12)	169(7)
C(24)	1998(9)	-2159(9)	5704(8)	76(3)
C(25)	2595(11)	-3035(9)	5973(10)	93(3)
C(26)	1820(20)	-4106(13)	5160(20)	350(20)
C(27)	2930(30)	-2990(20)	6964(13)	340(20)

Table S4.3. Bond lengths [Å] and angles [°] for **4**.

Ti(1)-O(5)	1.786(6)
Ti(1)-O(4)	1.860(5)
Ti(1)-O(3)	1.870(5)
Ti(1)-O(1)	2.025(6)
Ti(1)-O(2)	2.053(6)
Ti(1)-O(6)	2.138(5)
Ti(1)-Ti(3)	3.052(2)
Ti(1)-Ti(2)	3.068(2)
Ti(2)-O(9)	1.797(6)
Ti(2)-O(3)#1	1.853(5)
Ti(2)-O(6)	1.911(5)
Ti(2)-O(8)	2.009(6)
Ti(2)-O(7)	2.053(6)
Ti(2)-O(4)	2.145(5)
Ti(2)-Ti(3)#1	3.052(2)
Ti(3)-O(12)	1.781(5)
Ti(3)-O(6)	1.863(5)
Ti(3)-O(4)#1	1.895(5)
Ti(3)-O(11)	2.043(6)
Ti(3)-O(10)	2.075(6)
Ti(3)-O(3)	2.149(5)
Ti(3)-Ti(2)#1	3.052(2)
O(1)-C(1)	1.243(11)
O(2)-C(5)	1.248(10)
O(3)-Ti(2)#1	1.853(5)
O(4)-Ti(3)#1	1.895(5)
O(5)-C(9)	1.188(16)
O(7)-C(1)	1.234(10)
O(8)-C(24)#1	1.206(10)
O(9)-C(14)	1.246(15)
O(10)-C(24)	1.198(10)
O(11)-C(5)	1.219(10)
O(12)-C(19)	1.392(10)
C(1)-C(2)	1.519(13)
C(2)-C(3)	1.34(2)

C(2)-C(4)	1.354(19)
C(5)-C(6)	1.529(13)
C(6)-C(8)	1.404(16)
C(6)-C(7)	1.442(16)
C(9)-C(10)	1.543(16)
C(10)-C(11)	1.346(19)
C(10)-C(12)	1.40(2)
C(10)-C(13)	1.53(2)
C(14)-C(15)	1.560(16)
C(15)-C(17)	1.450(19)
C(15)-C(16)	1.511(17)
C(15)-C(18)	1.520(18)
C(19)-C(20)	1.461(12)
C(20)-C(23)	1.486(13)
C(20)-C(21)	1.509(14)
C(20)-C(22)	1.609(16)
C(24)-O(8)#1	1.206(10)
C(24)-C(25)	1.574(14)
C(25)-C(27)	1.282(16)
C(25)-C(26)	1.41(2)

O(5)-Ti(1)-O(4)	97.9(3)
O(5)-Ti(1)-O(3)	97.5(2)
O(4)-Ti(1)-O(3)	101.3(2)
O(5)-Ti(1)-O(1)	95.4(3)
O(4)-Ti(1)-O(1)	89.2(2)
O(3)-Ti(1)-O(1)	162.1(2)
O(5)-Ti(1)-O(2)	94.9(3)
O(4)-Ti(1)-O(2)	162.3(2)
O(3)-Ti(1)-O(2)	89.1(2)
O(1)-Ti(1)-O(2)	77.4(3)
O(5)-Ti(1)-O(6)	174.6(2)
O(4)-Ti(1)-O(6)	79.26(19)
O(3)-Ti(1)-O(6)	78.73(19)
O(1)-Ti(1)-O(6)	89.1(2)
O(2)-Ti(1)-O(6)	88.9(2)
O(5)-Ti(1)-Ti(3)	140.3(2)

O(4)-Ti(1)-Ti(3)	99.53(14)
O(3)-Ti(1)-Ti(3)	44.14(14)
O(1)-Ti(1)-Ti(3)	120.16(19)
O(2)-Ti(1)-Ti(3)	77.90(18)
O(6)-Ti(1)-Ti(3)	37.05(13)
O(5)-Ti(1)-Ti(2)	140.4(2)
O(4)-Ti(1)-Ti(2)	43.58(14)
O(3)-Ti(1)-Ti(2)	99.27(15)
O(1)-Ti(1)-Ti(2)	78.25(18)
O(2)-Ti(1)-Ti(2)	120.97(18)
O(6)-Ti(1)-Ti(2)	38.05(13)
Ti(3)-Ti(1)-Ti(2)	69.76(5)
O(9)-Ti(2)-O(3)#1	99.5(2)
O(9)-Ti(2)-O(6)	95.3(3)
O(3)#1-Ti(2)-O(6)	101.4(2)
O(9)-Ti(2)-O(8)	97.6(3)
O(3)#1-Ti(2)-O(8)	90.3(2)
O(6)-Ti(2)-O(8)	161.0(2)
O(9)-Ti(2)-O(7)	94.3(3)
O(3)#1-Ti(2)-O(7)	163.0(2)
O(6)-Ti(2)-O(7)	87.1(2)
O(8)-Ti(2)-O(7)	78.0(3)
O(9)-Ti(2)-O(4)	172.7(3)
O(3)#1-Ti(2)-O(4)	79.26(19)
O(6)-Ti(2)-O(4)	77.98(19)
O(8)-Ti(2)-O(4)	89.7(2)
O(7)-Ti(2)-O(4)	88.2(2)
O(9)-Ti(2)-Ti(3)#1	142.72(19)
O(3)#1-Ti(2)-Ti(3)#1	44.06(14)
O(6)-Ti(2)-Ti(3)#1	99.50(14)
O(8)-Ti(2)-Ti(3)#1	78.4(2)
O(7)-Ti(2)-Ti(3)#1	120.34(18)
O(4)-Ti(2)-Ti(3)#1	37.96(12)
O(9)-Ti(2)-Ti(1)	137.5(2)
O(3)#1-Ti(2)-Ti(1)	99.20(15)
O(6)-Ti(2)-Ti(1)	43.59(14)
O(8)-Ti(2)-Ti(1)	120.13(19)

O(7)-Ti(2)-Ti(1)	76.69(17)
O(4)-Ti(2)-Ti(1)	36.69(13)
Ti(3)#1-Ti(2)-Ti(1)	69.66(5)
O(12)-Ti(3)-O(6)	99.9(2)
O(12)-Ti(3)-O(4)#1	98.1(2)
O(6)-Ti(3)-O(4)#1	100.8(2)
O(12)-Ti(3)-O(11)	95.2(2)
O(6)-Ti(3)-O(11)	89.7(2)
O(4)#1-Ti(3)-O(11)	161.4(2)
O(12)-Ti(3)-O(10)	93.5(3)
O(6)-Ti(3)-O(10)	163.3(2)
O(4)#1-Ti(3)-O(10)	87.1(2)
O(11)-Ti(3)-O(10)	79.1(3)
O(12)-Ti(3)-O(3)	175.6(2)
O(6)-Ti(3)-O(3)	78.58(19)
O(4)#1-Ti(3)-O(3)	78.26(18)
O(11)-Ti(3)-O(3)	88.9(2)
O(10)-Ti(3)-O(3)	88.8(2)
O(12)-Ti(3)-Ti(2)#1	140.41(17)
O(6)-Ti(3)-Ti(2)#1	99.17(14)
O(4)#1-Ti(3)-Ti(2)#1	44.14(14)
O(11)-Ti(3)-Ti(2)#1	119.31(18)
O(10)-Ti(3)-Ti(2)#1	76.23(19)
O(3)-Ti(3)-Ti(2)#1	36.83(12)
O(12)-Ti(3)-Ti(1)	142.30(18)
O(6)-Ti(3)-Ti(1)	43.75(14)
O(4)#1-Ti(3)-Ti(1)	98.63(14)
O(11)-Ti(3)-Ti(1)	78.25(18)
O(10)-Ti(3)-Ti(1)	120.88(19)
O(3)-Ti(3)-Ti(1)	37.29(13)
Ti(2)#1-Ti(3)-Ti(1)	69.17(5)
C(1)-O(1)-Ti(1)	129.7(6)
C(5)-O(2)-Ti(1)	127.8(6)
Ti(2)#1-O(3)-Ti(1)	137.1(3)
Ti(2)#1-O(3)-Ti(3)	99.1(2)
Ti(1)-O(3)-Ti(3)	98.6(2)
Ti(1)-O(4)-Ti(3)#1	137.1(3)

Ti(1)-O(4)-Ti(2)	99.7(2)
Ti(3)#1-O(4)-Ti(2)	97.9(2)
C(9)-O(5)-Ti(1)	156.6(10)
Ti(3)-O(6)-Ti(2)	136.0(3)
Ti(3)-O(6)-Ti(1)	99.2(2)
Ti(2)-O(6)-Ti(1)	98.4(2)
C(1)-O(7)-Ti(2)	130.9(6)
C(24)#1-O(8)-Ti(2)	128.2(7)
C(14)-O(9)-Ti(2)	147.9(8)
C(24)-O(10)-Ti(3)	128.4(7)
C(5)-O(11)-Ti(3)	128.7(6)
C(19)-O(12)-Ti(3)	154.3(7)
O(7)-C(1)-O(1)	124.0(8)
O(7)-C(1)-C(2)	117.8(10)
O(1)-C(1)-C(2)	118.1(9)
C(3)-C(2)-C(4)	125.2(14)
C(3)-C(2)-C(1)	117.9(13)
C(4)-C(2)-C(1)	116.7(11)
O(11)-C(5)-O(2)	127.0(9)
O(11)-C(5)-C(6)	116.9(9)
O(2)-C(5)-C(6)	116.1(8)
C(8)-C(6)-C(7)	116.7(16)
C(8)-C(6)-C(5)	107.8(10)
C(7)-C(6)-C(5)	113.4(10)
O(5)-C(9)-C(10)	119.7(15)
C(11)-C(10)-C(12)	115(2)
C(11)-C(10)-C(13)	117(2)
C(12)-C(10)-C(13)	102.3(19)
C(11)-C(10)-C(9)	112.3(13)
C(12)-C(10)-C(9)	101.8(13)
C(13)-C(10)-C(9)	106.9(15)
O(9)-C(14)-C(15)	116.2(12)
C(17)-C(15)-C(16)	114.4(16)
C(17)-C(15)-C(18)	117.2(16)
C(16)-C(15)-C(18)	102.2(14)
C(17)-C(15)-C(14)	111.8(11)
C(16)-C(15)-C(14)	101.8(12)

C(18)-C(15)-C(14)	107.9(12)
O(12)-C(19)-C(20)	115.7(8)
C(19)-C(20)-C(23)	112.6(10)
C(19)-C(20)-C(21)	112.6(9)
C(23)-C(20)-C(21)	107.6(10)
C(19)-C(20)-C(22)	104.1(9)
C(23)-C(20)-C(22)	108.0(10)
C(21)-C(20)-C(22)	111.9(11)
O(10)-C(24)-O(8)#1	128.0(11)
O(10)-C(24)-C(25)	116.1(10)
O(8)#1-C(24)-C(25)	115.9(9)
C(27)-C(25)-C(26)	114.4(17)
C(27)-C(25)-C(24)	116.1(11)
C(26)-C(25)-C(24)	110.2(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table S4.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Ti(1)	56(1)	66(1)	61(1)	29(1)	28(1)	6(1)
Ti(2)	59(1)	68(1)	48(1)	26(1)	18(1)	11(1)
Ti(3)	68(1)	52(1)	56(1)	12(1)	28(1)	16(1)
O(1)	68(4)	86(4)	72(4)	46(4)	33(4)	11(3)
O(2)	62(4)	79(5)	84(4)	25(4)	43(3)	12(3)
O(3)	42(3)	50(3)	49(3)	16(2)	21(2)	8(2)
O(4)	55(3)	36(3)	41(3)	10(2)	23(2)	0(2)
O(5)	42(3)	68(4)	70(4)	18(3)	-2(3)	-3(3)
O(6)	60(3)	42(3)	34(3)	11(2)	25(2)	11(2)
O(7)	70(4)	90(4)	64(4)	46(3)	31(3)	20(3)
O(8)	81(5)	74(4)	71(4)	23(4)	24(4)	29(3)
O(9)	65(4)	78(4)	39(3)	3(3)	12(3)	1(3)
O(10)	83(5)	73(4)	82(5)	22(4)	31(4)	32(3)
O(11)	69(4)	72(4)	71(4)	9(3)	36(3)	16(3)
O(12)	70(4)	35(3)	49(3)	-2(2)	28(3)	9(2)
C(1)	87(8)	77(6)	64(6)	35(5)	46(6)	28(6)
C(2)	114(10)	140(11)	109(10)	90(9)	44(8)	-2(8)
C(3)	450(40)	220(20)	158(18)	134(18)	60(20)	-20(20)
C(4)	280(30)	480(40)	146(16)	210(20)	-22(18)	-170(30)
C(5)	62(6)	57(6)	67(6)	18(5)	17(5)	5(5)
C(6)	80(7)	120(9)	89(7)	38(7)	63(7)	42(6)
C(7)	112(12)	270(20)	230(20)	-65(17)	112(14)	-48(13)
C(8)	178(18)	700(60)	116(14)	160(20)	98(14)	220(30)
C(9)	168(17)	121(12)	220(20)	75(13)	37(15)	-8(12)
C(10)	68(7)	54(6)	114(9)	18(6)	34(7)	-8(5)
C(11)	290(30)	330(30)	270(30)	-90(20)	230(20)	-190(20)
C(12)	153(17)	106(14)	580(50)	50(20)	160(30)	-12(13)
C(13)	270(30)	300(30)	300(30)	150(30)	-100(30)	-30(20)
C(14)	103(11)	149(13)	150(14)	4(11)	-7(10)	39(9)
C(15)	83(8)	105(9)	54(6)	19(6)	-3(6)	14(6)
C(16)	88(11)	370(30)	101(11)	35(15)	-6(9)	-5(14)
C(17)	240(20)	270(20)	127(14)	112(16)	-35(13)	-81(18)

C(18)	250(20)	280(20)	115(13)	-51(15)	-12(14)	140(20)
C(19)	125(10)	76(7)	97(8)	9(6)	65(8)	25(6)
C(20)	100(8)	46(5)	85(7)	-4(5)	39(6)	17(5)
C(21)	205(14)	100(9)	101(9)	37(8)	96(10)	64(9)
C(22)	162(14)	129(12)	159(13)	-5(10)	54(12)	85(10)
C(23)	225(17)	50(7)	143(13)	-12(8)	56(12)	-11(8)
C(24)	66(6)	87(7)	44(5)	13(5)	19(5)	0(5)
C(25)	113(9)	72(7)	115(9)	52(7)	48(7)	50(7)
C(26)	330(30)	92(13)	380(40)	99(18)	-130(30)	34(15)
C(27)	730(60)	340(30)	105(12)	128(17)	150(20)	440(40)

Table S4.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4**.

	x	y	z	U(eq)
H(2)	1188	1716	1817	146
H(3A)	2492	3101	3143	465
H(3B)	1704	3767	2644	465
H(3C)	2227	3034	1943	465
H(4A)	-757	1133	936	563
H(4B)	155	1802	542	563
H(4C)	-641	2356	1072	563
H(6)	3621	-1313	2926	106
H(7A)	5158	263	4213	378
H(7B)	4672	932	3508	378
H(7C)	5253	59	3082	378
H(8A)	1973	-1403	1541	460
H(8B)	3250	-988	1407	460
H(8C)	2614	-145	1788	460
H(9A)	4427	2154	6714	229
H(9B)	3879	2944	7314	229
H(11A)	5537	2923	5648	560
H(11B)	5684	4136	5725	560
H(11C)	4323	3199	5104	560
H(12A)	4390	4637	7559	465
H(12B)	3601	4270	6291	465
H(12C)	4974	5189	6885	465
H(13A)	5964	4279	8341	546
H(13B)	6795	4777	7789	546
H(13C)	6570	3558	7725	546
H(14A)	-3054	-2291	1523	197
H(14B)	-1969	-1584	1313	197
H(16A)	-5135	-2643	629	342
H(16B)	-5697	-2012	-92	342
H(16C)	-4881	-1379	1178	342
H(17A)	-4117	-681	-474	401

H(17B)	-2653	-481	106	401
H(17C)	-3368	-35	801	401
H(18A)	-4232	-3334	-386	393
H(18B)	-3267	-2648	-724	393
H(18C)	-4725	-2805	-1240	393
H(19A)	-2263	-3903	2021	122
H(19B)	-1204	-4132	2861	122
H(21A)	-811	-4121	114	187
H(21B)	-547	-3000	1028	187
H(21C)	-1961	-3818	270	187
H(22A)	698	-4620	1555	241
H(22B)	387	-4705	2549	241
H(22C)	960	-3540	2521	241
H(23A)	-1610	-5842	272	253
H(23B)	-2751	-5551	463	253
H(23C)	-1841	-5896	1308	253
H(25)	3397	-2852	5881	111
H(26A)	1539	-4061	4447	522
H(26B)	1092	-4400	5295	522
H(26C)	2316	-4581	5184	522
H(27A)	3469	-2243	7465	512
H(27B)	3388	-3479	7070	512
H(27C)	2176	-3204	7098	512

Table S5.1. Crystal data and structure refinement for **5**

Empirical formula	$C_{40}H_{84}O_{10}Ti_2$
Formula weight	820.87
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P(-1)
Unit cell dimensions	a = 10.1515(6)Å α = 75.453(1)°
	b = 11.5415(7)Å β = 69.296(1)°
	c = 11.5495(7)Å γ = 87.026(1)°
Volume, Z	1224.2(1) $Å^3$, 1
Density (calculated)	1.113 Mg/m^3
Absorption coefficient	0.372 mm^{-1}
Absorption correction	empirical (SADABS; Sheldrick, 1997)
Tmax./Tmin.	0.94/0.92
F(000)	448
Crystal size	0.16 x 0.21 x 0.29 mm
Theta range for data collection	2.0° to 26.4°
Limiting indices	-11<=h<=12, -13<=k<=13, 0<=l<=14
Reflections collected	6389
Independent reflections	4597 [R(int) = 0.0134]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4597 / 0 / 235
Goodness-of-fit	1.479 (on F^2)
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1280
R indices (all data)	R1 = 0.0511, wR2 = 0.1318
Largest diff. peak and hole	0.747 and -0.438 $eÅ^{-3}$

Table S5.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **5**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ti(1)	4226(1)	6193(1)	9852(1)	25(1)
O(1)	4113(2)	7431(1)	10553(1)	36(1)
O(2)	3153(1)	6808(1)	8924(1)	36(1)
O(3)	2822(1)	5141(1)	11496(1)	29(1)
O(4)	6061(1)	6595(1)	8283(1)	30(1)
O(5)	4345(1)	4604(1)	9358(1)	27(1)
C(1)	3654(2)	8548(2)	10794(2)	41(1)
C(2)	2393(2)	8457(2)	12033(2)	42(1)
C(3)	2086(4)	9728(3)	12172(4)	82(1)
C(4)	2751(4)	7726(4)	13159(3)	80(1)
C(5)	1114(3)	7891(3)	11973(3)	64(1)
C(6)	2332(2)	7686(2)	8446(2)	46(1)
C(7)	3151(3)	8499(2)	7137(2)	51(1)
C(8)	4301(3)	9223(3)	7229(3)	65(1)
C(9)	2105(4)	9349(4)	6718(4)	100(1)
C(10)	3808(4)	7748(3)	6175(3)	81(1)
C(11)	2909(2)	4066(2)	12063(2)	28(1)
C(12)	1692(2)	3535(2)	13309(2)	33(1)
C(13)	1650(5)	2224(3)	13647(5)	156(3)
C(14)	1943(5)	3981(5)	14338(3)	123(2)
C(15)	313(3)	4038(5)	13224(4)	122(2)
C(16)	4205(2)	4440(2)	8216(2)	33(1)
C(17)	2848(2)	3735(2)	8456(2)	42(1)
C(18)	1551(3)	4371(3)	9100(3)	56(1)
C(19)	2869(4)	3710(3)	7127(3)	75(1)
C(20)	2811(3)	2473(3)	9267(3)	65(1)

Table S5.3. Bond lengths [Å] and angles [°] for **5**.

Ti(1)-O(2)	1.7897(14)
Ti(1)-O(1)	1.7918(14)
Ti(1)-O(5)	2.0387(14)
Ti(1)-O(5)#1	2.0393(13)
Ti(1)-O(3)	2.0541(14)
Ti(1)-O(4)	2.0612(13)
Ti(1)-Ti(1)#1	3.1026(7)
O(1)-C(1)	1.408(3)
O(2)-C(6)	1.408(2)
O(3)-C(11)	1.264(2)
O(4)-C(11)#1	1.269(2)
O(5)-C(16)	1.434(2)
O(5)-Ti(1)#1	2.0393(13)
C(1)-C(2)	1.529(3)
C(2)-C(4)	1.512(4)
C(2)-C(5)	1.514(4)
C(2)-C(3)	1.519(3)
C(6)-C(7)	1.528(3)
C(7)-C(8)	1.519(4)
C(7)-C(10)	1.526(4)
C(7)-C(9)	1.530(4)
C(11)-O(4)#1	1.269(2)
C(11)-C(12)	1.533(3)
C(12)-C(13)	1.464(4)
C(12)-C(14)	1.508(4)
C(12)-C(15)	1.514(4)
C(16)-C(17)	1.539(3)
C(17)-C(20)	1.515(4)
C(17)-C(18)	1.519(4)
C(17)-C(19)	1.535(3)
O(2)-Ti(1)-O(1)	95.76(7)
O(2)-Ti(1)-O(5)	92.34(6)
O(1)-Ti(1)-O(5)	169.93(6)
O(2)-Ti(1)-O(5)#1	170.24(6)
O(1)-Ti(1)-O(5)#1	91.73(6)
O(5)-Ti(1)-O(5)#1	80.93(5)

O(2)-Ti(1)-O(3)	103.42(6)
O(1)-Ti(1)-O(3)	92.82(6)
O(5)-Ti(1)-O(3)	79.45(5)
O(5)#1-Ti(1)-O(3)	82.40(5)
O(2)-Ti(1)-O(4)	92.66(6)
O(1)-Ti(1)-O(4)	103.04(6)
O(5)-Ti(1)-O(4)	82.51(5)
O(5)#1-Ti(1)-O(4)	79.52(5)
O(3)-Ti(1)-O(4)	156.19(6)
O(2)-Ti(1)-Ti(1)#1	132.42(5)
O(1)-Ti(1)-Ti(1)#1	131.82(5)
O(5)-Ti(1)-Ti(1)#1	40.47(4)
O(5)#1-Ti(1)-Ti(1)#1	40.46(4)
O(3)-Ti(1)-Ti(1)#1	78.03(4)
O(4)-Ti(1)-Ti(1)#1	78.16(4)
C(1)-O(1)-Ti(1)	155.5(2)
C(6)-O(2)-Ti(1)	155.2(2)
C(11)-O(3)-Ti(1)	129.38(12)
C(11)#1-O(4)-Ti(1)	128.75(13)
C(16)-O(5)-Ti(1)	125.59(13)
C(16)-O(5)-Ti(1)#1	125.63(12)
Ti(1)-O(5)-Ti(1)#1	99.07(5)
O(1)-C(1)-C(2)	113.8(2)
C(4)-C(2)-C(5)	109.6(3)
C(4)-C(2)-C(3)	109.8(3)
C(5)-C(2)-C(3)	109.5(2)
C(4)-C(2)-C(1)	110.1(2)
C(5)-C(2)-C(1)	110.9(2)
C(3)-C(2)-C(1)	106.8(2)
O(2)-C(6)-C(7)	113.6(2)
C(8)-C(7)-C(10)	109.6(3)
C(8)-C(7)-C(6)	110.2(2)
C(10)-C(7)-C(6)	110.1(2)
C(8)-C(7)-C(9)	109.4(3)
C(10)-C(7)-C(9)	110.1(3)
C(6)-C(7)-C(9)	107.4(2)
O(3)-C(11)-O(4)#1	125.7(2)
O(3)-C(11)-C(12)	117.0(2)
O(4)#1-C(11)-C(12)	117.3(2)
C(13)-C(12)-C(14)	109.3(4)

C(13)-C(12)-C(15)	112.4(4)
C(14)-C(12)-C(15)	106.3(3)
C(13)-C(12)-C(11)	112.0(2)
C(14)-C(12)-C(11)	106.4(2)
C(15)-C(12)-C(11)	110.1(2)
O(5)-C(16)-C(17)	113.8(2)
C(20)-C(17)-C(18)	109.5(2)
C(20)-C(17)-C(19)	110.5(3)
C(18)-C(17)-C(19)	108.9(2)
C(20)-C(17)-C(16)	111.3(2)
C(18)-C(17)-C(16)	110.9(2)
C(19)-C(17)-C(16)	105.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table S5.4. Anisotropic displacement parameters ($Å^2 x10^3$) for **5**.

	U11	U22	U33	U23	U13	U12
Ti(1)	24(1)	28(1)	22(1)	-6(1)	-8(1)	2(1)
O(1)	36(1)	31(1)	39(1)	-13(1)	-8(1)	1(1)
O(2)	32(1)	39(1)	35(1)	-1(1)	-15(1)	4(1)
O(3)	27(1)	33(1)	25(1)	-7(1)	-6(1)	0(1)
O(4)	28(1)	32(1)	25(1)	-4(1)	-7(1)	1(1)
O(5)	27(1)	34(1)	22(1)	-8(1)	-11(1)	0(1)
C(1)	43(1)	30(1)	45(1)	-9(1)	-8(1)	1(1)
C(2)	41(1)	35(1)	46(1)	-17(1)	-6(1)	2(1)
C(3)	69(2)	53(2)	110(3)	-46(2)	0(2)	5(2)
C(4)	79(2)	111(3)	39(2)	-24(2)	-8(1)	27(2)
C(5)	42(1)	72(2)	74(2)	-34(2)	-4(1)	-2(1)
C(6)	36(1)	45(2)	51(1)	3(1)	-20(1)	6(1)
C(7)	50(1)	52(2)	46(1)	8(1)	-26(1)	1(1)
C(8)	68(2)	55(2)	61(2)	11(1)	-25(2)	-13(1)
C(9)	82(2)	91(3)	104(3)	38(2)	-51(2)	11(2)
C(10)	118(3)	77(2)	40(2)	4(2)	-28(2)	-12(2)
C(11)	28(1)	34(1)	23(1)	-9(1)	-9(1)	-2(1)
C(12)	29(1)	38(1)	26(1)	-6(1)	-3(1)	-4(1)
C(13)	149(4)	41(2)	144(4)	-8(2)	102(3)	-13(2)
C(14)	118(3)	202(5)	32(2)	-34(2)	10(2)	-82(3)
C(15)	35(2)	194(5)	75(2)	47(3)	1(2)	-3(2)
C(16)	35(1)	46(1)	24(1)	-12(1)	-14(1)	1(1)
C(17)	41(1)	53(2)	44(1)	-17(1)	-24(1)	-1(1)
C(18)	37(1)	71(2)	71(2)	-24(2)	-26(1)	-1(1)
C(19)	75(2)	111(3)	65(2)	-42(2)	-42(2)	-6(2)
C(20)	57(2)	52(2)	99(2)	-14(2)	-43(2)	-9(1)

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

Table S5.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 5.

	x	y	z	U(eq)
H(1A)	3401(2)	9016(2)	10085(2)	50
H(1B)	4430(2)	8975(2)	10833(2)	50
H(3A)	1859(4)	10188(3)	11455(4)	122
H(3B)	2900(4)	10088(3)	12203(4)	122
H(3C)	1303(4)	9710(3)	12946(4)	122
H(4A)	3562(4)	8087(4)	13194(3)	120
H(4B)	2951(4)	6926(4)	13063(3)	120
H(4C)	1967(4)	7701(4)	13934(3)	120
H(5A)	889(3)	8357(3)	11258(3)	96
H(5B)	329(3)	7866(3)	12748(3)	96
H(5C)	1313(3)	7092(3)	11877(3)	96
H(6A)	1946(2)	8177(2)	9049(2)	55
H(6B)	1547(2)	7292(2)	8384(2)	55
H(8A)	3887(3)	9695(3)	7834(3)	98
H(8B)	4795(3)	9742(3)	6406(3)	98
H(8C)	4950(3)	8689(3)	7505(3)	98
H(9A)	1377(4)	8892(4)	6660(4)	149
H(9B)	2589(4)	9877(4)	5898(4)	149
H(9C)	1692(4)	9812(4)	7332(4)	149
H(10A)	3079(4)	7291(3)	6118(3)	122
H(10B)	4456(4)	7214(3)	6450(3)	122
H(10C)	4301(4)	8267(3)	5352(3)	122
H(13A)	1490(5)	1938(3)	12993(5)	234
H(13B)	900(5)	1927(3)	14447(5)	234
H(13C)	2531(5)	1946(3)	13721(5)	234
H(14A)	1971(5)	4841(5)	14118(3)	185
H(14B)	2824(5)	3703(5)	14412(3)	185
H(14C)	1193(5)	3684(5)	15138(3)	185
H(15A)	390(3)	4897(5)	13002(4)	183
H(15B)	-429(3)	3762(5)	14035(4)	183
H(15C)	102(3)	3773(5)	12582(4)	183
H(16A)	5010(2)	4019(2)	7790(2)	40
H(16B)	4220(2)	5220(2)	7646(2)	40
H(18A)	1575(3)	5170(3)	8586(3)	84
H(18B)	1538(3)	4403(3)	9927(3)	84

H(18C)	719(3)	3941(3)	9196(3)	84
H(19A)	2892(4)	4515(3)	6626(3)	112
H(19B)	2038(4)	3285(3)	7213(3)	112
H(19C)	3690(4)	3315(3)	6710(3)	112
H(20A)	3631(3)	2072(3)	8859(3)	98
H(20B)	1980(3)	2043(3)	9362(3)	98
H(20C)	2799(3)	2504(3)	10093(3)	98

Table S5a.1. Crystal data and structure refinement for **5a**.

Empirical formula	$C_{31} H_{68} O_{11} Ti_2$	
Formula weight	712.65	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 21.443(3) Å	α= 90°.
	b = 15.229(2) Å	β= 90°.
	c = 25.168(4) Å	γ = 90°.
Volume	8219(2) $Å^3$	
Z	8	
Density (calculated)	1.152 Mg/m^3	
Absorption coefficient	0.436 mm^{-1}	
F(000)	3088	
Crystal size	0.34 x 0.30 x 0.24 mm^3	
Theta range for data collection	2.06 to 22.50°.	
Index ranges	$-9 \le h \le 23$, $-16 \le k \le 15$, $-27 \le l \le 11$	
Reflections collected	5608	
Independent reflections	5608 [R(int) = 0.0000]	
Completeness to theta = 22.50°	99.8 %	
Absorption correction	None	
Max. and min. transmission	0.9026 and 0.8660	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5608 / 0 / 319	
Goodness-of-fit on F^2	1.033	
Final R indices [I > 2sigma(I)]	R1 = 0.1092, wR2 = 0.2781	
R indices (all data)	R1 = 0.2364, wR2 = 0.3588	
Largest diff. peak and hole	1.142 and -0.541 $e.Å^{-3}$	

Table S5a.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Ti(1)	5578(1)	2500	6034(1)	30(1)
Ti(2)	4340(1)	2500	6768(1)	26(1)
O(1)	5927(5)	2500	6783(4)	36(3)
O(2)	5093(5)	2500	7300(4)	33(3)
O(3)	4887(3)	1702(5)	6308(3)	28(2)
O(4)	6065(3)	1603(6)	5835(3)	45(2)
O(5)	5084(5)	2500	5342(4)	38(3)
O(6)	3671(5)	2500	6227(4)	32(3)
O(7)	3920(5)	2500	5355(4)	52(4)
O(8)	4000(3)	1608(5)	7132(3)	34(2)
C(1)	5672(8)	2500	7232(7)	34(4)
C(2)	6092(8)	2500	7719(7)	36(4)
C(3)	5721(9)	2500	8242(8)	57(5)
C(4)	6503(9)	1642(13)	7671(8)	108(7)
C(5)	4884(5)	756(8)	6206(4)	37(3)
C(6)	4215(6)	465(8)	6064(5)	46(3)
C(7)	5145(6)	289(9)	6699(5)	53(4)
C(8)	6629(9)	1165(13)	5702(7)	97(6)
C(9)	7063(9)	1131(13)	6169(7)	95(6)
C(10)	6491(8)	239(12)	5479(6)	83(5)
C(11)	5288(10)	2500	4790(8)	63(6)
C(12)	5054(9)	1676(14)	4537(8)	107(7)
C(13)	3533(9)	2500	5742(8)	45(5)
C(14)	2826(9)	2500	5608(8)	53(5)
C(15)	2736(10)	2500	4986(8)	60(6)
C(16)	2548(8)	1657(12)	5863(7)	91(6)
C(17)	3804(11)	950(16)	7504(9)	33(6)
C(18)	3109(14)	1060(20)	7627(12)	53(8)
C(19)	4225(12)	926(17)	7998(10)	38(6)
C(17B)	3529(16)	1440(20)	7549(12)	68(9)
C(19B)	3951(17)	1270(30)	8044(14)	83(11)
C(18B)	3079(16)	780(20)	7382(14)	77(11)
Ti(3)	179(2)	2500	3804(1)	39(1)

Ti(4)	-1307(1)	2500	3635(1)	36(1)
O(9)	-147(6)	2500	4566(4)	41(3)
O(10)	-1187(5)	2500	4453(5)	47(3)
O(11)	-541(3)	1705(5)	3619(3)	32(2)
O(12)	703(4)	1620(5)	3944(3)	47(2)
O(13)	342(5)	2500	2999(5)	56(4)
O(14)	-1375(5)	2500	2846(4)	44(3)
O(15)	-524(7)	2500	2335(5)	86(5)
O(16)	-1841(4)	1610(6)	3702(3)	56(3)
C(20)	-696(9)	2500	4739(7)	37(4)
C(21)	-808(12)	2500	5350(9)	73(7)
C(22)	-1450(20)	2500	5494(18)	74(14)
C(23)	-362(15)	1680(20)	5561(12)	73(9)
C(22B)	-1200(20)	1690(40)	5460(20)	150(20)
C(23B)	-260(30)	2500	5670(20)	105(18)
C(24)	-494(7)	776(10)	3526(6)	62(4)
C(25)	-770(11)	527(16)	3022(9)	130(8)
C(26)	-623(8)	289(11)	4054(6)	77(5)
C(27)	1078(14)	960(20)	4146(11)	57(8)
C(27B)	1266(16)	1460(20)	4261(13)	70(9)
C(28)	1698(9)	916(12)	3901(7)	91(6)
C(29)	1090(8)	1026(13)	4762(7)	94(6)
C(30)	930(9)	2500	2727(8)	53(5)
C(31)	952(10)	1649(15)	2393(9)	126(8)
C(32)	-1122(10)	2500	2413(8)	54(5)
C(33)	-1573(17)	2500	1914(14)	128(11)
C(34)	-1347(19)	1730(30)	1550(15)	103(12)
C(35)	-2213(19)	2500	2069(15)	50(10)
C(34B)	-1930(30)	1610(40)	2000(30)	200(30)
C(35B)	-1110(30)	2500	1400(20)	102(18)
C(36)	-2490(20)	1400(40)	3730(20)	118(16)
C(37)	-2598(17)	540(30)	3301(15)	79(11)
C(38)	-2680(20)	1280(30)	4249(18)	106(14)
C(36B)	-2250(20)	910(30)	3887(17)	96(12)
C(37B)	-2720(30)	840(40)	3560(20)	150(20)
C(38B)	-2390(20)	910(40)	4410(20)	131(18)

Table S5a.3. Bond lengths [Å] and angles [°] for **5a**.

Ti(1)-O(4)#1	1.793(8)
Ti(1)-O(4)	1.793(8)
Ti(1)-O(1)	2.028(11)
Ti(1)-O(3)#1	2.035(7)
Ti(1)-O(3)	2.035(7)
Ti(1)-O(5)	2.038(10)
Ti(1)-Ti(2)	3.233(4)
Ti(2)-O(8)	1.794(7)
Ti(2)-O(8)#1	1.794(7)
Ti(2)-O(6)	1.977(10)
Ti(2)-O(3)	2.048(7)
Ti(2)-O(3)#1	2.048(7)
Ti(2)-O(2)	2.099(11)
O(1)-C(1)	1.255(18)
O(2)-C(1)	1.253(19)
O(3)-C(5)	1.464(13)
O(4)-C(8)	1.42(2)
O(5)-C(11)	1.46(2)
O(6)-C(13)	1.25(2)
O(7)-C(13)	1.28(2)
O(8)-C(17)	1.43(2)
O(8)-C(17B)	1.48(3)
C(1)-C(2)	1.52(2)
C(2)-C(3)	1.54(2)
C(2)-C(4)	1.58(2)
C(2)-C(4)#1	1.58(2)
C(5)-C(7)	1.535(17)
C(5)-C(6)	1.545(17)
C(8)-C(9)	1.50(2)
C(8)-C(10)	1.55(2)
C(11)-C(12)	1.49(2)
C(11)-C(12)#1	1.49(2)
C(13)-C(14)	1.55(3)
C(14)-C(16)#1	1.55(2)
C(14)-C(16)	1.55(2)

C(14)-C(15)	1.58(3)
C(17)-C(18)	1.53(4)
C(17)-C(19)	1.54(3)
C(17B)-C(18B)	1.46(5)
C(17B)-C(19B)	1.56(5)
Ti(3)-O(12)	1.784(8)
Ti(3)-O(12)#1	1.784(8)
Ti(3)-O(11)	2.016(7)
Ti(3)-O(11)#1	2.016(7)
Ti(3)-O(9)	2.042(11)
Ti(3)-O(13)	2.056(13)
Ti(3)-Ti(4)	3.214(4)
Ti(4)-O(16)#1	1.782(9)
Ti(4)-O(16)	1.782(9)
Ti(4)-O(14)	1.991(10)
Ti(4)-O(11)#1	2.040(7)
Ti(4)-O(11)	2.040(7)
Ti(4)-O(10)	2.076(12)
O(9)-C(20)	1.254(19)
O(10)-C(20)	1.28(2)
O(11)-C(24)	1.439(16)
O(12)-C(27)	1.38(3)
O(12)-C(27B)	1.47(3)
O(13)-C(30)	1.44(2)
O(14)-C(32)	1.22(2)
O(15)-C(32)	1.30(2)
O(16)-C(36)	1.44(5)
O(16)-C(36B)	1.45(4)
C(20)-C(21)	1.55(3)
C(21)-C(23B)	1.43(6)
C(21)-C(22)	1.43(5)
C(21)-C(22B)#1	1.52(6)
C(21)-C(22B)	1.52(6)
C(21)-C(23)#1	1.66(4)
C(21)-C(23)	1.66(4)
C(24)-C(25)	1.45(2)
C(24)-C(26)	1.55(2)

C(27)-C(27B)	0.91(4)
C(27)-C(28)	1.47(3)
C(27)-C(29)	1.55(3)
C(27B)-C(29)	1.47(3)
C(27B)-C(28)	1.54(4)
C(30)-C(31)#1	1.55(2)
C(30)-C(31)	1.55(2)
C(32)-C(33)	1.59(4)
C(33)-C(35)	1.43(5)
C(33)-C(34)#1	1.56(4)
C(33)-C(34)	1.56(4)
C(33)-C(34B)	1.58(7)
C(33)-C(34B)#1	1.58(7)
C(33)-C(35B)	1.64(6)
C(36)-C(38)	1.38(6)
C(36)-C(37)	1.71(7)
C(36B)-C(37B)	1.30(7)
C(36B)-C(38B)	1.35(6)

O(4)#1-Ti(1)-O(4)	99.3(5)
O(4)#1-Ti(1)-O(1)	92.5(3)
O(4)-Ti(1)-O(1)	92.5(3)
O(4)#1-Ti(1)-O(3)#1	93.7(3)
O(4)-Ti(1)-O(3)#1	167.0(3)
O(1)-Ti(1)-O(3)#1	87.4(3)
O(4)#1-Ti(1)-O(3)	167.0(3)
O(4)-Ti(1)-O(3)	93.7(3)
O(1)-Ti(1)-O(3)	87.4(3)
O(3)#1-Ti(1)-O(3)	73.3(4)
O(4)#1-Ti(1)-O(5)	93.7(3)
O(4)-Ti(1)-O(5)	93.7(3)
O(1)-Ti(1)-O(5)	170.4(4)
O(3)#1-Ti(1)-O(5)	84.9(3)
O(3)-Ti(1)-O(5)	84.9(3)
O(4)#1-Ti(1)-Ti(2)	129.7(3)
O(4)-Ti(1)-Ti(2)	129.7(3)
O(1)-Ti(1)-Ti(2)	76.9(3)

O(3)#1-Ti(1)-Ti(2)	37.8(2)
O(3)-Ti(1)-Ti(2)	37.8(2)
O(5)-Ti(1)-Ti(2)	93.5(3)
O(8)-Ti(2)-O(8)#1	98.5(5)
O(8)-Ti(2)-O(6)	93.3(3)
O(8)#1-Ti(2)-O(6)	93.3(3)
O(8)-Ti(2)-O(3)	94.2(3)
O(8)#1-Ti(2)-O(3)	166.2(3)
O(6)-Ti(2)-O(3)	91.5(3)
O(8)-Ti(2)-O(3)#1	166.2(3)
O(8)#1-Ti(2)-O(3)#1	94.2(3)
O(6)-Ti(2)-O(3)#1	91.5(3)
O(3)-Ti(2)-O(3)#1	72.8(4)
O(8)-Ti(2)-O(2)	89.2(3)
O(8)#1-Ti(2)-O(2)	89.2(3)
O(6)-Ti(2)-O(2)	176.1(4)
O(3)-Ti(2)-O(2)	85.4(3)
O(3)#1-Ti(2)-O(2)	85.4(3)
O(8)-Ti(2)-Ti(1)	128.7(2)
O(8)#1-Ti(2)-Ti(1)	128.7(2)
O(6)-Ti(2)-Ti(1)	101.6(3)
O(3)-Ti(2)-Ti(1)	37.5(2)
O(3)#1-Ti(2)-Ti(1)	37.5(2)
O(2)-Ti(2)-Ti(1)	74.5(3)
C(1)-O(1)-Ti(1)	132.5(11)
C(1)-O(2)-Ti(2)	132.4(10)
C(5)-O(3)-Ti(1)	122.1(6)
C(5)-O(3)-Ti(2)	132.9(7)
Ti(1)-O(3)-Ti(2)	104.7(3)
C(8)-O(4)-Ti(1)	156.9(10)
C(11)-O(5)-Ti(1)	131.2(11)
C(13)-O(6)-Ti(2)	147.2(11)
C(17)-O(8)-C(17B)	38.4(13)
C(17)-O(8)-Ti(2)	169.1(10)
C(17B)-O(8)-Ti(2)	140.5(14)
O(2)-C(1)-O(1)	123.7(15)
O(2)-C(1)-C(2)	118.4(15)

O(1)-C(1)-C(2)	117.9(15)
C(1)-C(2)-C(3)	112.6(14)
C(1)-C(2)-C(4)	105.5(11)
C(3)-C(2)-C(4)	110.7(11)
C(1)-C(2)-C(4)#1	105.5(11)
C(3)-C(2)-C(4)#1	110.7(11)
C(4)-C(2)-C(4)#1	111.5(18)
O(3)-C(5)-C(7)	108.3(10)
O(3)-C(5)-C(6)	109.1(9)
C(7)-C(5)-C(6)	113.1(10)
O(4)-C(8)-C(9)	111.2(15)
O(4)-C(8)-C(10)	110.5(15)
C(9)-C(8)-C(10)	111.8(16)
O(5)-C(11)-C(12)	107.8(13)
O(5)-C(11)-C(12)#1	107.8(13)
C(12)-C(11)-C(12)#1	114(2)
O(6)-C(13)-O(7)	125.9(17)
O(6)-C(13)-C(14)	116.3(16)
O(7)-C(13)-C(14)	117.9(16)
C(13)-C(14)-C(16)#1	106.6(12)
C(13)-C(14)-C(16)	106.6(12)
C(16)#1-C(14)-C(16)	111.3(18)
C(13)-C(14)-C(15)	109.6(16)
C(16)#1-C(14)-C(15)	111.3(11)
C(16)-C(14)-C(15)	111.3(11)
O(8)-C(17)-C(18)	110(2)
O(8)-C(17)-C(19)	111.9(18)
C(18)-C(17)-C(19)	114(2)
C(18B)-C(17B)-O(8)	112(3)
C(18B)-C(17B)-C(19B)	120(3)
O(8)-C(17B)-C(19B)	102(2)
O(12)-Ti(3)-O(12)#1	97.4(5)
O(12)-Ti(3)-O(11)	94.4(3)
O(12)#1-Ti(3)-O(11)	168.2(3)
O(12)-Ti(3)-O(11)#1	168.2(3)
O(12)#1-Ti(3)-O(11)#1	94.4(3)
O(11)-Ti(3)-O(11)#1	73.8(4)

O(12)-Ti(3)-O(9)	91.7(4)
O(12)#1-Ti(3)-O(9)	91.7(4)
O(11)-Ti(3)-O(9)	87.4(3)
O(11)#1-Ti(3)-O(9)	87.4(3)
O(12)-Ti(3)-O(13)	95.0(4)
O(12)#1-Ti(3)-O(13)	95.0(4)
O(11)-Ti(3)-O(13)	84.4(4)
O(11)#1-Ti(3)-O(13)	84.4(4)
O(9)-Ti(3)-O(13)	169.8(5)
O(12)-Ti(3)-Ti(4)	130.6(3)
O(12)#1-Ti(3)-Ti(4)	130.6(3)
O(11)-Ti(3)-Ti(4)	37.8(2)
O(11)#1-Ti(3)-Ti(4)	37.8(2)
O(9)-Ti(3)-Ti(4)	77.6(3)
O(13)-Ti(3)-Ti(4)	92.2(4)
O(16)#1-Ti(4)-O(16)	99.0(6)
O(16)#1-Ti(4)-O(14)	92.7(4)
O(16)-Ti(4)-O(14)	92.7(4)
O(16)#1-Ti(4)-O(11)#1	93.9(4)
O(16)-Ti(4)-O(11)#1	165.9(4)
O(14)-Ti(4)-O(11)#1	92.3(3)
O(16)#1-Ti(4)-O(11)	165.9(4)
O(16)-Ti(4)-O(11)	93.9(4)
O(14)-Ti(4)-O(11)	92.3(3)
O(11)#1-Ti(4)-O(11)	72.8(4)
O(16)#1-Ti(4)-O(10)	89.2(4)
O(16)-Ti(4)-O(10)	89.2(4)
O(14)-Ti(4)-O(10)	177.1(5)
O(11)#1-Ti(4)-O(10)	85.4(3)
O(11)-Ti(4)-O(10)	85.4(3)
O(16)#1-Ti(4)-Ti(3)	128.6(3)
O(16)-Ti(4)-Ti(3)	128.6(3)
O(14)-Ti(4)-Ti(3)	101.8(3)
O(11)#1-Ti(4)-Ti(3)	37.3(2)
O(11)-Ti(4)-Ti(3)	37.3(2)
O(10)-Ti(4)-Ti(3)	75.2(3)
C(20)-O(9)-Ti(3)	130.3(11)

C(20)-O(10)-Ti(4)	131.6(11)
C(24)-O(11)-Ti(3)	125.0(8)
C(24)-O(11)-Ti(4)	130.1(7)
Ti(3)-O(11)-Ti(4)	104.8(3)
C(27)-O(12)-C(27B)	37.1(15)
C(27)-O(12)-Ti(3)	169.8(14)
C(27B)-O(12)-Ti(3)	138.6(15)
C(30)-O(13)-Ti(3)	128.3(11)
C(32)-O(14)-Ti(4)	149.3(13)
C(36)-O(16)-C(36B)	40(2)
C(36)-O(16)-Ti(4)	143(2)
C(36B)-O(16)-Ti(4)	166.7(18)
O(9)-C(20)-O(10)	125.3(16)
O(9)-C(20)-C(21)	119.2(17)
O(10)-C(20)-C(21)	115.5(17)
C(23B)-C(21)-C(22)	131(4)
C(23B)-C(21)-C(22B)#1	110(3)
C(22)-C(21)-C(22B)#1	55(2)
C(23B)-C(21)-C(22B)	110(3)
C(22)-C(21)-C(22B)	55(2)
C(22B)#1-C(21)-C(22B)	109(4)
C(23B)-C(21)-C(20)	116(3)
C(22)-C(21)-C(20)	114(3)
C(22B)#1-C(21)-C(20)	106(2)
C(22B)-C(21)-C(20)	106(2)
C(23B)-C(21)-C(23)#1	49.1(13)
C(22)-C(21)-C(23)#1	118.3(18)
C(22B)#1-C(21)-C(23)#1	69(2)
C(22B)-C(21)-C(23)#1	151(3)
C(20)-C(21)-C(23)#1	103.1(16)
C(23B)-C(21)-C(23)	49.1(13)
C(22)-C(21)-C(23)	118.3(18)
C(22B)#1-C(21)-C(23)	151(3)
C(22B)-C(21)-C(23)	69(2)
C(20)-C(21)-C(23)	103.1(16)
C(23)#1-C(21)-C(23)	98(3)
O(11)-C(24)-C(25)	111.8(14)

O(11)-C(24)-C(26)	108.6(12)
C(25)-C(24)-C(26)	123.6(15)
C(27B)-C(27)-O(12)	76(3)
C(27B)-C(27)-C(28)	77(3)
O(12)-C(27)-C(28)	114(2)
C(27B)-C(27)-C(29)	68(3)
O(12)-C(27)-C(29)	109(2)
C(28)-C(27)-C(29)	114(2)
C(27)-C(27B)-O(12)	67(3)
C(27)-C(27B)-C(29)	77(3)
O(12)-C(27B)-C(29)	109(2)
C(27)-C(27B)-C(28)	68(3)
O(12)-C(27B)-C(28)	105(2)
C(29)-C(27B)-C(28)	115(2)
C(27)-C(28)-C(27B)	35.2(15)
C(27B)-C(29)-C(27)	34.9(15)
O(13)-C(30)-C(31)#1	106.6(13)
O(13)-C(30)-C(31)	106.6(13)
C(31)#1-C(30)-C(31)	114(2)
O(14)-C(32)-O(15)	125.3(19)
O(14)-C(32)-C(33)	116(2)
O(15)-C(32)-C(33)	119(2)
C(35)-C(33)-C(34)#1	117(2)
C(35)-C(33)-C(34)	117(2)
C(34)#1-C(33)-C(34)	97(4)
C(35)-C(33)-C(34B)	59(3)
C(34)#1-C(33)-C(34B)	152(4)
C(34)-C(33)-C(34B)	66(3)
C(35)-C(33)-C(34B)#1	59(3)
C(34)#1-C(33)-C(34B)#1	66(3)
C(34)-C(33)-C(34B)#1	152(4)
C(34B)-C(33)-C(34B)#1	118(5)
C(35)-C(33)-C(32)	112(3)
C(34)#1-C(33)-C(32)	106(2)
C(34)-C(33)-C(32)	106(2)
C(34B)-C(33)-C(32)	101(3)
C(34B)#1-C(33)-C(32)	101(3)

C(35)-C(33)-C(35B)	143(4)
C(34)#1-C(33)-C(35B)	49.2(18)
C(34)-C(33)-C(35B)	49.2(18)
C(34B)-C(33)-C(35B)	114(3)
C(34B)#1-C(33)-C(35B)	114(3)
C(32)-C(33)-C(35B)	105(3)
C(38)-C(36)-O(16)	111(4)
C(38)-C(36)-C(37)	118(4)
O(16)-C(36)-C(37)	106(3)
C(37B)-C(36B)-C(38B)	116(5)
C(37B)-C(36B)-O(16)	109(4)
C(38B)-C(36B)-O(16)	117(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table S5a.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Ti(1)	25(2)	41(2)	26(2)	0	2(1)	0
Ti(2)	24(2)	37(2)	18(2)	0	3(1)	0
O(1)	35(7)	43(7)	29(6)	0	-1(5)	0
O(2)	26(6)	50(7)	23(6)	0	5(5)	0
O(3)	26(4)	29(4)	30(4)	-11(3)	3(3)	-1(4)
O(4)	31(5)	63(6)	41(5)	-14(5)	11(4)	8(4)
O(5)	23(6)	77(9)	15(6)	0	7(5)	0
O(6)	24(6)	50(7)	22(6)	0	-2(5)	0
O(7)	45(8)	97(11)	13(6)	0	-4(5)	0
O(8)	28(4)	41(5)	34(4)	3(4)	4(3)	-5(4)
Ti(3)	32(2)	43(2)	43(2)	0	-9(2)	0
Ti(4)	31(2)	47(2)	28(2)	0	0(1)	0
O(9)	52(8)	47(8)	24(6)	0	-15(6)	0
O(10)	43(8)	51(8)	49(7)	0	0(6)	0
O(11)	35(5)	21(4)	40(5)	-5(4)	-6(4)	-2(4)
O(12)	34(5)	39(5)	69(6)	3(5)	-18(4)	7(4)
O(13)	34(7)	74(10)	61(8)	0	23(6)	0
O(14)	33(7)	82(10)	18(6)	0	10(5)	0
O(15)	58(10)	154(16)	45(9)	0	15(7)	0
O(16)	36(5)	69(6)	62(6)	4(5)	1(4)	-27(5)

Table S6.1. Crystal data and structure refinement for **6.**

Empirical formula	$C_{52} H_{110} O_{13} Ti_3$	
Formula weight	1087.10	
Temperature	158 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 15.4865(7) Å	α= 90°.
	b = 20.9548(10) Å	β= 91.3170(10)°.
	c = 19.8993(9) Å	γ = 90°.
Volume	6455.9(5) $Å^3$	
Z	4	
Density (calculated)	1.118 Mg/m^3	
Absorption coefficient	0.413 mm^{-1}	
F(000)	2368	
Crystal size	0.32 x 0.27 x 0.24 mm^3	
Theta range for data collection	1.41 to 28.34°.	
Index ranges	$-1 \le h \le 20$, $-27 \le k \le 27$, $-26 \le l \le 25$	
Reflections collected	64420	
Independent reflections	15610 [R(int) = 0.0503]	
Completeness to theta = 28.34°	97.0 %	
Absorption correction	Semi-empirical via SADABS	
Max. and min. transmission	0.9073 and 0.8791	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15610 / 0 / 614	
Goodness-of-fit on F^2	1.107	
Final R indices [I > 2sigma(I)]	R1 = 0.0545, wR2 = 0.1127	
R indices (all data)	R1 = 0.0804, wR2 = 0.1230	
Extinction coefficient	0.00072(11)	
Largest diff. peak and hole	0.562 and -0.377 $e.Å^{-3}$	

Table S6.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Ti(1)	6786(1)	2031(1)	9867(1)	19(1)
Ti(2)	8213(1)	3392(1)	9822(1)	20(1)
Ti(3)	7146(1)	3007(1)	11040(1)	18(1)
O(1)	7271(1)	2117(1)	8928(1)	24(1)
O(2)	8135(1)	2970(1)	8899(1)	29(1)
O(3)	6007(1)	2839(1)	9557(1)	23(1)
O(4)	6241(1)	3512(1)	10416(1)	22(1)
O(5)	5851(1)	1588(1)	9577(1)	26(1)
O(6)	6398(1)	2250(1)	10804(1)	20(1)
O(7)	7445(1)	1345(1)	10067(1)	25(1)
O(8)	7965(1)	3707(1)	10739(1)	20(1)
O(9)	7820(1)	4102(1)	9417(1)	33(1)
O(10)	9359(1)	3313(1)	9852(1)	33(1)
O(11)	6651(1)	3397(1)	11738(1)	26(1)
O(12)	7938(1)	2561(1)	11528(1)	25(1)
O(13)	7631(1)	2691(1)	10155(1)	17(1)
C(1)	7821(1)	2463(1)	8651(1)	21(1)
C(2)	8144(1)	2251(1)	7975(1)	27(1)
C(3)	7480(2)	2267(1)	7385(1)	28(1)
C(4)	7147(2)	2943(1)	7281(1)	48(1)
C(5)	7958(2)	2043(1)	6758(1)	41(1)
C(6)	6727(2)	1810(1)	7506(1)	40(1)
C(7)	5874(1)	3356(1)	9865(1)	21(1)
C(8)	5226(1)	3822(1)	9558(1)	25(1)
C(9)	4336(1)	3834(1)	9895(1)	27(1)
C(10)	4427(2)	4062(1)	10625(1)	37(1)
C(11)	3756(2)	4303(1)	9503(1)	39(1)
C(12)	3924(2)	3173(1)	9884(2)	41(1)
C(13)	5066(2)	1676(1)	9213(1)	33(1)
C(14)	4599(2)	1049(1)	9074(1)	38(1)
C(15)	4396(2)	730(2)	9739(2)	69(1)
C(16)	3754(2)	1201(2)	8694(2)	60(1)
C(17)	5160(2)	618(2)	8651(2)	67(1)

C(18)	5572(1)	2089(1)	11068(1)	25(1)
C(19)	5631(2)	1601(1)	11640(1)	29(1)
C(20)	6183(2)	1035(1)	11431(1)	34(1)
C(21)	6014(2)	1906(1)	12279(1)	40(1)
C(22)	4710(2)	1373(1)	11773(2)	48(1)
C(23)	7432(2)	675(1)	10030(2)	43(1)
C(24)	8180(2)	389(1)	9663(1)	35(1)
C(25)	9005(3)	579(2)	10023(3)	124(2)
C(26)	8113(3)	-334(1)	9680(2)	75(1)
C(27)	8188(4)	626(2)	8957(2)	139(3)
C(28)	7890(1)	4360(1)	10956(1)	25(1)
C(29)	8741(2)	4640(1)	11228(1)	28(1)
C(30)	9368(2)	4755(1)	10669(1)	39(1)
C(31)	9149(2)	4192(2)	11744(2)	66(1)
C(32)	8527(2)	5281(2)	11553(2)	63(1)
C(33)	7298(2)	4345(1)	8890(1)	30(1)
C(34)	7778(2)	4807(1)	8442(1)	29(1)
C(35)	8088(2)	5385(1)	8848(1)	32(1)
C(36)	8547(2)	4472(1)	8136(2)	49(1)
C(37)	7131(2)	5020(2)	7890(2)	60(1)
C(38)	10096(2)	3279(1)	9444(1)	36(1)
C(39)	10711(2)	2754(1)	9677(1)	35(1)
C(40)	10244(2)	2116(1)	9644(2)	63(1)
C(41)	11023(2)	2890(2)	10392(2)	72(1)
C(42)	11474(2)	2748(2)	9199(2)	55(1)
C(43)	6735(2)	3606(1)	12409(1)	30(1)
C(44)	5995(2)	4050(1)	12610(1)	29(1)
C(45)	5945(2)	4623(1)	12142(2)	44(1)
C(46)	5143(2)	3683(1)	12578(1)	41(1)
C(47)	6185(2)	4266(2)	13335(1)	51(1)
C(48)	8591(2)	2118(1)	11386(1)	44(1)
C(49)	9065(2)	1863(1)	12009(1)	40(1)
C(50)	9770(3)	1407(2)	11779(2)	92(2)
C(51)	9477(3)	2403(2)	12385(2)	96(2)
C(52)	8453(3)	1504(3)	12432(3)	135(3)

Table S6.3. Bond lengths [Å] and angles [°] for **6**.

Ti(1)-O(7)	1.8023(15)
Ti(1)-O(5)	1.8042(15)
Ti(1)-O(13)	1.9795(14)
Ti(1)-O(6)	2.0240(14)
Ti(1)-O(1)	2.0377(14)
Ti(1)-O(3)	2.1613(15)
Ti(1)-Ti(3)	3.1433(5)
Ti(2)-O(10)	1.7823(17)
Ti(2)-O(9)	1.7911(16)
Ti(2)-O(13)	1.8535(14)
Ti(2)-O(8)	1.9871(14)
Ti(2)-O(2)	2.0394(15)
Ti(2)-Ti(3)	3.0743(5)
Ti(3)-O(11)	1.7966(15)
Ti(3)-O(12)	1.8069(15)
Ti(3)-O(6)	2.0131(14)
Ti(3)-O(8)	2.0387(14)
Ti(3)-O(13)	2.0422(14)
Ti(3)-O(4)	2.1324(15)
O(1)-C(1)	1.256(3)
O(2)-C(1)	1.264(3)
O(3)-C(7)	1.263(3)
O(4)-C(7)	1.267(3)
O(5)-C(13)	1.413(3)
O(6)-C(18)	1.435(2)
O(7)-C(23)	1.407(3)
O(8)-C(28)	1.440(2)
O(9)-C(33)	1.406(3)
O(10)-C(38)	1.418(3)
O(11)-C(43)	1.410(3)
O(12)-C(48)	1.405(3)
C(1)-C(2)	1.513(3)
C(2)-C(3)	1.543(3)
C(3)-C(4)	1.521(4)
C(3)-C(6)	1.532(3)

C(3)-C(5)	1.538(3)
C(7)-C(8)	1.518(3)
C(8)-C(9)	1.547(3)
C(9)-C(12)	1.525(3)
C(9)-C(10)	1.531(3)
C(9)-C(11)	1.533(3)
C(13)-C(14)	1.521(3)
C(14)-C(17)	1.521(4)
C(14)-C(15)	1.522(4)
C(14)-C(16)	1.529(4)
C(18)-C(19)	1.531(3)
C(19)-C(20)	1.524(3)
C(19)-C(21)	1.530(3)
C(19)-C(22)	1.534(3)
C(23)-C(24)	1.506(3)
C(24)-C(27)	1.490(4)
C(24)-C(25)	1.504(5)
C(24)-C(26)	1.519(4)
C(28)-C(29)	1.529(3)
C(29)-C(30)	1.513(3)
C(29)-C(31)	1.519(4)
C(29)-C(32)	1.531(4)
C(33)-C(34)	1.521(3)
C(34)-C(36)	1.522(4)
C(34)-C(35)	1.527(3)
C(34)-C(37)	1.536(4)
C(38)-C(39)	1.521(4)
C(39)-C(40)	1.520(4)
C(39)-C(41)	1.520(4)
C(39)-C(42)	1.534(4)
C(43)-C(44)	1.535(3)
C(44)-C(45)	1.521(4)
C(44)-C(46)	1.527(3)
C(44)-C(47)	1.533(3)
C(48)-C(49)	1.524(3)
C(49)-C(52)	1.487(5)
C(49)-C(51)	1.492(4)

C(49)-C(50)	1.529(5)
O(7)-Ti(1)-O(5)	96.08(7)
O(7)-Ti(1)-O(13)	97.29(7)
O(5)-Ti(1)-O(13)	166.57(7)
O(7)-Ti(1)-O(6)	99.01(7)
O(5)-Ti(1)-O(6)	99.10(6)
O(13)-Ti(1)-O(6)	77.53(6)
O(7)-Ti(1)-O(1)	93.10(7)
O(5)-Ti(1)-O(1)	93.54(7)
O(13)-Ti(1)-O(1)	87.03(6)
O(6)-Ti(1)-O(1)	161.41(6)
O(7)-Ti(1)-O(3)	176.11(6)
O(5)-Ti(1)-O(3)	82.71(6)
O(13)-Ti(1)-O(3)	84.03(6)
O(6)-Ti(1)-O(3)	84.84(6)
O(1)-Ti(1)-O(3)	83.30(6)
O(7)-Ti(1)-Ti(3)	105.40(5)
O(5)-Ti(1)-Ti(3)	134.41(5)
O(13)-Ti(1)-Ti(3)	39.31(4)
O(6)-Ti(1)-Ti(3)	38.74(4)
O(1)-Ti(1)-Ti(3)	124.12(4)
O(3)-Ti(1)-Ti(3)	77.94(4)
O(10)-Ti(2)-O(9)	114.93(8)
O(10)-Ti(2)-O(13)	113.94(7)
O(9)-Ti(2)-O(13)	130.92(8)
O(10)-Ti(2)-O(8)	102.31(7)
O(9)-Ti(2)-O(8)	93.79(7)
O(13)-Ti(2)-O(8)	80.13(6)
O(10)-Ti(2)-O(2)	91.62(7)
O(9)-Ti(2)-O(2)	86.73(7)
O(13)-Ti(2)-O(2)	87.66(6)
O(8)-Ti(2)-O(2)	164.29(6)
O(10)-Ti(2)-Ti(3)	120.11(6)
O(9)-Ti(2)-Ti(3)	112.88(6)
O(13)-Ti(2)-Ti(3)	40.11(4)
O(8)-Ti(2)-Ti(3)	40.84(4)

O(2)-Ti(2)-Ti(3)	125.09(5)
O(11)-Ti(3)-O(12)	96.72(7)
O(11)-Ti(3)-O(6)	106.57(6)
O(12)-Ti(3)-O(6)	95.61(7)
O(11)-Ti(3)-O(8)	100.34(6)
O(12)-Ti(3)-O(8)	96.37(6)
O(6)-Ti(3)-O(8)	148.94(6)
O(11)-Ti(3)-O(13)	170.30(7)
O(12)-Ti(3)-O(13)	92.14(6)
O(6)-Ti(3)-O(13)	76.36(5)
O(8)-Ti(3)-O(13)	74.65(5)
O(11)-Ti(3)-O(4)	86.44(7)
O(12)-Ti(3)-O(4)	176.84(6)
O(6)-Ti(3)-O(4)	83.59(6)
O(8)-Ti(3)-O(4)	82.89(6)
O(13)-Ti(3)-O(4)	84.70(6)
O(11)-Ti(3)-Ti(2)	137.44(5)
O(12)-Ti(3)-Ti(2)	100.88(5)
O(6)-Ti(3)-Ti(2)	109.83(4)
O(8)-Ti(3)-Ti(2)	39.60(4)
O(13)-Ti(3)-Ti(2)	35.78(4)
O(4)-Ti(3)-Ti(2)	76.58(4)
O(11)-Ti(3)-Ti(1)	142.90(5)
O(12)-Ti(3)-Ti(1)	99.71(5)
O(6)-Ti(3)-Ti(1)	38.99(4)
O(8)-Ti(3)-Ti(1)	110.52(4)
O(13)-Ti(3)-Ti(1)	37.89(4)
O(4)-Ti(3)-Ti(1)	77.74(4)
Ti(2)-Ti(3)-Ti(1)	70.986(12)
C(1)-O(1)-Ti(1)	136.17(14)
C(1)-O(2)-Ti(2)	136.85(14)
C(7)-O(3)-Ti(1)	128.92(14)
C(7)-O(4)-Ti(3)	130.64(13)
C(13)-O(5)-Ti(1)	140.53(14)
C(18)-O(6)-Ti(3)	127.80(12)
C(18)-O(6)-Ti(1)	124.76(13)
Ti(3)-O(6)-Ti(1)	102.27(6)

C(23)-O(7)-Ti(1)	141.09(17)
C(28)-O(8)-Ti(2)	127.53(12)
C(28)-O(8)-Ti(3)	122.71(12)
Ti(2)-O(8)-Ti(3)	99.57(6)
C(33)-O(9)-Ti(2)	145.13(15)
C(38)-O(10)-Ti(2)	143.04(16)
C(43)-O(11)-Ti(3)	147.34(15)
C(48)-O(12)-Ti(3)	135.72(15)
Ti(2)-O(13)-Ti(1)	140.73(8)
Ti(2)-O(13)-Ti(3)	104.11(6)
Ti(1)-O(13)-Ti(3)	102.80(6)
O(1)-C(1)-O(2)	124.97(19)
O(1)-C(1)-C(2)	117.57(19)
O(2)-C(1)-C(2)	117.46(19)
C(1)-C(2)-C(3)	116.28(18)
C(4)-C(3)-C(6)	110.3(2)
C(4)-C(3)-C(5)	110.0(2)
C(6)-C(3)-C(5)	108.6(2)
C(4)-C(3)-C(2)	109.9(2)
C(6)-C(3)-C(2)	111.3(2)
C(5)-C(3)-C(2)	106.63(19)
O(3)-C(7)-O(4)	124.59(19)
O(3)-C(7)-C(8)	117.96(19)
O(4)-C(7)-C(8)	117.45(18)
C(7)-C(8)-C(9)	115.07(17)
C(12)-C(9)-C(10)	109.0(2)
C(12)-C(9)-C(11)	109.6(2)
C(10)-C(9)-C(11)	108.9(2)
C(12)-C(9)-C(8)	110.74(19)
C(10)-C(9)-C(8)	110.68(19)
C(11)-C(9)-C(8)	107.91(19)
O(5)-C(13)-C(14)	112.4(2)
C(13)-C(14)-C(17)	109.7(2)
C(13)-C(14)-C(15)	109.2(2)
C(17)-C(14)-C(15)	110.6(3)
C(13)-C(14)-C(16)	108.0(2)
C(17)-C(14)-C(16)	110.1(3)

C(15)-C(14)-C(16)	109.2(3)
O(6)-C(18)-C(19)	112.99(18)
C(20)-C(19)-C(21)	110.1(2)
C(20)-C(19)-C(18)	109.94(18)
C(21)-C(19)-C(18)	110.75(19)
C(20)-C(19)-C(22)	109.5(2)
C(21)-C(19)-C(22)	109.4(2)
C(18)-C(19)-C(22)	107.2(2)
O(7)-C(23)-C(24)	114.3(2)
C(27)-C(24)-C(25)	109.5(4)
C(27)-C(24)-C(23)	110.5(3)
C(25)-C(24)-C(23)	108.6(3)
C(27)-C(24)-C(26)	110.8(3)
C(25)-C(24)-C(26)	108.1(3)
C(23)-C(24)-C(26)	109.4(2)
O(8)-C(28)-C(29)	113.31(18)
C(30)-C(29)-C(31)	109.4(2)
C(30)-C(29)-C(28)	111.31(19)
C(31)-C(29)-C(28)	110.1(2)
C(30)-C(29)-C(32)	108.7(2)
C(31)-C(29)-C(32)	110.3(3)
C(28)-C(29)-C(32)	107.1(2)
O(9)-C(33)-C(34)	112.79(19)
C(33)-C(34)-C(36)	109.8(2)
C(33)-C(34)-C(35)	110.27(19)
C(36)-C(34)-C(35)	109.7(2)
C(33)-C(34)-C(37)	106.5(2)
C(36)-C(34)-C(37)	110.6(2)
C(35)-C(34)-C(37)	109.9(2)
O(10)-C(38)-C(39)	111.5(2)
C(40)-C(39)-C(41)	110.3(3)
C(40)-C(39)-C(38)	109.3(2)
C(41)-C(39)-C(38)	109.4(2)
C(40)-C(39)-C(42)	109.7(2)
C(41)-C(39)-C(42)	110.4(3)
C(38)-C(39)-C(42)	107.6(2)
O(11)-C(43)-C(44)	112.47(19)

C(45)-C(44)-C(46)	109.9(2)
C(45)-C(44)-C(47)	110.4(2)
C(46)-C(44)-C(47)	109.6(2)
C(45)-C(44)-C(43)	110.28(19)
C(46)-C(44)-C(43)	109.5(2)
C(47)-C(44)-C(43)	107.2(2)
O(12)-C(48)-C(49)	113.8(2)
C(52)-C(49)-C(51)	111.8(4)
C(52)-C(49)-C(48)	109.7(3)
C(51)-C(49)-C(48)	109.5(2)
C(52)-C(49)-C(50)	108.8(3)
C(51)-C(49)-C(50)	108.9(3)
C(48)-C(49)-C(50)	108.0(3)

Table S6.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Ti(1)	21(1)	16(1)	19(1)	-2(1)	2(1)	-3(1)
Ti(2)	21(1)	19(1)	19(1)	1(1)	4(1)	-4(1)
Ti(3)	21(1)	17(1)	16(1)	0(1)	2(1)	-2(1)
O(1)	28(1)	27(1)	18(1)	-3(1)	5(1)	-4(1)
O(2)	39(1)	27(1)	20(1)	-1(1)	6(1)	-8(1)
O(3)	23(1)	21(1)	23(1)	-2(1)	-1(1)	0(1)
O(4)	22(1)	19(1)	24(1)	-2(1)	1(1)	1(1)
O(5)	27(1)	23(1)	27(1)	-4(1)	-1(1)	-8(1)
O(6)	22(1)	19(1)	20(1)	0(1)	5(1)	-3(1)
O(7)	29(1)	17(1)	30(1)	-2(1)	3(1)	2(1)
O(8)	23(1)	17(1)	20(1)	-1(1)	2(1)	-3(1)
O(9)	52(1)	24(1)	24(1)	3(1)	0(1)	0(1)
O(10)	23(1)	41(1)	36(1)	-6(1)	8(1)	-6(1)
O(11)	33(1)	25(1)	21(1)	-4(1)	8(1)	-4(1)
O(12)	29(1)	23(1)	21(1)	3(1)	-2(1)	-1(1)
O(13)	18(1)	17(1)	17(1)	-1(1)	2(1)	-1(1)
C(1)	21(1)	24(1)	19(1)	0(1)	0(1)	3(1)
C(2)	25(1)	34(1)	20(1)	-5(1)	5(1)	1(1)
C(3)	30(1)	34(1)	21(1)	-6(1)	2(1)	1(1)
C(4)	60(2)	45(2)	39(2)	-1(1)	-13(1)	14(1)
C(5)	43(2)	57(2)	23(1)	-11(1)	3(1)	-6(1)
C(6)	33(1)	53(2)	35(1)	-14(1)	1(1)	-9(1)
C(7)	16(1)	22(1)	24(1)	4(1)	5(1)	-2(1)
C(8)	24(1)	28(1)	24(1)	6(1)	2(1)	3(1)
C(9)	21(1)	29(1)	32(1)	4(1)	1(1)	4(1)
C(10)	32(1)	47(2)	33(1)	0(1)	7(1)	12(1)
C(11)	29(1)	44(2)	44(2)	9(1)	-2(1)	12(1)
C(12)	24(1)	39(1)	61(2)	4(1)	3(1)	-4(1)
C(13)	33(1)	29(1)	37(1)	2(1)	-9(1)	-9(1)
C(14)	37(1)	40(1)	37(1)	1(1)	-10(1)	-20(1)
C(15)	69(2)	76(2)	60(2)	25(2)	-17(2)	-50(2)
C(16)	50(2)	69(2)	61(2)	1(2)	-21(2)	-23(2)

C(17)	65(2)	55(2)	80(2)	-34(2)	-13(2)	-15(2)
C(18)	24(1)	25(1)	27(1)	1(1)	7(1)	-4(1)
C(19)	34(1)	23(1)	29(1)	2(1)	11(1)	-6(1)
C(20)	46(2)	23(1)	33(1)	2(1)	8(1)	-4(1)
C(21)	66(2)	31(1)	24(1)	3(1)	8(1)	-6(1)
C(22)	45(2)	44(2)	57(2)	9(1)	23(1)	-12(1)
C(23)	48(2)	20(1)	62(2)	-5(1)	18(1)	0(1)
C(24)	43(2)	24(1)	37(1)	3(1)	10(1)	10(1)
C(25)	44(2)	79(3)	249(7)	-62(4)	-12(3)	18(2)
C(26)	99(3)	28(2)	100(3)	-6(2)	36(2)	14(2)
C(27)	264(7)	98(3)	59(2)	27(2)	77(4)	113(4)
C(28)	27(1)	19(1)	29(1)	-5(1)	4(1)	-3(1)
C(29)	33(1)	29(1)	23(1)	-4(1)	2(1)	-11(1)
C(30)	34(1)	46(2)	37(1)	-9(1)	8(1)	-19(1)
C(31)	65(2)	76(2)	55(2)	27(2)	-34(2)	-39(2)
C(32)	54(2)	50(2)	84(2)	-41(2)	20(2)	-25(2)
C(33)	28(1)	28(1)	32(1)	5(1)	6(1)	0(1)
C(34)	37(1)	28(1)	23(1)	5(1)	2(1)	-2(1)
C(35)	37(1)	26(1)	34(1)	4(1)	2(1)	1(1)
C(36)	57(2)	42(2)	48(2)	-9(1)	31(1)	-11(1)
C(37)	87(3)	47(2)	44(2)	15(1)	-27(2)	-13(2)
C(38)	25(1)	41(1)	43(1)	6(1)	12(1)	-2(1)
C(39)	35(1)	41(1)	30(1)	-1(1)	2(1)	6(1)
C(40)	80(3)	38(2)	71(2)	-2(2)	22(2)	5(2)
C(41)	58(2)	111(3)	44(2)	-12(2)	-14(2)	20(2)
C(42)	37(2)	70(2)	60(2)	5(2)	12(1)	18(2)
C(43)	34(1)	34(1)	21(1)	-3(1)	4(1)	-3(1)
C(44)	31(1)	31(1)	27(1)	-9(1)	7(1)	-4(1)
C(45)	44(2)	33(1)	57(2)	-4(1)	11(1)	1(1)
C(46)	37(2)	45(2)	43(2)	-9(1)	11(1)	-6(1)
C(47)	54(2)	62(2)	38(2)	-23(1)	12(1)	-8(2)
C(48)	46(2)	49(2)	36(1)	-5(1)	-14(1)	20(1)
C(49)	41(2)	32(1)	45(2)	10(1)	-17(1)	1(1)
C(50)	86(3)	88(3)	98(3)	-11(2)	-46(2)	52(2)
C(51)	111(3)	60(2)	113(3)	-26(2)	-85(3)	20(2)
C(52)	64(3)	161(5)	179(6)	140(5)	-12(3)	-1(3)

Table S6.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6**.

H(2A)	8365	1810	8021	32
H(2B)	8638	2526	7857	32
H(4A)	6842	3081	7681	72
H(4B)	6751	2954	6890	72
H(4C)	7635	3230	7204	72
H(5A)	7558	2045	6369	61
H(5B)	8178	1610	6832	61
H(5C)	8441	2332	6674	61
H(6A)	6417	1947	7905	61
H(6B)	6951	1377	7577	61
H(6C)	6332	1814	7114	61
H(8A)	5137	3713	9077	30
H(8B)	5477	4256	9581	30
H(10A)	3857	4064	10830	56
H(10B)	4669	4494	10635	56
H(10C)	4812	3772	10876	56
H(11A)	3186	4319	9707	59
H(11B)	3693	4161	9035	59
H(11C)	4017	4729	9516	59
H(12A)	3363	3191	10101	62
H(12B)	4302	2872	10126	62
H(12C)	3844	3032	9417	62
H(13A)	5187	1887	8780	39
H(13B)	4686	1960	9470	39
H(15A)	4031	1013	10003	103
H(15B)	4935	644	9990	103
H(15C)	4091	327	9652	103
H(16A)	3396	1477	8971	90
H(16B)	3443	803	8595	90
H(16C)	3882	1419	8273	90
H(17A)	5700	524	8899	100
H(17B)	5291	833	8228	100
H(17C)	4852	219	8555	100

H(18A)	5200	1914	10701	30
H(18B)	5293	2482	11235	30
H(20A)	6772	1181	11348	51
H(20B)	5935	845	11020	51
H(20C)	6195	716	11791	51
H(21A)	6603	2053	12195	60
H(21B)	6027	1591	12643	60
H(21C)	5657	2271	12408	60
H(22A)	4465	1176	11364	72
H(22B)	4353	1737	11901	72
H(22C)	4723	1059	12138	72
H(23A)	6888	539	9802	52
H(23B)	7433	500	10493	52
H(25A)	9063	1045	10015	186
H(25B)	9497	386	9797	186
H(25C)	8994	431	10489	186
H(26A)	8597	-520	9440	113
H(26B)	7567	-467	9464	113
H(26C)	8130	-480	10148	113
H(27A)	8231	1092	8957	208
H(27B)	7655	495	8721	208
H(27C)	8686	444	8728	208
H(28A)	7454	4384	11311	30
H(28B)	7680	4622	10572	30
H(30A)	9513	4347	10458	58
H(30B)	9895	4953	10854	58
H(30C)	9102	5039	10332	58
H(31A)	9284	3785	11529	99
H(31B)	8744	4119	12108	99
H(31C)	9681	4383	11928	99
H(32A)	9059	5476	11734	94
H(32B)	8124	5213	11919	94
H(32C)	8262	5565	11216	94
H(33A)	6795	4567	9082	35
H(33B)	7075	3986	8613	35
H(35A)	8502	5246	9198	48
H(35B)	7593	5590	9058	48

H(35C)	8368	5689	8549	48
H(36A)	8953	4340	8495	73
H(36B)	8837	4765	7831	73
H(36C)	8347	4096	7885	73
H(37A)	6935	4647	7631	90
H(37B)	7412	5323	7590	90
H(37C)	6634	5225	8097	90
H(38A)	10402	3694	9459	43
H(38B)	9910	3198	8972	43
H(40A)	9759	2122	9951	94
H(40B)	10645	1774	9775	94
H(40C)	10027	2041	9184	94
H(41A)	10528	2895	10691	107
H(41B)	11312	3306	10409	107
H(41C)	11430	2557	10539	107
H(42A)	11774	3159	9222	83
H(42B)	11260	2674	8738	83
H(42C)	11875	2406	9330	83
H(43A)	7291	3835	12470	35
H(43B)	6747	3231	12711	35
H(45A)	5822	4478	11682	66
H(45B)	6498	4851	12158	66
H(45C)	5484	4910	12285	66
H(46A)	5022	3545	12115	62
H(46B)	4675	3960	12727	62
H(46C)	5185	3308	12872	62
H(47A)	6731	4502	13354	77
H(47B)	6229	3892	13628	77
H(47C)	5717	4542	13484	77
H(48A)	9015	2324	11090	53
H(48B)	8331	1755	11136	53
H(50A)	10084	1236	12172	138
H(50B)	10172	1637	11493	138
H(50C)	9506	1055	11523	138
H(51A)	9029	2695	12539	144
H(51B)	9868	2632	12089	144
H(51C)	9806	2236	12774	144

H(52A)	7998	1792	12583	202
H(52B)	8764	1327	12824	202
H(52C)	8193	1155	12169	202

Table S6.6. Torsion angles [°] for **6**.

O(10)-Ti(2)-Ti(3)-O(11)	98.76(10)
O(9)-Ti(2)-Ti(3)-O(11)	-41.91(10)
O(13)-Ti(2)-Ti(3)-O(11)	-168.97(11)
O(8)-Ti(2)-Ti(3)-O(11)	25.85(10)
O(2)-Ti(2)-Ti(3)-O(11)	-144.66(10)
O(10)-Ti(2)-Ti(3)-O(12)	-13.92(8)
O(9)-Ti(2)-Ti(3)-O(12)	-154.59(8)
O(13)-Ti(2)-Ti(3)-O(12)	78.36(8)
O(8)-Ti(2)-Ti(3)-O(12)	-86.83(8)
O(2)-Ti(2)-Ti(3)-O(12)	102.66(8)
O(10)-Ti(2)-Ti(3)-O(6)	-114.01(8)
O(9)-Ti(2)-Ti(3)-O(6)	105.32(8)
O(13)-Ti(2)-Ti(3)-O(6)	-21.73(8)
O(8)-Ti(2)-Ti(3)-O(6)	173.08(8)
O(2)-Ti(2)-Ti(3)-O(6)	2.57(8)
O(10)-Ti(2)-Ti(3)-O(8)	72.91(9)
O(9)-Ti(2)-Ti(3)-O(8)	-67.76(9)
O(13)-Ti(2)-Ti(3)-O(8)	165.19(9)
O(2)-Ti(2)-Ti(3)-O(8)	-170.51(9)
O(10)-Ti(2)-Ti(3)-O(13)	-92.28(9)
O(9)-Ti(2)-Ti(3)-O(13)	127.06(9)
O(8)-Ti(2)-Ti(3)-O(13)	-165.19(9)
O(2)-Ti(2)-Ti(3)-O(13)	24.30(9)
O(10)-Ti(2)-Ti(3)-O(4)	168.01(8)
O(9)-Ti(2)-Ti(3)-O(4)	27.34(7)
O(13)-Ti(2)-Ti(3)-O(4)	-99.72(8)
O(8)-Ti(2)-Ti(3)-O(4)	95.09(8)
O(2)-Ti(2)-Ti(3)-O(4)	-75.42(7)
O(10)-Ti(2)-Ti(3)-Ti(1)	-110.55(7)
O(9)-Ti(2)-Ti(3)-Ti(1)	108.78(6)
O(13)-Ti(2)-Ti(3)-Ti(1)	-18.27(7)
O(8)-Ti(2)-Ti(3)-Ti(1)	176.54(7)
O(2)-Ti(2)-Ti(3)-Ti(1)	6.03(6)
O(7)-Ti(1)-Ti(3)-O(11)	-113.32(10)
O(5)-Ti(1)-Ti(3)-O(11)	1.74(12)

O(13)-Ti(1)-Ti(3)-O(11)	164.08(11)
O(6)-Ti(1)-Ti(3)-O(11)	-28.12(11)
O(1)-Ti(1)-Ti(3)-O(11)	141.94(10)
O(3)-Ti(1)-Ti(3)-O(11)	68.73(10)
O(7)-Ti(1)-Ti(3)-O(12)	1.72(7)
O(5)-Ti(1)-Ti(3)-O(12)	116.78(9)
O(13)-Ti(1)-Ti(3)-O(12)	-80.89(8)
O(6)-Ti(1)-Ti(3)-O(12)	86.91(8)
O(1)-Ti(1)-Ti(3)-O(12)	-103.02(7)
O(3)-Ti(1)-Ti(3)-O(12)	-176.23(6)
O(7)-Ti(1)-Ti(3)-O(6)	-85.20(8)
O(5)-Ti(1)-Ti(3)-O(6)	29.87(10)
O(13)-Ti(1)-Ti(3)-O(6)	-167.80(9)
O(1)-Ti(1)-Ti(3)-O(6)	170.07(9)
O(3)-Ti(1)-Ti(3)-O(6)	96.86(8)
O(7)-Ti(1)-Ti(3)-O(8)	102.33(7)
O(5)-Ti(1)-Ti(3)-O(8)	-142.61(8)
O(13)-Ti(1)-Ti(3)-O(8)	19.73(8)
O(6)-Ti(1)-Ti(3)-O(8)	-172.47(8)
O(1)-Ti(1)-Ti(3)-O(8)	-2.41(7)
O(3)-Ti(1)-Ti(3)-O(8)	-75.62(6)
O(7)-Ti(1)-Ti(3)-O(13)	82.61(8)
O(5)-Ti(1)-Ti(3)-O(13)	-162.33(10)
O(6)-Ti(1)-Ti(3)-O(13)	167.80(9)
O(1)-Ti(1)-Ti(3)-O(13)	-22.13(8)
O(3)-Ti(1)-Ti(3)-O(13)	-95.34(8)
O(7)-Ti(1)-Ti(3)-O(4)	179.82(7)
O(5)-Ti(1)-Ti(3)-O(4)	-65.12(8)
O(13)-Ti(1)-Ti(3)-O(4)	97.21(8)
O(6)-Ti(1)-Ti(3)-O(4)	-94.99(8)
O(1)-Ti(1)-Ti(3)-O(4)	75.08(7)
O(3)-Ti(1)-Ti(3)-O(4)	1.87(6)
O(7)-Ti(1)-Ti(3)-Ti(2)	99.98(5)
O(5)-Ti(1)-Ti(3)-Ti(2)	-144.96(7)
O(13)-Ti(1)-Ti(3)-Ti(2)	17.37(6)
O(6)-Ti(1)-Ti(3)-Ti(2)	-174.83(7)
O(1)-Ti(1)-Ti(3)-Ti(2)	-4.76(6)

O(3)-Ti(1)-Ti(3)-Ti(2)	-77.97(4)
O(7)-Ti(1)-O(1)-C(1)	-100.9(2)
O(5)-Ti(1)-O(1)-C(1)	162.8(2)
O(13)-Ti(1)-O(1)-C(1)	-3.8(2)
O(6)-Ti(1)-O(1)-C(1)	29.8(3)
O(3)-Ti(1)-O(1)-C(1)	80.6(2)
Ti(3)-Ti(1)-O(1)-C(1)	10.0(2)
O(10)-Ti(2)-O(2)-C(1)	114.9(2)
O(9)-Ti(2)-O(2)-C(1)	-130.3(2)
O(13)-Ti(2)-O(2)-C(1)	1.0(2)
O(8)-Ti(2)-O(2)-C(1)	-37.9(4)
Ti(3)-Ti(2)-O(2)-C(1)	-14.4(2)
O(7)-Ti(1)-O(3)-C(7)	-153.8(9)
O(5)-Ti(1)-O(3)-C(7)	134.13(17)
O(13)-Ti(1)-O(3)-C(7)	-43.71(16)
O(6)-Ti(1)-O(3)-C(7)	34.25(17)
O(1)-Ti(1)-O(3)-C(7)	-131.41(17)
Ti(3)-Ti(1)-O(3)-C(7)	-4.35(16)
O(11)-Ti(3)-O(4)-C(7)	-147.02(18)
O(12)-Ti(3)-O(4)-C(7)	35.6(13)
O(6)-Ti(3)-O(4)-C(7)	-39.89(17)
O(8)-Ti(3)-O(4)-C(7)	112.09(17)
O(13)-Ti(3)-O(4)-C(7)	36.94(17)
Ti(2)-Ti(3)-O(4)-C(7)	72.31(17)
Ti(1)-Ti(3)-O(4)-C(7)	-0.78(16)
O(7)-Ti(1)-O(5)-C(13)	-165.2(2)
O(13)-Ti(1)-O(5)-C(13)	20.4(4)
O(6)-Ti(1)-O(5)-C(13)	94.7(2)
O(1)-Ti(1)-O(5)-C(13)	-71.7(2)
O(3)-Ti(1)-O(5)-C(13)	11.1(2)
Ti(3)-Ti(1)-O(5)-C(13)	76.3(2)
O(11)-Ti(3)-O(6)-C(18)	7.62(17)
O(12)-Ti(3)-O(6)-C(18)	106.36(16)
O(8)-Ti(3)-O(6)-C(18)	-141.37(16)
O(13)-Ti(3)-O(6)-C(18)	-162.80(17)
O(4)-Ti(3)-O(6)-C(18)	-76.71(16)
Ti(2)-Ti(3)-O(6)-C(18)	-149.92(15)

Ti(1)-Ti(3)-O(6)-C(18)	-155.12(19)
O(11)-Ti(3)-O(6)-Ti(1)	162.74(7)
O(12)-Ti(3)-O(6)-Ti(1)	-98.52(7)
O(8)-Ti(3)-O(6)-Ti(1)	13.75(15)
O(13)-Ti(3)-O(6)-Ti(1)	-7.67(6)
O(4)-Ti(3)-O(6)-Ti(1)	78.41(7)
Ti(2)-Ti(3)-O(6)-Ti(1)	5.20(7)
O(7)-Ti(1)-O(6)-C(18)	-100.45(15)
O(5)-Ti(1)-O(6)-C(18)	-2.75(16)
O(13)-Ti(1)-O(6)-C(18)	164.01(16)
O(1)-Ti(1)-O(6)-C(18)	129.5(2)
O(3)-Ti(1)-O(6)-C(18)	79.00(15)
Ti(3)-Ti(1)-O(6)-C(18)	156.13(18)
O(7)-Ti(1)-O(6)-Ti(3)	103.42(7)
O(5)-Ti(1)-O(6)-Ti(3)	-158.88(7)
O(13)-Ti(1)-O(6)-Ti(3)	7.88(6)
O(1)-Ti(1)-O(6)-Ti(3)	-26.6(2)
O(3)-Ti(1)-O(6)-Ti(3)	-77.13(7)
O(5)-Ti(1)-O(7)-C(23)	3.5(3)
O(13)-Ti(1)-O(7)-C(23)	-177.8(2)
O(6)-Ti(1)-O(7)-C(23)	103.8(2)
O(1)-Ti(1)-O(7)-C(23)	-90.4(2)
O(3)-Ti(1)-O(7)-C(23)	-68.1(10)
Ti(3)-Ti(1)-O(7)-C(23)	142.9(2)
O(10)-Ti(2)-O(8)-C(28)	92.68(16)
O(9)-Ti(2)-O(8)-C(28)	-23.86(17)
O(13)-Ti(2)-O(8)-C(28)	-154.77(16)
O(2)-Ti(2)-O(8)-C(28)	-115.3(3)
Ti(3)-Ti(2)-O(8)-C(28)	-145.14(19)
O(10)-Ti(2)-O(8)-Ti(3)	-122.18(7)
O(9)-Ti(2)-O(8)-Ti(3)	121.28(8)
O(13)-Ti(2)-O(8)-Ti(3)	-9.62(6)
O(2)-Ti(2)-O(8)-Ti(3)	29.9(3)
O(11)-Ti(3)-O(8)-C(28)	-15.15(16)
O(12)-Ti(3)-O(8)-C(28)	-113.20(15)
O(6)-Ti(3)-O(8)-C(28)	134.72(15)
O(13)-Ti(3)-O(8)-C(28)	156.32(16)

O(4)-Ti(3)-O(8)-C(28)	69.89(15)
Ti(2)-Ti(3)-O(8)-C(28)	147.41(18)
Ti(1)-Ti(3)-O(8)-C(28)	143.91(14)
O(11)-Ti(3)-O(8)-Ti(2)	-162.56(7)
O(12)-Ti(3)-O(8)-Ti(2)	99.39(7)
O(6)-Ti(3)-O(8)-Ti(2)	-12.68(15)
O(13)-Ti(3)-O(8)-Ti(2)	8.92(6)
O(4)-Ti(3)-O(8)-Ti(2)	-77.52(6)
Ti(1)-Ti(3)-O(8)-Ti(2)	-3.49(7)
O(10)-Ti(2)-O(9)-C(33)	121.2(3)
O(13)-Ti(2)-O(9)-C(33)	-53.1(3)
O(8)-Ti(2)-O(9)-C(33)	-133.3(3)
O(2)-Ti(2)-O(9)-C(33)	31.0(3)
Ti(3)-Ti(2)-O(9)-C(33)	-96.0(3)
O(9)-Ti(2)-O(10)-C(38)	-58.7(3)
O(13)-Ti(2)-O(10)-C(38)	116.6(3)
O(8)-Ti(2)-O(10)-C(38)	-158.8(3)
O(2)-Ti(2)-O(10)-C(38)	28.5(3)
Ti(3)-Ti(2)-O(10)-C(38)	161.4(2)
O(12)-Ti(3)-O(11)-C(43)	23.2(3)
O(6)-Ti(3)-O(11)-C(43)	121.1(3)
O(8)-Ti(3)-O(11)-C(43)	-74.6(3)
O(13)-Ti(3)-O(11)-C(43)	-132.6(4)
O(4)-Ti(3)-O(11)-C(43)	-156.7(3)
Ti(2)-Ti(3)-O(11)-C(43)	-91.0(3)
Ti(1)-Ti(3)-O(11)-C(43)	139.1(2)
O(11)-Ti(3)-O(12)-C(48)	178.7(2)
O(6)-Ti(3)-O(12)-C(48)	71.2(2)
O(8)-Ti(3)-O(12)-C(48)	-80.1(2)
O(13)-Ti(3)-O(12)-C(48)	-5.3(2)
O(4)-Ti(3)-O(12)-C(48)	-3.9(13)
Ti(2)-Ti(3)-O(12)-C(48)	-40.3(2)
Ti(1)-Ti(3)-O(12)-C(48)	32.0(2)
O(10)-Ti(2)-O(13)-Ti(1)	-119.10(12)
O(9)-Ti(2)-O(13)-Ti(1)	55.27(15)
O(8)-Ti(2)-O(13)-Ti(1)	141.72(13)
O(2)-Ti(2)-O(13)-Ti(1)	-28.36(12)

Ti(3)-Ti(2)-O(13)-Ti(1)	131.95(15)
O(10)-Ti(2)-O(13)-Ti(3)	108.96(8)
O(9)-Ti(2)-O(13)-Ti(3)	-76.67(10)
O(8)-Ti(2)-O(13)-Ti(3)	9.77(6)
O(2)-Ti(2)-O(13)-Ti(3)	-160.30(7)
O(7)-Ti(1)-O(13)-Ti(2)	122.26(12)
O(5)-Ti(1)-O(13)-Ti(2)	-63.3(3)
O(6)-Ti(1)-O(13)-Ti(2)	-140.08(13)
O(1)-Ti(1)-O(13)-Ti(2)	29.51(12)
O(3)-Ti(1)-O(13)-Ti(2)	-54.06(12)
Ti(3)-Ti(1)-O(13)-Ti(2)	-132.29(15)
O(7)-Ti(1)-O(13)-Ti(3)	-105.45(7)
O(5)-Ti(1)-O(13)-Ti(3)	69.0(3)
O(6)-Ti(1)-O(13)-Ti(3)	-7.78(6)
O(1)-Ti(1)-O(13)-Ti(3)	161.80(7)
O(3)-Ti(1)-O(13)-Ti(3)	78.23(6)
O(11)-Ti(3)-O(13)-Ti(2)	50.2(4)
O(12)-Ti(3)-O(13)-Ti(2)	-105.75(7)
O(6)-Ti(3)-O(13)-Ti(2)	159.00(8)
O(8)-Ti(3)-O(13)-Ti(2)	-9.73(6)
O(4)-Ti(3)-O(13)-Ti(2)	74.33(7)
Ti(1)-Ti(3)-O(13)-Ti(2)	151.13(10)
O(11)-Ti(3)-O(13)-Ti(1)	-101.0(4)
O(12)-Ti(3)-O(13)-Ti(1)	103.12(7)
O(6)-Ti(3)-O(13)-Ti(1)	7.86(6)
O(8)-Ti(3)-O(13)-Ti(1)	-160.86(7)
O(4)-Ti(3)-O(13)-Ti(1)	-76.80(6)
Ti(2)-Ti(3)-O(13)-Ti(1)	-151.13(10)
Ti(1)-O(1)-C(1)-O(2)	-14.3(4)
Ti(1)-O(1)-C(1)-C(2)	164.74(15)
Ti(2)-O(2)-C(1)-O(1)	16.8(4)
Ti(2)-O(2)-C(1)-C(2)	-162.24(16)
O(1)-C(1)-C(2)-C(3)	67.3(3)
O(2)-C(1)-C(2)-C(3)	-113.6(2)
C(1)-C(2)-C(3)-C(4)	60.0(3)
C(1)-C(2)-C(3)-C(6)	-62.5(3)
C(1)-C(2)-C(3)-C(5)	179.2(2)

Ti(1)-O(3)-C(7)-O(4)	5.4(3)
Ti(1)-O(3)-C(7)-C(8)	-174.33(13)
Ti(3)-O(4)-C(7)-O(3)	-2.2(3)
Ti(3)-O(4)-C(7)-C(8)	177.60(13)
O(3)-C(7)-C(8)-C(9)	103.3(2)
O(4)-C(7)-C(8)-C(9)	-76.5(2)
C(7)-C(8)-C(9)-C(12)	-57.4(3)
C(7)-C(8)-C(9)-C(10)	63.6(3)
C(7)-C(8)-C(9)-C(11)	-177.3(2)
Ti(1)-O(5)-C(13)-C(14)	173.00(17)
O(5)-C(13)-C(14)-C(17)	-61.3(3)
O(5)-C(13)-C(14)-C(15)	60.0(3)
O(5)-C(13)-C(14)-C(16)	178.7(2)
Ti(3)-O(6)-C(18)-C(19)	-96.9(2)
Ti(1)-O(6)-C(18)-C(19)	113.10(18)
O(6)-C(18)-C(19)-C(20)	-49.7(3)
O(6)-C(18)-C(19)-C(21)	72.1(2)
O(6)-C(18)-C(19)-C(22)	-168.61(19)
Ti(1)-O(7)-C(23)-C(24)	124.9(2)
O(7)-C(23)-C(24)-C(27)	-60.0(4)
O(7)-C(23)-C(24)-C(25)	60.1(4)
O(7)-C(23)-C(24)-C(26)	177.9(3)
Ti(2)-O(8)-C(28)-C(29)	-92.2(2)
Ti(3)-O(8)-C(28)-C(29)	129.85(15)
O(8)-C(28)-C(29)-C(30)	71.6(3)
O(8)-C(28)-C(29)-C(31)	-49.9(3)
O(8)-C(28)-C(29)-C(32)	-169.8(2)
Ti(2)-O(9)-C(33)-C(34)	-125.7(2)
O(9)-C(33)-C(34)-C(36)	59.4(3)
O(9)-C(33)-C(34)-C(35)	-61.7(3)
O(9)-C(33)-C(34)-C(37)	179.1(2)
Ti(2)-O(10)-C(38)-C(39)	-135.7(2)
O(10)-C(38)-C(39)-C(40)	59.8(3)
O(10)-C(38)-C(39)-C(41)	-61.0(3)
O(10)-C(38)-C(39)-C(42)	178.9(2)
Ti(3)-O(11)-C(43)-C(44)	168.38(19)
O(11)-C(43)-C(44)-C(45)	-57.3(3)

O(11)-C(43)-C(44)-C(46)	63.8(3)
O(11)-C(43)-C(44)-C(47)	-177.4(2)
Ti(3)-O(12)-C(48)-C(49)	-177.85(16)
O(12)-C(48)-C(49)-C(52)	63.3(4)
O(12)-C(48)-C(49)-C(51)	-59.7(4)
O(12)-C(48)-C(49)-C(50)	-178.2(3)

Table 1. Crystal data and structure refinement for 6a

Formula	$C_{60}H_{128}O_{24}Ti_6$
fw	1521.02
a	13.033(3) Å
b	15.667(3) Å
c	20.798(4) Å
α	69.570(13)°
β	84.748(13)°
γ	83.680(13)°
V	3948.9(14) Å^3
Z	2
Space group	$P\bar{1}$
T	158 K
λ	0.71073 Å
ρ (calcd)	1.279 g/cm^3
μ	0.644mm^{-1}
R1,wR2[I>2σ(I)]	0.0679,0.1277
R1,wR2(all data)	0.1307,0.1573

$$R1 = \sum||F_o|-|F_c||/\sum|F_o|$$

$$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$$

Table 2. Crystal data and structure refinement for 6a

Empirical formula	$C_{60}H_{128}O_{24}Ti_6$
Formula weight	1521.02
Temperature	158 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.033(3) Å α = 69.570(13)° b = 15.667(3) Å β = 84.748(13)° c = 20.798(4) Å γ = 83.680(13)°
Volume, Z	3948.9(14) $Å^3$, 2
Density (calculated)	1.279 Mg/m^3
Absorption coefficient	0.644 mm^{-1}
F(000)	1624
Crystal size	0.20 x 0.20 x 0.16 mm
θ range for data collection	2.01 to 22.50°
Limiting indices	$-13 \le h \le 14$, $-15 \le k \le 15$, $-22 \le l \le 22$
Reflections collected	10660
Independent reflections	10125 (R_{int} = 0.0371)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10124 / 0 / 811
Goodness-of-fit on F^2	1.089
Final R indices [$I>2\sigma(I)$]	R1 = 0.0679, wR2 = 0.1277
R indices (all data)	R1 = 0.1307, wR2 = 0.1573
Largest diff. peak and hole	1.031 and -0.442 $eÅ^{-3}$

$$R1 = \sum||F_o|-|F_c||/\sum|F_o|$$

$$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$$

Crystal data.

Empirical formula	$C_{60}H_{128}O_{24}Ti_6$
Formula weight	1521.02
Crystal Description	Prism
Crystal Color	Colorless
Crystal size	0.20 x 0.20 x 0.16 mm
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	a = 13.033(3) Å
	b = 15.667(3) Å
	c = 20.798(4) Å
	α = 69.570(13)°
	β = 84.748(13)°
	γ = 83.680(13)°
Volume	3948.9(14) $Å^3$
Z	2
Density (calculated)	1.279 Mg/m^3
Absorption coefficient	0.644 mm^{-1}
F(000)	1624

Data Collection and Reduction.

Diffractometer type	Siemens P4
Radiation source	rotating-anode
Monochromator type	graphite
Radiation	MoKα
Wavelength	0.71073 Å
Temperature	158 K
Cell measurement reflections	30 ($5.07^{\circ} < \theta < 10.60^{\circ}$)
Intensity measurement method	$2\theta/\omega$ scans
θ range for data collection	2.01 to 22.50°
Limiting indices	$-13 \leq h \leq 14$, $-15 \leq k \leq 15$, $-22 \leq l \leq 22$
Scan width (in ω)	1.2° plus α_1,α_2 separation
Scan speed (in ω)	3.0°/min
Reflections collected	10660
Independent reflections	10125 ($R_{int} = 0.0371$)
Observed reflections	6235 (I >2sigma(I))
Number of standards	2
Interval between standards	98
Decay of standards	none
Absorption correction	None

Unit cell refinement and data collection were carried out by use of the Siemens XSCAnS system, Version 2.10b. Data were processed with a local version of CARESS (R.W. Broach et al.), which employs a modified version of the Lehman-Larsen algorithm to obtain integrated intensities and standard deviations from the measured 96-step peak profiles.

Structure Solution and Refinement.

Structure solution method	direct methods
Refinement method	Full-matrix least-squares on F^2
Scattering Factor Source	International Tables Vol C Tables 4.2.6.8 and 6.1.1.4
Final refinement: Data	10124
Restraints	0
Parameters	811
Final R indices [$I>2\sigma(I)$]	R1 = 0.0679, wR2 = 0.1277
R indices (all data)	R1 = 0.1307, wR2 = 0.1573
Goodness-of-fit on F^2	1.089
Largest diff. peak and hole	1.031 and -0.442 $e\text{Å}^{-3}$
Maximum Δ/σ in final cycle	0.000
Mean Δ/σ in final cycle	0.000

Final weighting scheme:

calc $w=1/[\sigma^2(Fo^2)+(0.0256P)^2+22.5336P]$

where $P=(Fo^2+2Fc^2)/3$

R-factor definitions:

$R1 = \sum||F_o|-|F_c||/\sum|F_o|$

$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Structure solution, refinement, and generation of figures and tables were carried out by use of Version 5.03 of the Siemens SHELXTL program package.

Table 3. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. 6a

	x	y	z	U(eq)
Ti(1)	6797(1)	1040(1)	-44(1)	18(1)
Ti(2)	4559(1)	811(1)	267(1)	17(1)
Ti(3)	5841(1)	1036(1)	1387(1)	21(1)
O(1)	6264(4)	1990(3)	-930(2)	22(1)
O(2)	4584(4)	1735(3)	-736(2)	19(1)
O(3)	7484(4)	2117(3)	74(2)	23(1)
O(4)	6898(4)	1995(3)	1150(3)	26(1)
O(5)	7964(4)	745(3)	-470(2)	22(1)
O(6)	3303(4)	1328(3)	393(2)	23(1)
O(7)	6297(4)	348(3)	2230(2)	25(1)
O(8)	7039(3)	388(3)	913(2)	19(1)
O(9)	4825(4)	211(3)	1259(2)	18(1)
O(10)	4916(4)	1766(3)	1653(2)	28(1)
O(11)	5563(3)	1519(3)	389(2)	17(1)
O(12)	4101(3)	-225(3)	102(2)	14(1)
C(1)	5327(7)	2191(5)	-1071(4)	25(2)
C(2)	5072(6)	3035(5)	-1681(4)	28(2)
C(3)	5271(7)	3927(5)	-1581(4)	34(2)
C(4)	4796(7)	3951(6)	-898(4)	41(2)
C(5)	6423(7)	4047(6)	-1628(4)	40(2)
C(6)	4782(8)	4711(5)	-2167(4)	50(3)
C(7)	7481(6)	2307(5)	617(4)	28(2)
C(8)	8279(6)	2938(5)	635(4)	31(2)
C(9)	7847(7)	3878(5)	658(4)	34(2)
C(10)	7318(7)	3787(6)	1356(4)	43(2)
C(11)	8720(8)	4488(6)	523(5)	57(3)
C(12)	7091(8)	4311(6)	96(5)	58(3)
C(13)	8891(6)	929(6)	-877(4)	31(2)
C(14)	8645(7)	1542(6)	-1595(4)	53(3)
C(15)	9618(6)	1323(6)	-553(5)	39(2)
C(16)	2297(6)	1636(6)	153(4)	31(2)

C(17)	1534(6)	1516(6)	755(5)	46(2)
C(18)	2263(7)	2579(6)	-332(5)	56(3)
C(19)	6163(7)	378(6)	2901(4)	38(2)
C(20)	6767(9)	1128(7)	2939(5)	67(3)
C(21)	6534(8)	-529(7)	3409(4)	60(3)
C(22)	7932(6)	-239(5)	1172(4)	27(2)
C(23)	8616(6)	174(6)	1526(4)	34(2)
C(24)	7586(7)	-1151(5)	1632(4)	38(2)
C(25)	4134(6)	-386(5)	1738(4)	28(2)
C(26)	4757(6)	-1191(5)	2237(4)	34(2)
C(27)	3402(6)	125(6)	2121(4)	35(2)
C(28)	4178(10)	2473(7)	1621(5)	73(4)
C(29)	4094(11)	3183(8)	1006(6)	106(5)
C(30)	4161(10)	2737(8)	2239(5)	83(4)
Ti(4)	9048(1)	4879(1)	4617(1)	23(1)
Ti(5)	10727(1)	3528(1)	4432(1)	25(1)
Ti(6)	8551(1)	2859(1)	4969(1)	25(1)
O(13)	10922(4)	4545(4)	3492(3)	27(1)
O(14)	9751(4)	5619(3)	3674(2)	26(1)
O(15)	10577(4)	2678(3)	3859(3)	30(1)
O(16)	9068(4)	2135(3)	4340(3)	29(1)
O(17)	7873(4)	5533(3)	4310(3)	29(1)
O(18)	12072(4)	3161(4)	4449(3)	33(1)
O(19)	8151(4)	1868(3)	5664(3)	30(1)
O(20)	7366(4)	3156(3)	4551(3)	31(1)
O(21)	8418(4)	3870(3)	5388(2)	25(1)
O(22)	10149(4)	2602(3)	5217(2)	26(1)
O(23)	9251(4)	3889(3)	4278(2)	23(1)
O(24)	9408(4)	5586(3)	5148(2)	24(1)
C(31)	10386(7)	5300(5)	3295(4)	28(2)
C(32)	10538(6)	5859(5)	2539(4)	32(2)
C(33)	10208(7)	5404(5)	2051(4)	35(2)
C(34)	10203(8)	6148(6)	1331(4)	52(3)
C(35)	10966(7)	4608(6)	2038(4)	44(2)
C(36)	9113(7)	5105(7)	2261(5)	47(2)
C(37)	9882(6)	2124(5)	3964(4)	29(2)
C(38)	10028(7)	1381(5)	3649(4)	38(2)
C(39)	10382(6)	1628(5)	2891(4)	31(2)
C(40)	11476(7)	1894(7)	2741(5)	53(3)

C(41)	10312(7)	788(6)	2690(5)	46(2)
C(42)	9653(7)	2396(6)	2466(5)	54(3)
C(43)	7366(6)	6418(6)	3975(5)	40(2)
C(44)	6314(8)	6486(8)	4265(6)	86(4)
C(45)	7417(9)	6600(7)	3219(5)	69(3)
C(46)	12930(8)	2863(7)	4082(6)	76(4)
C(47)	13417(7)	3640(7)	3601(5)	60(3)
C(48)	13432(9)	2027(8)	4446(6)	97(5)
C(49)	7483(7)	1147(6)	5874(5)	46(2)
C(50)	6397(7)	1505(7)	5927(5)	60(3)
C(51)	7645(8)	629(6)	5369(5)	60(3)
C(52)	6937(7)	3721(6)	3925(4)	40(2)
C(53)	6995(11)	3208(9)	3441(6)	106(5)
C(54)	5876(8)	4093(9)	4064(5)	85(4)
C(55)	7715(6)	3996(5)	5942(4)	28(2)
C(56)	6614(6)	4124(6)	5751(4)	42(2)
C(57)	7904(7)	3223(5)	6600(4)	38(2)
C(58)	10724(7)	1886(5)	5723(4)	32(2)
C(59)	10722(7)	990(5)	5597(5)	41(2)
C(60)	10336(7)	1845(6)	6431(4)	42(2)

Table 4. Bond lengths [Å] and angles [°] for 6a

Ti(1)-O(5)	1.787(5)	Ti(1)-O(12)#1	1.864(5)
Ti(1)-O(8)	1.932(5)	Ti(1)-O(11)	1.975(5)
Ti(1)-O(1)	2.047(5)	Ti(1)-O(3)	2.090(5)
Ti(1)-Ti(2)	2.963(2)	Ti(1)-Ti(3)	3.117(2)
Ti(2)-O(6)	1.784(5)	Ti(2)-O(11)	1.893(5)
Ti(2)-O(12)	1.936(4)	Ti(2)-O(9)	1.992(5)
Ti(2)-O(2)	2.082(5)	Ti(2)-O(12)#1	2.090(5)
Ti(2)-Ti(3)	3.124(2)	Ti(2)-Ti(2)#1	3.177(3)
Ti(3)-O(10)	1.757(5)	Ti(3)-O(7)	1.823(5)
Ti(3)-O(11)	1.998(5)	Ti(3)-O(9)	2.044(5)
Ti(3)-O(4)	2.052(5)	Ti(3)-O(8)	2.123(5)
O(1)-C(1)	1.262(9)	O(2)-C(1)	1.271(9)
O(3)-C(7)	1.263(9)	O(4)-C(7)	1.264(9)
O(5)-C(13)	1.406(8)	O(6)-C(16)	1.420(9)
O(7)-C(19)	1.408(9)	O(8)-C(22)	1.449(9)
O(9)-C(25)	1.431(8)	O(10)-C(28)	1.372(11)
O(12)-Ti(1)#1	1.864(5)	O(12)-Ti(2)#1	2.090(5)
C(1)-C(2)	1.509(10)	C(2)-C(3)	1.534(10)
C(3)-C(4)	1.509(11)	C(3)-C(5)	1.523(11)
C(3)-C(6)	1.525(11)	C(7)-C(8)	1.524(10)
C(8)-C(9)	1.533(11)	C(9)-C(11)	1.510(11)
C(9)-C(10)	1.516(11)	C(9)-C(12)	1.519(12)
C(13)-C(15)	1.507(11)	C(13)-C(14)	1.508(11)
C(16)-C(18)	1.468(11)	C(16)-C(17)	1.497(11)
C(19)-C(21)	1.505(12)	C(19)-C(20)	1.512(12)
C(22)-C(24)	1.507(10)	C(22)-C(23)	1.528(10)
C(25)-C(27)	1.526(10)	C(25)-C(26)	1.531(10)
C(28)-C(29)	1.374(14)	C(28)-C(30)	1.480(12)

Ti(4)-O(17)	1.783(5)	Ti(4)-O(23)	1.900(5)
Ti(4)-O(24)	1.932(5)	Ti(4)-O(21)	2.005(5)
Ti(4)-O(14)	2.085(5)	Ti(4)-O(24)#2	2.104(5)
Ti(4)-Ti(5)	2.968(2)	Ti(4)-Ti(6)	3.117(2)
Ti(4)-Ti(4)#2	3.193(3)	Ti(5)-O(18)	1.783(5)
Ti(5)-O(24)#2	1.866(5)	Ti(5)-O(22)	1.924(5)
Ti(5)-O(23)	1.967(5)	Ti(5)-O(13)	2.061(5)
Ti(5)-O(15)	2.109(5)	Ti(5)-Ti(6)	3.106(2)
Ti(6)-O(20)	1.778(5)	Ti(6)-O(19)	1.801(5)
Ti(6)-O(23)	1.991(5)	Ti(6)-O(16)	2.039(5)
Ti(6)-O(21)	2.043(5)	Ti(6)-O(22)	2.153(5)

O(13)-C(31)	1.260(9)	O(14)-C(31)	1.273(9)
O(15)-C(37)	1.275(9)	O(16)-C(37)	1.261(9)
O(17)-C(43)	1.433(9)	O(18)-C(46)	1.424(10)
O(19)-C(49)	1.424(9)	O(20)-C(52)	1.419(9)
O(21)-C(55)	1.459(9)	O(22)-C(58)	1.435(9)
O(24)-Ti(5)#2	1.866(5)	O(24)-Ti(4)#2	2.104(5)
C(31)-C(32)	1.516(10)	C(32)-C(33)	1.541(10)
C(33)-C(35)	1.511(12)	C(33)-C(36)	1.528(11)
C(33)-C(34)	1.543(11)	C(37)-C(38)	1.510(11)
C(38)-C(39)	1.526(11)	C(39)-C(40)	1.504(11)
C(39)-C(42)	1.514(11)	C(39)-C(41)	1.528(11)
C(43)-C(44)	1.455(12)	C(43)-C(45)	1.493(12)
C(46)-C(48)	1.388(13)	C(46)-C(47)	1.446(13)
C(49)-C(50)	1.472(12)	C(49)-C(51)	1.524(12)
C(52)-C(53)	1.484(12)	C(52)-C(54)	1.485(12)
C(55)-C(56)	1.497(11)	C(55)-C(57)	1.497(11)
C(58)-C(60)	1.495(11)	C(58)-C(59)	1.515(10)

O(5)-Ti(1)-O(12)#1	103.0(2)	O(5)-Ti(1)-O(8)	102.6(2)
O(12)#1-Ti(1)-O(8)	94.5(2)	O(5)-Ti(1)-O(11)	173.0(2)
O(12)#1-Ti(1)-O(11)	83.2(2)	O(8)-Ti(1)-O(11)	80.0(2)
O(5)-Ti(1)-O(1)	93.0(2)	O(12)#1-Ti(1)-O(1)	89.9(2)
O(8)-Ti(1)-O(1)	162.4(2)	O(11)-Ti(1)-O(1)	83.5(2)
O(5)-Ti(1)-O(3)	90.0(2)	O(12)#1-Ti(1)-O(3)	166.5(2)
O(8)-Ti(1)-O(3)	86.3(2)	O(11)-Ti(1)-O(3)	83.7(2)
O(1)-Ti(1)-O(3)	85.6(2)	O(6)-Ti(2)-O(11)	108.9(2)
O(6)-Ti(2)-O(12)	96.6(2)	O(11)-Ti(2)-O(12)	154.5(2)
O(6)-Ti(2)-O(9)	96.3(2)	O(11)-Ti(2)-O(9)	77.6(2)
O(12)-Ti(2)-O(9)	98.5(2)	O(6)-Ti(2)-O(2)	87.4(2)
O(11)-Ti(2)-O(2)	84.1(2)	O(12)-Ti(2)-O(2)	99.1(2)
O(9)-Ti(2)-O(2)	161.5(2)	O(6)-Ti(2)-O(12)#1	166.5(2)
O(11)-Ti(2)-O(12)#1	79.4(2)	O(12)-Ti(2)-O(12)#1	75.9(2)
O(9)-Ti(2)-O(12)#1	96.0(2)	O(2)-Ti(2)-O(12)#1	82.8(2)
O(10)-Ti(3)-O(7)	97.7(2)	O(10)-Ti(3)-O(11)	97.6(2)
O(7)-Ti(3)-O(11)	164.3(2)	O(10)-Ti(3)-O(9)	96.7(2)
O(7)-Ti(3)-O(9)	101.0(2)	O(11)-Ti(3)-O(9)	74.0(2)
O(10)-Ti(3)-O(4)	90.4(2)	O(7)-Ti(3)-O(4)	96.6(2)
O(11)-Ti(3)-O(4)	86.5(2)	O(9)-Ti(3)-O(4)	160.0(2)
O(10)-Ti(3)-O(8)	169.0(2)	O(7)-Ti(3)-O(8)	90.2(2)
O(11)-Ti(3)-O(8)	75.1(2)	O(9)-Ti(3)-O(8)	89.3(2)
O(4)-Ti(3)-O(8)	81.0(2)	Ti(1)-Ti(3)-Ti(2)	56.67(4)
Ti(1)-Ti(2)-Ti(3)	61.55(4)	Ti(2)-Ti(1)-Ti(3)	61.78(4)

C(1)-O(1)-Ti(1)	125.6(5)	C(1)-O(2)-Ti(2)	127.7(5)
C(7)-O(3)-Ti(1)	127.0(5)	C(7)-O(4)-Ti(3)	130.6(5)
C(13)-O(5)-Ti(1)	154.7(5)	C(16)-O(6)-Ti(2)	148.0(5)
C(19)-O(7)-Ti(3)	136.8(5)	C(22)-O(8)-Ti(1)	125.6(4)
C(22)-O(8)-Ti(3)	133.2(4)	Ti(1)-O(8)-Ti(3)	100.4(2)
C(25)-O(9)-Ti(2)	122.7(4)	C(25)-O(9)-Ti(3)	131.5(4)
Ti(2)-O(9)-Ti(3)	101.4(2)	C(28)-O(10)-Ti(3)	160.2(6)
Ti(2)-O(11)-Ti(1)	100.0(2)	Ti(2)-O(11)-Ti(3)	106.8(2)
Ti(1)-O(11)-Ti(3)	103.4(2)	Ti(1)#1-O(12)-Ti(2)	159.0(3)
Ti(1)#1-O(12)-Ti(2)#1	96.9(2)	Ti(2)-O(12)-Ti(2)#1	104.1(2)

O(1)-C(1)-O(2)	124.7(7)	O(1)-C(1)-C(2)	117.5(7)
O(2)-C(1)-C(2)	117.7(7)	C(1)-C(2)-C(3)	113.6(6)
C(4)-C(3)-C(5)	109.7(7)	C(4)-C(3)-C(6)	110.3(7)
C(5)-C(3)-C(6)	107.6(7)	C(4)-C(3)-C(2)	110.4(6)
C(5)-C(3)-C(2)	111.6(7)	C(6)-C(3)-C(2)	107.1(7)
O(4)-C(7)-O(3)	125.6(7)	O(4)-C(7)-C(8)	117.5(7)
O(3)-C(7)-C(8)	116.9(7)	C(7)-C(8)-C(9)	115.8(7)
C(11)-C(9)-C(10)	109.2(7)	C(11)-C(9)-C(12)	108.2(7)
C(10)-C(9)-C(12)	110.6(8)	C(11)-C(9)-C(8)	109.4(7)
C(10)-C(9)-C(8)	110.3(7)	C(12)-C(9)-C(8)	109.2(7)
O(5)-C(13)-C(15)	110.7(6)	O(5)-C(13)-C(14)	109.2(6)
C(15)-C(13)-C(14)	112.9(7)	O(6)-C(16)-C(18)	111.3(7)
O(6)-C(16)-C(17)	109.2(6)	C(18)-C(16)-C(17)	113.0(7)
O(7)-C(19)-C(21)	110.0(7)	O(7)-C(19)-C(20)	108.7(7)
C(21)-C(19)-C(20)	110.4(8)	O(8)-C(22)-C(24)	109.9(6)
O(8)-C(22)-C(23)	110.5(6)	C(24)-C(22)-C(23)	112.9(7)
O(9)-C(25)-C(27)	111.2(6)	O(9)-C(25)-C(26)	109.6(6)
C(27)-C(25)-C(26)	111.2(6)	O(10)-C(28)-C(29)	118.1(9)
O(10)-C(28)-C(30)	110.8(9)	C(29)-C(28)-C(30)	115.8(10)

O(17)-Ti(4)-O(23)	108.5(2)	O(17)-Ti(4)-O(24)	97.6(2)
O(23)-Ti(4)-O(24)	153.8(2)	O(17)-Ti(4)-O(21)	97.4(2)
O(23)-Ti(4)-O(21)	77.7(2)	O(24)-Ti(4)-O(21)	98.1(2)
O(17)-Ti(4)-O(14)	86.8(2)	O(23)-Ti(4)-O(14)	84.6(2)
O(24)-Ti(4)-O(14)	98.3(2)	O(21)-Ti(4)-O(14)	162.3(2)
O(17)-Ti(4)-O(24)#2	165.9(2)	O(23)-Ti(4)-O(24)#2	79.2(2)
O(24)-Ti(4)-O(24)#2	75.5(2)	O(21)-Ti(4)-O(24)#2	95.7(2)
O(14)-Ti(4)-O(24)#2	82.1(2)	O(18)-Ti(5)-O(24)#2	104.2(2)
O(18)-Ti(5)-O(22)	102.6(2)	O(24)#2-Ti(5)-O(22)	94.5(2)
O(18)-Ti(5)-O(23)	170.9(2)	O(24)#2-Ti(5)-O(23)	83.6(2)
O(22)-Ti(5)-O(23)	81.1(2)	O(18)-Ti(5)-O(13)	92.3(2)
O(24)#2-Ti(5)-O(13)	89.1(2)	O(22)-Ti(5)-O(13)	163.2(2)
O(23)-Ti(5)-O(13)	83.1(2)	O(18)-Ti(5)-O(15)	87.4(2)
O(24)#2-Ti(5)-O(15)	167.4(2)	O(22)-Ti(5)-O(15)	87.6(2)
O(23)-Ti(5)-O(15)	84.4(2)	O(13)-Ti(5)-O(15)	85.5(2)
O(20)-Ti(6)-O(19)	97.1(2)	O(20)-Ti(6)-O(23)	93.7(2)
O(19)-Ti(6)-O(23)	169.2(2)	O(20)-Ti(6)-O(16)	89.1(2)
O(19)-Ti(6)-O(16)	93.8(2)	O(23)-Ti(6)-O(16)	85.7(2)
O(20)-Ti(6)-O(21)	97.6(2)	O(19)-Ti(6)-O(21)	104.3(2)
O(23)-Ti(6)-O(21)	74.8(2)	O(16)-Ti(6)-O(21)	159.7(2)
O(20)-Ti(6)-O(22)	165.7(2)	O(19)-Ti(6)-O(22)	94.1(2)
O(23)-Ti(6)-O(22)	75.1(2)	O(16)-Ti(6)-O(22)	81.4(2)
O(21)-Ti(6)-O(22)	88.1(2)	Ti(4)-Ti(5)-Ti(6)	61.70(5)
Ti(5)-Ti(6)-Ti(4)	56.96(4)	Ti(5)-Ti(4)-Ti(6)	61.34(5)

C(31)-O(13)-Ti(5)	125.3(5)	C(31)-O(14)-Ti(4)	126.8(5)
C(37)-O(15)-Ti(5)	126.0(5)	C(37)-O(16)-Ti(6)	133.4(5)
C(43)-O(17)-Ti(4)	147.2(5)	C(46)-O(18)-Ti(5)	144.6(7)
C(49)-O(19)-Ti(6)	145.3(5)	C(52)-O(20)-Ti(6)	141.6(5)
C(55)-O(21)-Ti(4)	125.1(4)	C(55)-O(21)-Ti(6)	130.0(4)
Ti(4)-O(21)-Ti(6)	100.7(2)	C(58)-O(22)-Ti(5)	125.9(5)
C(58)-O(22)-Ti(6)	134.1(5)	Ti(5)-O(22)-Ti(6)	99.1(2)
Ti(4)-O(23)-Ti(5)	100.2(2)	Ti(4)-O(23)-Ti(6)	106.4(2)
Ti(5)-O(23)-Ti(6)	103.4(2)	Ti(5)#2-O(24)-Ti(4)	158.8(3)
Ti(5)#2-O(24)-Ti(4)#2	96.6(2)	Ti(4)-O(24)-Ti(4)#2	104.5(2)

O(13)-C(31)-O(14)	125.6(7)	O(13)-C(31)-C(32)	115.4(8)
O(14)-C(31)-C(32)	119.0(7)	C(31)-C(32)-C(33)	114.1(6)
C(35)-C(33)-C(36)	111.2(7)	C(35)-C(33)-C(32)	110.9(7)
C(36)-C(33)-C(32)	110.2(7)	C(35)-C(33)-C(34)	109.7(7)
C(36)-C(33)-C(34)	108.7(7)	C(32)-C(33)-C(34)	106.0(6)
O(16)-C(37)-O(15)	123.8(7)	O(16)-C(37)-C(38)	116.3(7)
O(15)-C(37)-C(38)	119.9(7)	C(37)-C(38)-C(39)	118.9(7)
C(40)-C(39)-C(42)	110.0(8)	C(40)-C(39)-C(38)	113.2(7)
C(42)-C(39)-C(38)	109.2(7)	C(40)-C(39)-C(41)	108.5(7)
C(42)-C(39)-C(41)	108.3(7)	C(38)-C(39)-C(41)	107.4(7)
O(17)-C(43)-C(44)	110.6(7)	O(17)-C(43)-C(45)	109.0(7)
C(44)-C(43)-C(45)	113.0(9)	C(48)-C(46)-O(18)	114.8(9)
C(48)-C(46)-C(47)	125.9(10)	O(18)-C(46)-C(47)	110.3(8)
O(19)-C(49)-C(50)	110.8(7)	O(19)-C(49)-C(51)	109.0(7)
C(50)-C(49)-C(51)	111.6(8)	O(20)-C(52)-C(53)	109.8(8)
O(20)-C(52)-C(54)	109.8(7)	C(53)-C(52)-C(54)	114.0(9)
O(21)-C(55)-C(56)	110.9(6)	O(21)-C(55)-C(57)	110.3(6)
C(56)-C(55)-C(57)	112.8(7)	O(22)-C(58)-C(60)	110.5(6)
O(22)-C(58)-C(59)	110.2(6)	C(60)-C(58)-C(59)	114.0(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+2,-y+1,-z+1

Table 5. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 6a

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ti(1)	20(1)	18(1)	17(1)	-7(1)	0(1)	-3(1)
Ti(2)	17(1)	17(1)	18(1)	-8(1)	0(1)	-1(1)
Ti(3)	22(1)	24(1)	19(1)	-10(1)	0(1)	-4(1)
O(1)	24(3)	21(3)	16(3)	-1(2)	0(2)	-3(2)
O(2)	19(3)	18(3)	16(3)	-2(2)	-3(2)	0(2)
O(3)	24(3)	23(3)	26(3)	-11(2)	-3(2)	-9(2)
O(4)	27(3)	31(3)	24(3)	-15(3)	2(3)	-10(3)
O(5)	22(3)	23(3)	21(3)	-7(2)	-1(2)	-4(2)
O(6)	23(3)	19(3)	28(3)	-8(2)	1(2)	1(2)
O(7)	33(3)	31(3)	12(3)	-7(2)	-1(2)	-6(3)
O(8)	16(3)	25(3)	16(3)	-8(2)	-1(2)	-3(2)
O(9)	22(3)	21(3)	14(3)	-6(2)	-3(2)	-8(2)
O(10)	31(3)	26(3)	27(3)	-11(3)	2(3)	2(3)
O(11)	19(3)	16(3)	17(3)	-8(2)	2(2)	-5(2)
O(12)	18(3)	14(3)	10(3)	-3(2)	1(2)	-3(2)
C(1)	45(6)	18(4)	16(4)	-11(4)	1(4)	-2(4)
C(2)	35(5)	24(5)	15(4)	5(3)	-2(4)	-2(4)
C(3)	53(6)	13(4)	30(5)	0(4)	-2(4)	-3(4)
C(4)	52(6)	27(5)	49(6)	-20(4)	2(5)	1(4)
C(5)	55(6)	28(5)	39(5)	-11(4)	-2(5)	-11(5)
C(6)	70(7)	23(5)	44(6)	6(4)	-15(5)	1(5)
C(7)	37(5)	17(4)	35(5)	-13(4)	-11(4)	-2(4)
C(8)	25(5)	37(5)	38(5)	-20(4)	0(4)	-14(4)
C(9)	42(5)	23(5)	38(5)	-10(4)	-7(4)	-7(4)
C(10)	66(7)	27(5)	40(6)	-18(4)	-4(5)	-3(5)
C(11)	70(7)	51(7)	65(7)	-33(6)	6(6)	-36(6)
C(12)	80(8)	45(6)	50(6)	-14(5)	-14(6)	-11(6)
C(13)	21(5)	36(5)	31(5)	-7(4)	9(4)	-6(4)
C(14)	49(6)	60(7)	32(6)	3(5)	9(5)	-7(5)
C(15)	28(5)	31(5)	57(6)	-14(5)	3(4)	-5(4)
C(16)	24(5)	37(5)	36(5)	-19(4)	-10(4)	5(4)
C(17)	21(5)	63(7)	60(6)	-31(5)	1(5)	7(5)
C(18)	41(6)	57(7)	57(7)	-5(6)	-8(5)	15(5)
C(19)	40(5)	51(6)	28(5)	-17(4)	-5(4)	-8(5)
C(20)	108(10)	67(8)	36(6)	-26(6)	-16(6)	-9(7)
C(21)	85(8)	68(7)	25(5)	-8(5)	-15(5)	-14(6)
C(22)	28(5)	32(5)	21(4)	-9(4)	2(4)	2(4)
C(23)	28(5)	48(6)	26(5)	-15(4)	-10(4)	5(4)
C(24)	44(6)	30(5)	28(5)	0(4)	-6(4)	10(4)
C(25)	40(5)	24(5)	18(4)	-4(4)	5(4)	-16(4)
C(26)	49(6)	32(5)	24(5)	-11(4)	5(4)	-16(4)
C(27)	38(5)	42(5)	29(5)	-18(4)	11(4)	-11(4)
C(28)	113(10)	60(8)	49(7)	-30(6)	-23(7)	34(7)
C(29)	172(14)	65(8)	59(8)	-19(7)	-11(9)	73(9)
C(30)	121(11)	75(8)	70(8)	-58(7)	-10(7)	30(8)
Ti(4)	27(1)	19(1)	23(1)	-5(1)	-1(1)	-4(1)
Ti(5)	30(1)	23(1)	24(1)	-9(1)	0(1)	-6(1)

Ti(6)	29(1)	24(1)	22(1)	-8(1)	1(1)	-7(1)
O(13)	25(3)	27(3)	28(3)	-7(3)	-2(3)	-6(3)
O(14)	32(3)	25(3)	21(3)	-6(3)	1(3)	-10(3)
O(15)	37(3)	29(3)	28(3)	-14(3)	6(3)	-9(3)
O(16)	34(3)	33(3)	24(3)	-14(3)	4(3)	-9(3)
O(17)	36(3)	21(3)	27(3)	-4(2)	-1(3)	0(3)
O(18)	27(3)	34(3)	37(3)	-12(3)	3(3)	-2(3)
O(19)	34(3)	24(3)	32(3)	-9(3)	4(3)	-11(3)
O(20)	40(3)	32(3)	25(3)	-12(3)	-6(3)	-8(3)
O(21)	25(3)	32(3)	21(3)	-13(2)	4(2)	-9(2)
O(22)	35(3)	18(3)	25(3)	-6(2)	0(3)	-3(2)
O(23)	28(3)	22(3)	15(3)	-1(2)	-4(2)	-2(2)
O(24)	27(3)	19(3)	25(3)	-8(2)	-3(2)	-2(2)
C(31)	40(5)	24(5)	25(5)	-6(4)	-14(4)	-15(4)
C(32)	42(5)	27(5)	22(4)	0(4)	-9(4)	-9(4)
C(33)	58(6)	31(5)	15(4)	-5(4)	-10(4)	-8(5)
C(34)	84(8)	52(6)	21(5)	-7(5)	-7(5)	-18(6)
C(35)	63(7)	38(6)	36(5)	-17(5)	-3(5)	-8(5)
C(36)	41(6)	61(7)	49(6)	-27(5)	-10(5)	-12(5)
C(37)	29(5)	33(5)	27(5)	-12(4)	-2(4)	-5(4)
C(38)	57(6)	26(5)	39(5)	-18(4)	-3(5)	-8(4)
C(39)	34(5)	34(5)	34(5)	-21(4)	0(4)	-5(4)
C(40)	57(7)	60(7)	54(6)	-33(5)	5(5)	-15(5)
C(41)	49(6)	52(6)	47(6)	-31(5)	9(5)	-13(5)
C(42)	61(7)	48(6)	53(6)	-16(5)	-14(5)	3(5)
C(43)	33(5)	25(5)	54(6)	-4(4)	-11(5)	4(4)
C(44)	60(8)	82(9)	82(9)	0(7)	11(7)	31(7)
C(45)	83(8)	56(7)	40(6)	8(5)	2(6)	20(6)
C(46)	44(7)	58(8)	100(9)	-8(7)	35(7)	4(6)
C(47)	48(6)	72(8)	57(7)	-22(6)	19(5)	-9(6)
C(48)	90(10)	66(8)	97(10)	-2(7)	25(8)	40(7)
C(49)	49(6)	36(6)	46(6)	-4(5)	8(5)	-20(5)
C(50)	50(7)	80(8)	55(7)	-28(6)	25(5)	-41(6)
C(51)	69(7)	42(6)	79(8)	-29(6)	2(6)	-21(5)
C(52)	35(6)	45(6)	39(6)	-10(5)	-9(4)	-9(4)
C(53)	138(13)	125(12)	80(9)	-76(9)	-61(9)	68(10)
C(54)	60(8)	140(12)	44(7)	-26(7)	-24(6)	38(8)
C(55)	34(5)	23(5)	33(5)	-18(4)	-2(4)	-8(4)
C(56)	33(5)	51(6)	39(5)	-12(5)	3(4)	-7(5)
C(57)	58(6)	35(5)	28(5)	-20(4)	9(4)	-16(5)
C(58)	40(5)	20(5)	29(5)	0(4)	-9(4)	-3(4)
C(59)	50(6)	21(5)	51(6)	-9(4)	-13(5)	-4(4)
C(60)	54(6)	37(5)	25(5)	0(4)	-5(4)	5(5)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 6a

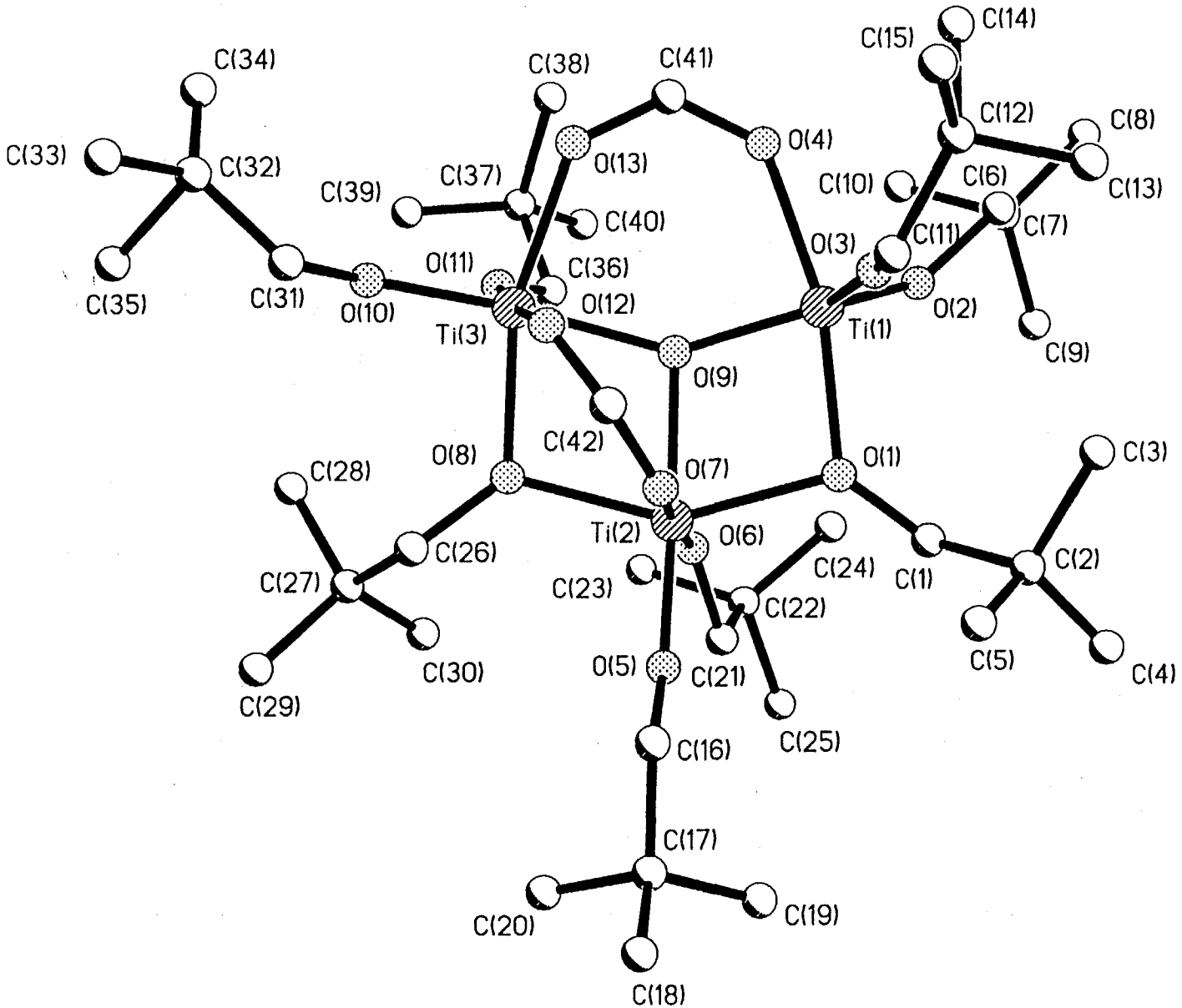
	x	y	z	U(eq)
H(2A)	4334(6)	3061(5)	-1771(4)	33
H(2B)	5490(6)	2987(5)	-2090(4)	33
H(4A)	4055(7)	3873(6)	-869(4)	62
H(4B)	4893(7)	4539(6)	-854(4)	62
H(4C)	5131(7)	3455(6)	-526(4)	62
H(5A)	6729(7)	4031(6)	-2072(4)	61
H(5B)	6760(7)	3551(6)	-1257(4)	61
H(5C)	6521(7)	4635(6)	-1585(4)	61
H(6A)	5096(8)	4689(5)	-2608(4)	74
H(6B)	4896(8)	5295(5)	-2121(4)	74
H(6C)	4037(8)	4655(5)	-2148(4)	74
H(8A)	8760(6)	3030(5)	224(4)	37
H(8B)	8687(6)	2626(5)	1044(4)	37
H(10A)	6751(7)	3391(6)	1446(4)	64
H(10B)	7044(7)	4392(6)	1363(4)	64
H(10C)	7820(7)	3517(6)	1711(4)	64
H(11A)	9064(8)	4549(6)	72(5)	85
H(11B)	9220(8)	4218(6)	879(5)	85
H(11C)	8444(8)	5092(6)	530(5)	85
H(12A)	6517(8)	3925(6)	174(5)	87
H(12B)	7447(8)	4370(6)	-352(5)	87
H(12C)	6822(8)	4918(6)	102(5)	87
H(13A)	9231(6)	337(6)	-903(4)	37
H(14A)	8172(7)	1254(6)	-1780(4)	79
H(14B)	9285(7)	1640(6)	-1888(4)	79
H(14C)	8319(7)	2131(6)	-1583(4)	79
H(15A)	9751(6)	899(6)	-89(5)	58
H(15B)	9304(6)	1909(6)	-526(5)	58
H(15C)	10271(6)	1419(6)	-832(5)	58
H(16A)	2122(6)	1237(6)	-99(4)	37
H(17A)	1591(6)	877(6)	1060(5)	69
H(17B)	833(6)	1683(6)	592(5)	69
H(17C)	1679(6)	1910(6)	1006(5)	69
H(18A)	2776(7)	2618(6)	-714(5)	84
H(18B)	2418(7)	2989(6)	-96(5)	84
H(18C)	1572(7)	2761(6)	-510(5)	84
H(19A)	5413(7)	516(6)	3009(4)	46
H(20A)	6517(9)	1714(7)	2606(5)	101
H(20B)	7503(9)	996(7)	2833(5)	101
H(20C)	6673(9)	1161(7)	3403(5)	101
H(21A)	6136(8)	-1008(7)	3379(4)	90
H(21B)	6439(8)	-503(7)	3875(4)	90
H(21C)	7269(8)	-668(7)	3305(4)	90
H(22A)	8346(6)	-333(5)	769(4)	33
H(23A)	8817(6)	764(6)	1204(4)	51
H(23B)	9237(6)	-241(6)	1671(4)	51
H(23C)	8232(6)	263(6)	1928(4)	51
H(24A)	7151(7)	-1383(5)	1380(4)	56

H(24B)	7189(7)	-1080(5)	2036(4)	56
H(24C)	8193(7)	-1584(5)	1779(4)	56
H(25A)	3710(6)	-632(5)	1475(4)	33
H(26A)	5220(6)	-1506(5)	1977(4)	51
H(26B)	4284(6)	-1618(5)	2546(4)	51
H(26C)	5167(6)	-965(5)	2506(4)	51
H(27A)	3014(6)	636(6)	1790(4)	52
H(27B)	3802(6)	360(6)	2390(4)	52
H(27C)	2918(6)	-293(6)	2430(4)	52
H(28A)	3514(10)	2183(7)	1679(5)	88
H(29A)	4113(11)	2938(8)	631(6)	158
H(29B)	4670(11)	3565(8)	934(6)	158
H(29C)	3438(11)	3552(8)	1016(6)	158
H(30A)	4225(10)	2186(8)	2648(5)	124
H(30B)	3507(10)	3094(8)	2280(5)	124
H(30C)	4739(10)	3107(8)	2198(5)	124
H(32A)	11278(6)	5971(5)	2433(4)	38
H(32B)	10137(6)	6459(5)	2449(4)	38
H(34A)	9710(8)	6663(6)	1342(4)	79
H(34B)	9999(8)	5893(6)	998(4)	79
H(34C)	10896(8)	6359(6)	1197(4)	79
H(35A)	11660(7)	4818(6)	1902(4)	67
H(35B)	10760(7)	4349(6)	1707(4)	67
H(35C)	10969(7)	4138(6)	2497(4)	67
H(36A)	8638(7)	5634(7)	2265(5)	71
H(36B)	9104(7)	4639(7)	2721(5)	71
H(36C)	8895(7)	4850(7)	1932(5)	71
H(38A)	9363(7)	1103(5)	3715(4)	46
H(38B)	10537(7)	901(5)	3917(4)	46
H(40A)	11943(7)	1394(7)	3018(5)	79
H(40B)	11529(7)	2444(7)	2854(5)	79
H(40C)	11670(7)	2018(7)	2252(5)	79
H(41A)	9602(7)	606(6)	2785(5)	69
H(41B)	10785(7)	285(6)	2958(5)	69
H(41C)	10503(7)	934(6)	2199(5)	69
H(42A)	8943(7)	2217(6)	2567(5)	81
H(42B)	9843(7)	2521(6)	1977(5)	81
H(42C)	9702(7)	2947(6)	2579(5)	81
H(43A)	7755(6)	6883(6)	4058(5)	48
H(44A)	6327(8)	6360(8)	4760(6)	130
H(44B)	5917(8)	6039(8)	4186(6)	130
H(44C)	5990(8)	7103(8)	4045(6)	130
H(45A)	8141(9)	6546(7)	3052(5)	104
H(45B)	7108(9)	7219(7)	2984(5)	104
H(45C)	7035(9)	6155(7)	3126(5)	104
H(46A)	12558(8)	2678(7)	3758(6)	91
H(47A)	12889(7)	4143(7)	3416(5)	90
H(47B)	13780(7)	3468(7)	3225(5)	90
H(47C)	13913(7)	3836(7)	3838(5)	90
H(48A)	12923(9)	1620(8)	4736(6)	145
H(48B)	13930(9)	2119(8)	4736(6)	145
H(48C)	13796(9)	1752(8)	4124(6)	145
H(49A)	7674(7)	716(6)	6338(5)	55
H(50A)	6321(7)	1833(7)	6255(5)	90
H(50B)	5954(7)	997(7)	6085(5)	90
H(50C)	6195(7)	1924(7)	5475(5)	90
H(51A)	8373(8)	401(6)	5347(5)	90
H(51B)	7453(8)	1041(6)	4912(5)	90

H(51C)	7212(8)	114(6)	5523(5)	90
H(52A)	7371(7)	4248(6)	3715(4)	48
H(53A)	7714(11)	2983(9)	3373(6)	160
H(53B)	6740(11)	3612(9)	2999(6)	160
H(53C)	6569(11)	2689(9)	3631(6)	160
H(54A)	5897(8)	4422(9)	4386(5)	128
H(54B)	5430(8)	3590(9)	4266(5)	128
H(54C)	5601(8)	4514(9)	3634(5)	128
H(55A)	7874(6)	4569(5)	6008(4)	33
H(56A)	6533(6)	4636(6)	5318(4)	63
H(56B)	6161(6)	4253(6)	6114(4)	63
H(56C)	6429(6)	3565(6)	5695(4)	63
H(57A)	8633(7)	3169(5)	6701(4)	57
H(57B)	7734(7)	2653(5)	6555(4)	57
H(57C)	7467(7)	3341(5)	6975(4)	57
H(58A)	11457(7)	2047(5)	5660(4)	38
H(59A)	10984(7)	1068(5)	5125(5)	61
H(59B)	10015(7)	804(5)	5665(5)	61
H(59C)	11166(7)	519(5)	5919(5)	61
H(60A)	10359(7)	2446(6)	6475(4)	63
H(60B)	10773(7)	1389(6)	6768(4)	63
H(60C)	9622(7)	1675(6)	6514(4)	63

Additional Figures

Compound 2


C(34)
C(33)
C(32)
C(35)
C(31)
O(10)
C(38)
C(41)
C(39)
C(37)
O(13)
O(4)
C(40)
O(11)
C(36)
O(12)
Ti(3)
O(3)
Ti(1)
C(15)
C(14)
C(12)
C(8)
C(10)
C(6)
C(13)
C(11)
C(7)
O(2)
C(9)
O(9)
C(42)
O(8)
O(7)
O(1)
C(3)
C(28)
Ti(2)
O(6)
C(26)
C(24)
C(1)
C(2)
C(27)
C(23)
C(22)
C(5)
C(30)
O(5)
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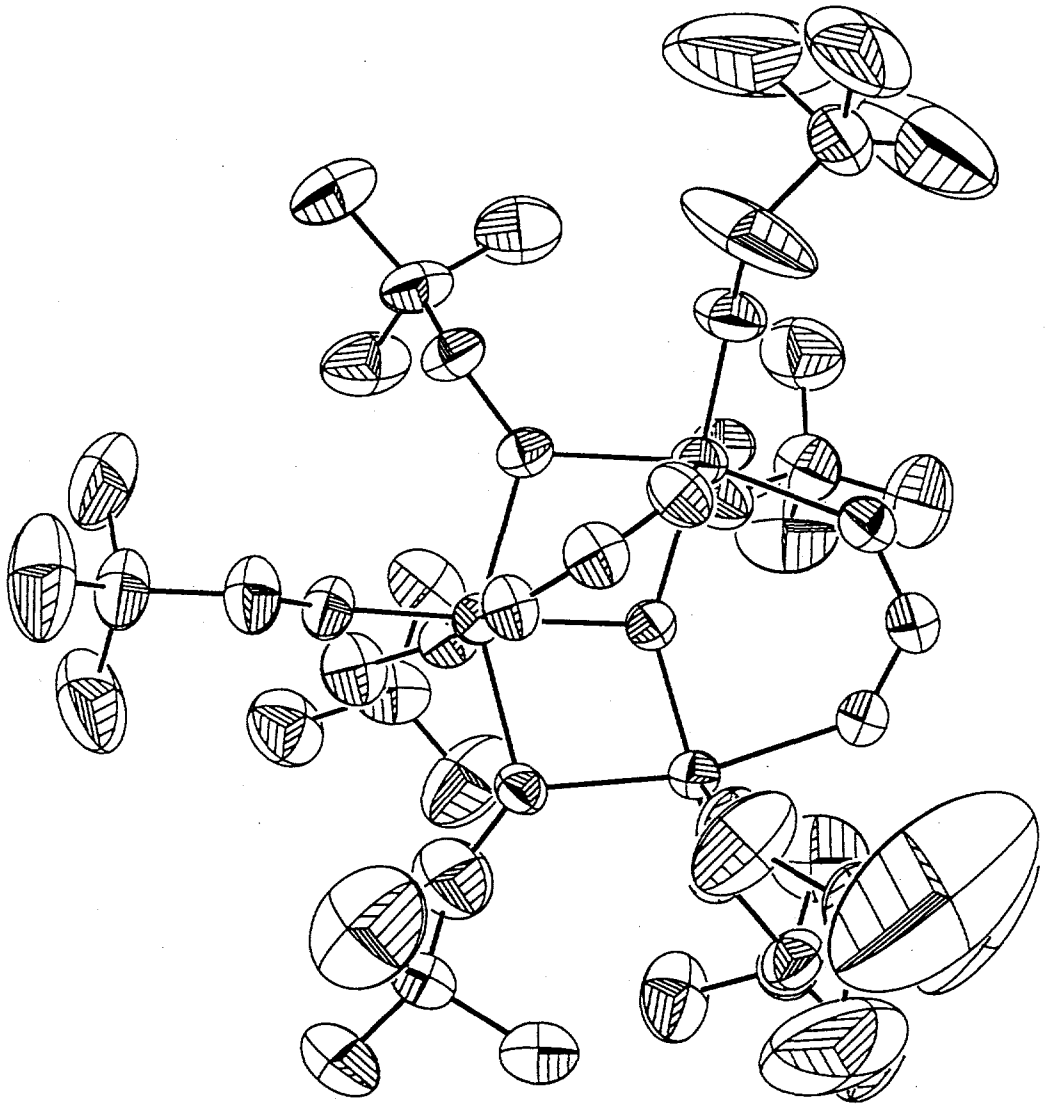
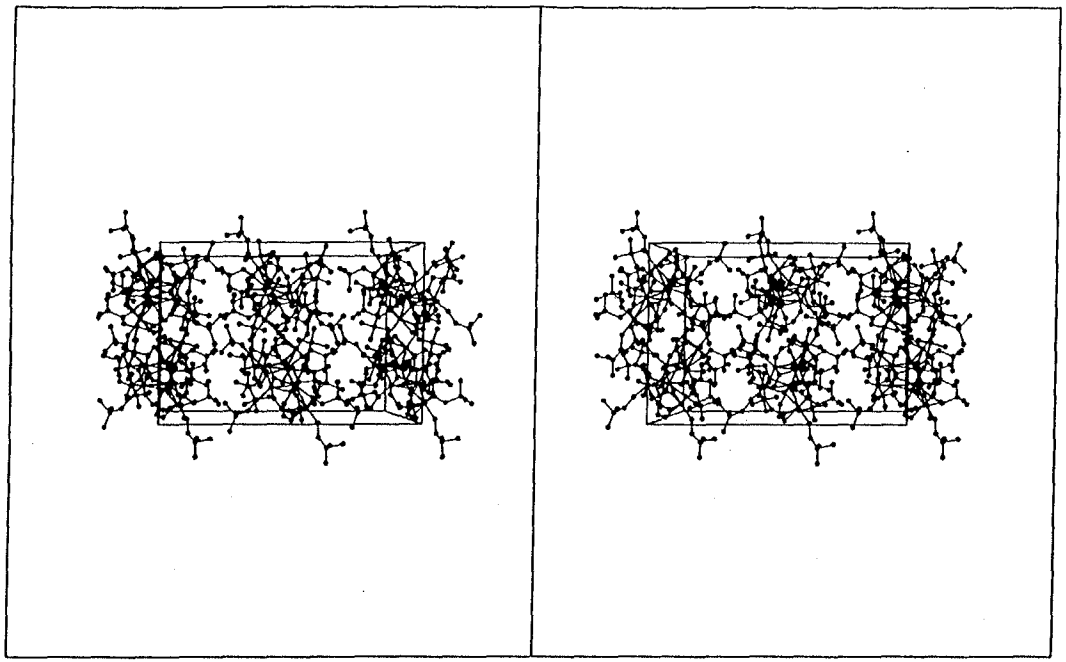
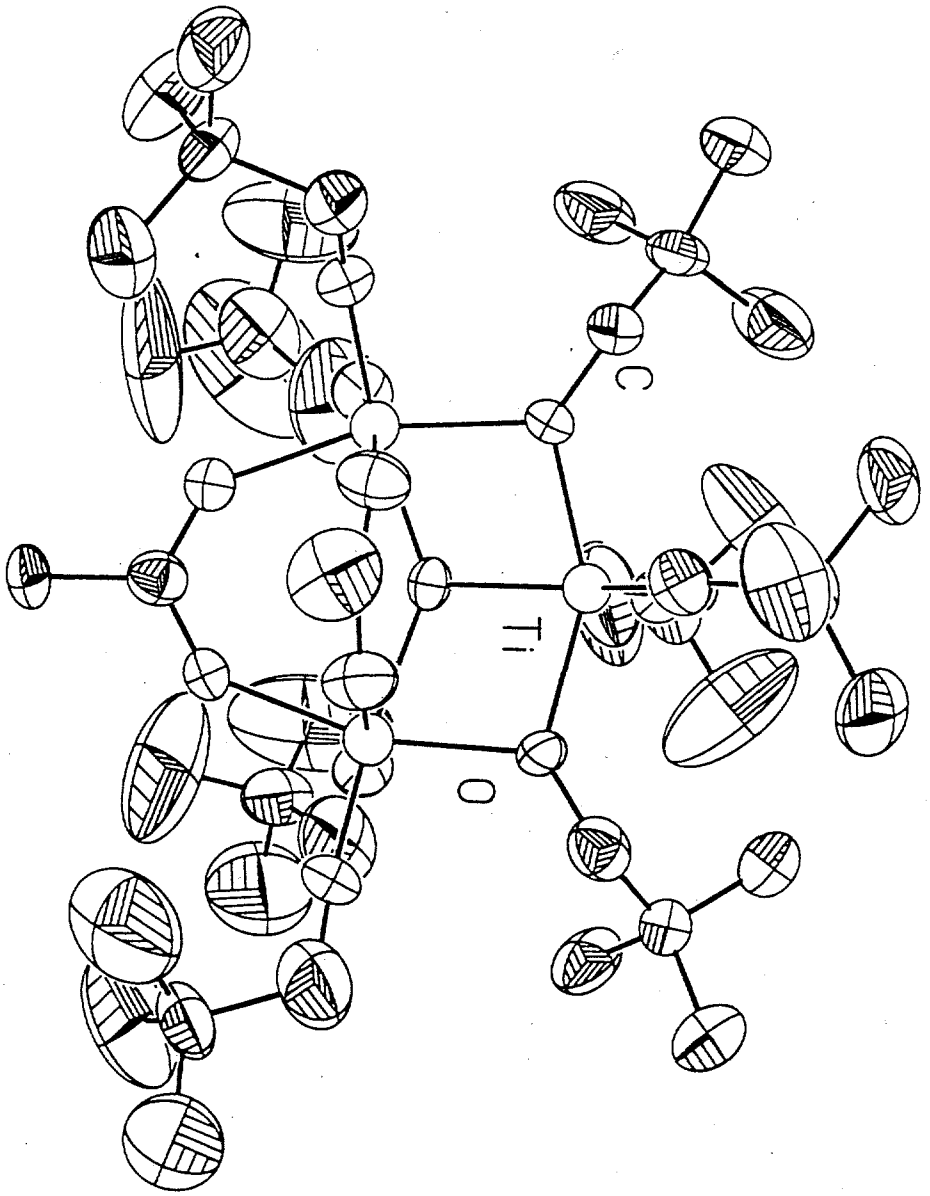
C(4)
C(29)
C(25)
C(16)
C(17)
C(20)
C(19)
C(18)



Compound 2

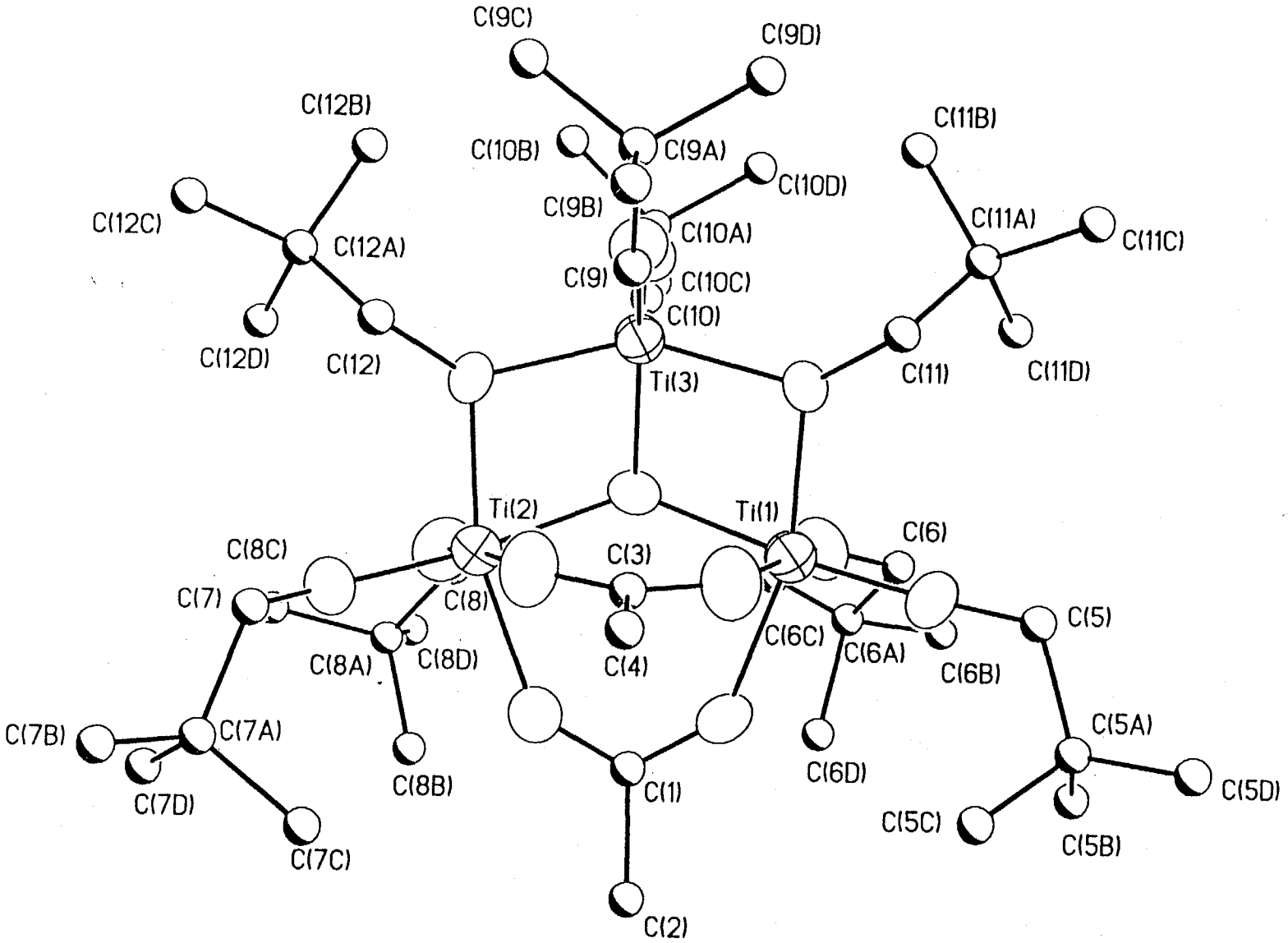


view down c-axis



Compound 3

Compound 3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C(9A)
C(11B)
C(10D)
C(9B)
C(12C)
C(12A)
C(10A)
C(11A)
C(11C)
C(9)
C(10C)
C(10)
C(12D)
C(12)
C(11)
C(11D)
Ti(3)
Ti(2)
Ti(1)
C(8C)
C(3)
C(6)
C(7)
C(8)
C(5)
C(6C)
C(6A)
C(8A)
C(8D)
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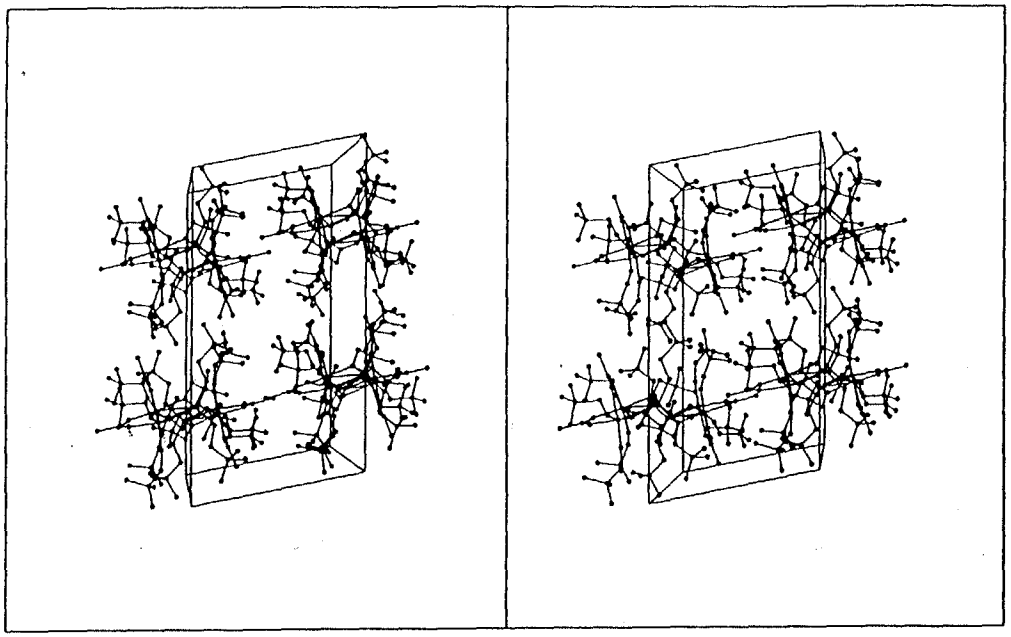
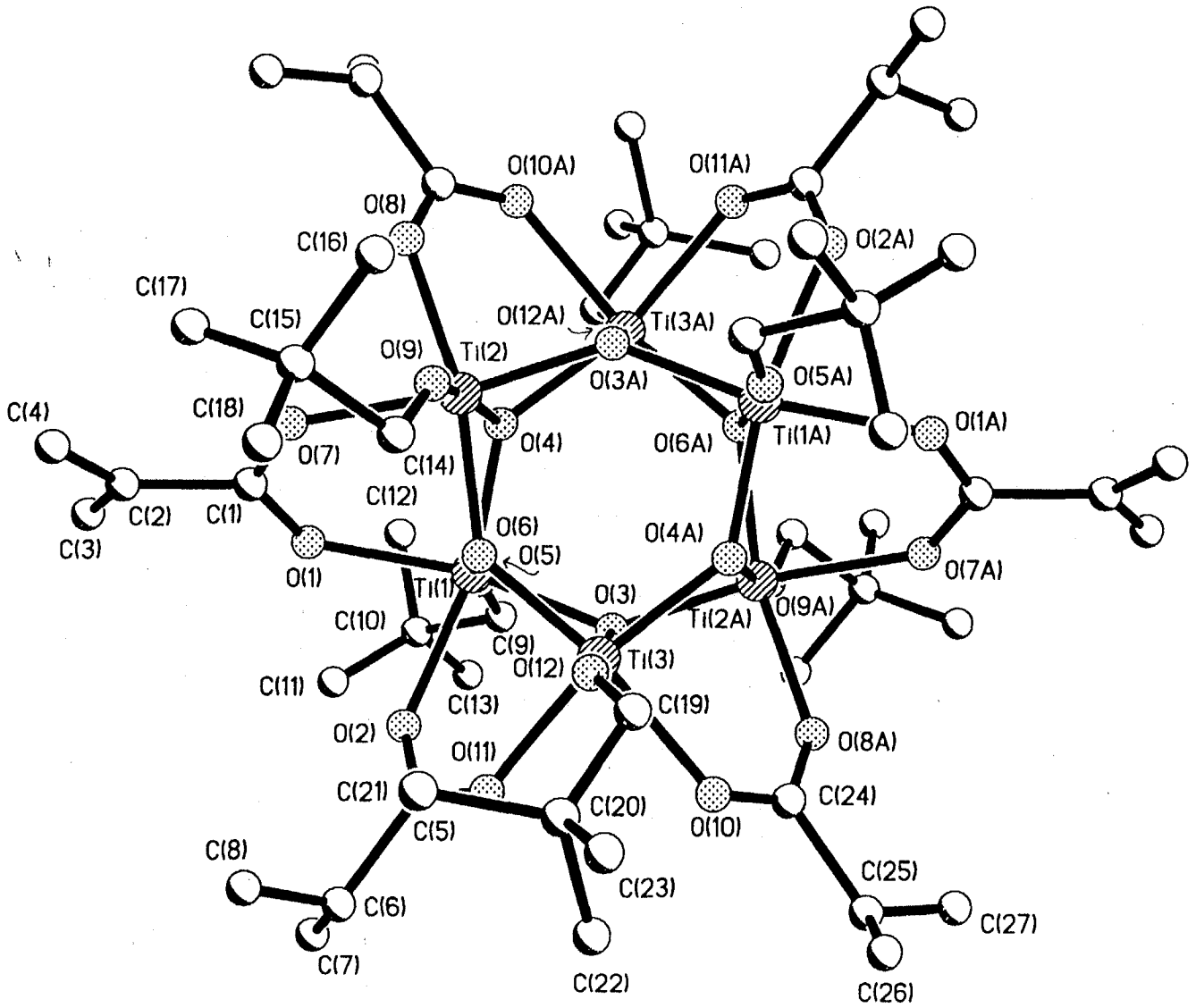
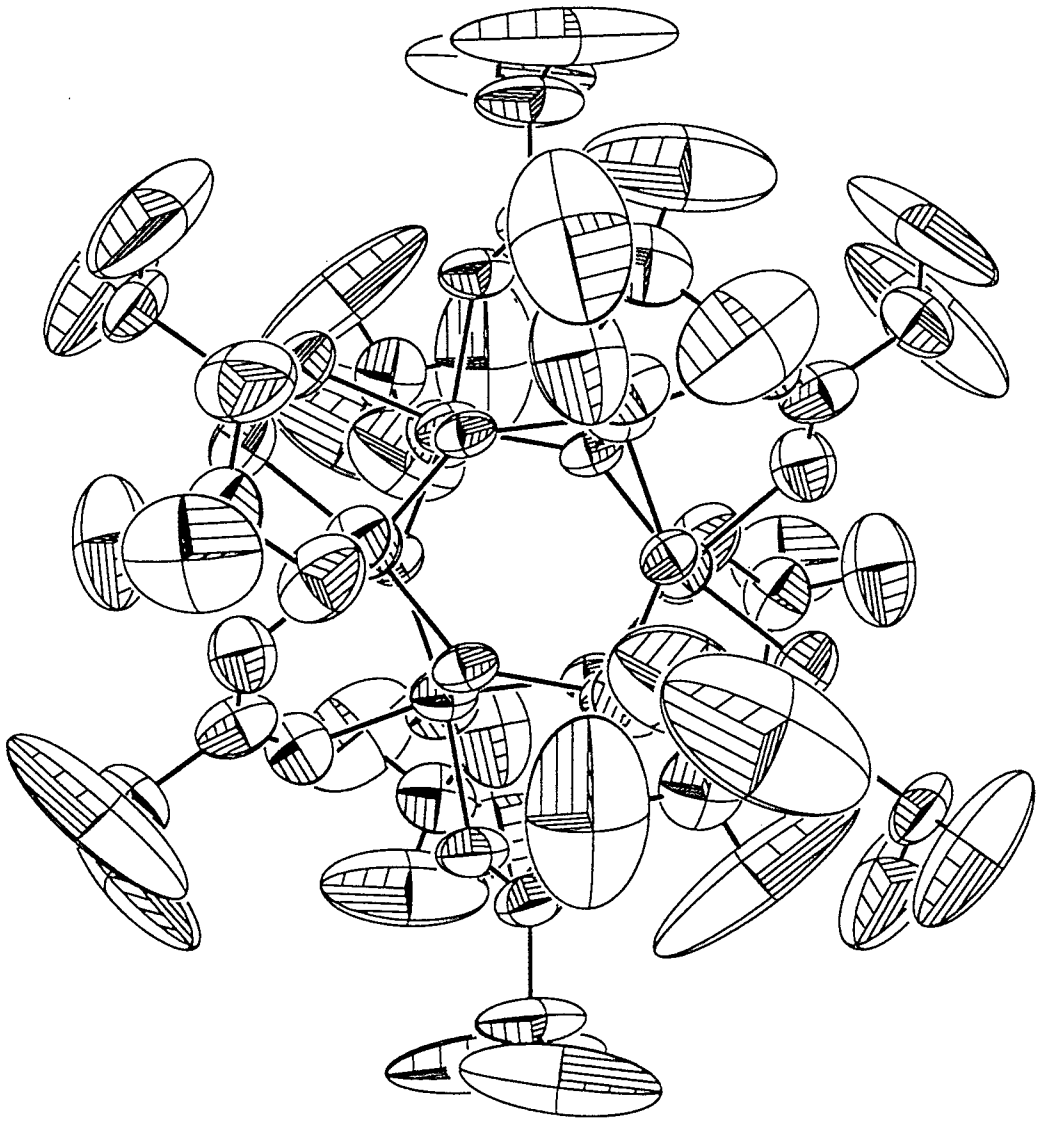
C(5C)
C(5B)
C(7C)
C(2)



b-axis projection

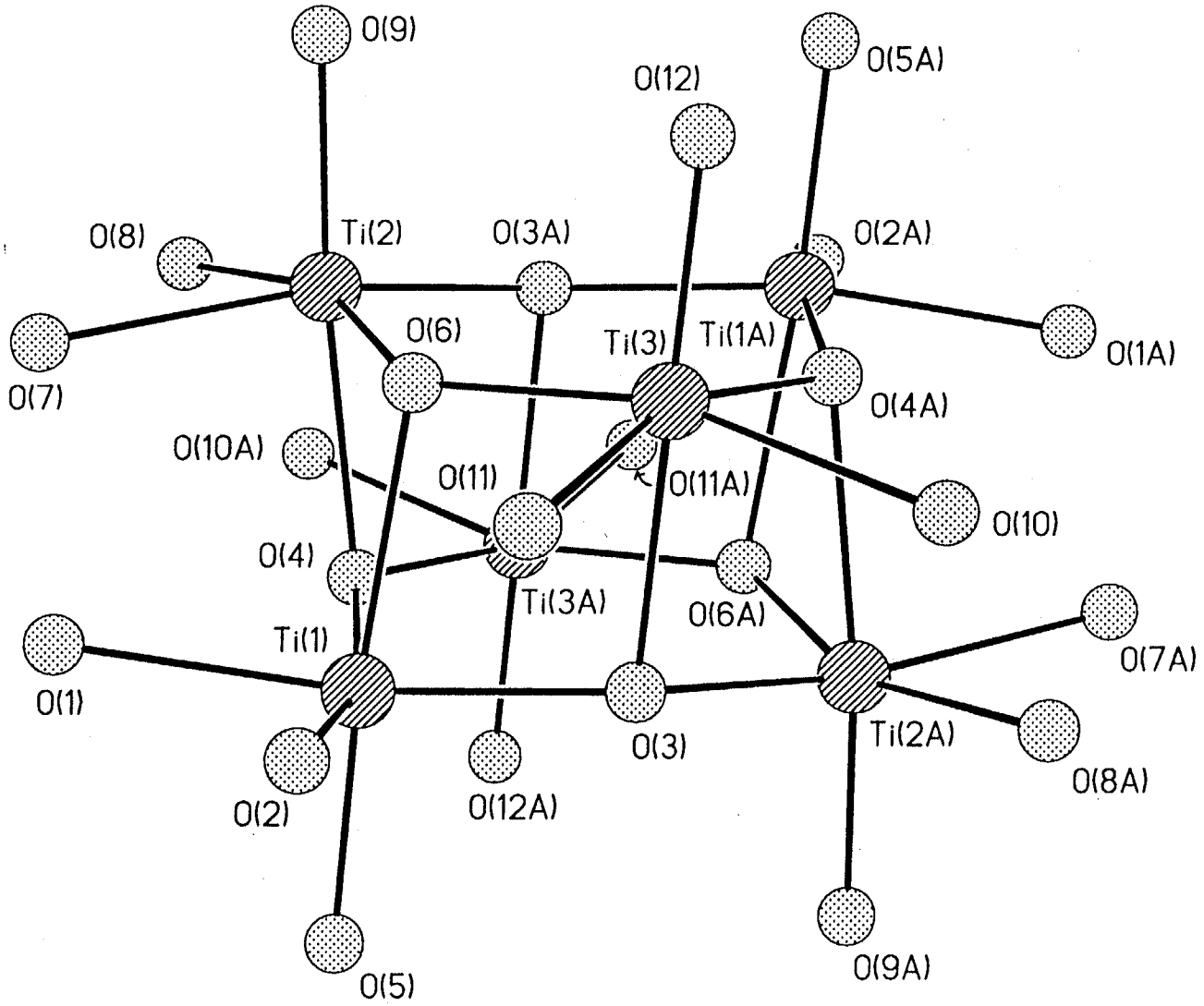
Compound 4


O(10A)
O(11A)
O(8)
C(16)
O(2A)
C(17)
C(15)
O(12A)
Ti(3A)
O(9)
Ti(2)
O(3A)
O(5A)
C(4)
C(18)
O(7)
C(14)
O(4)
O(6A)
Ti(1A)
O(1A)
C(12)
C(2)
C(1)
C(3)
O(6)
O(4A)
O(5)
O(7A)
O(1)
Ti(1)
O(3)
Ti(2A)
O(9A)
C(10)
C(9)
O(12)
Ti(3)
C(11)
C(13)
C(19)
O(2)
O(8A)
O(11)
C(21)
C(20)
C(24)
C(5)
O(10)
C(8)
C(25)
C(23)
C(6)
C(27)
C(7)
C(22)
C(26)



Compound 4

Compound 4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O(5A)
O(8)
Ti(2)
O(3A)
O(2A)
O(6)
Ti(3)
Ti(1A)
O(1A)
O(7)
O(4A)
O(10A)
O(11)
O(11A)
O(10)
O(4)
Ti(3A)
O(6A)
Ti(1)
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Ti(2A)
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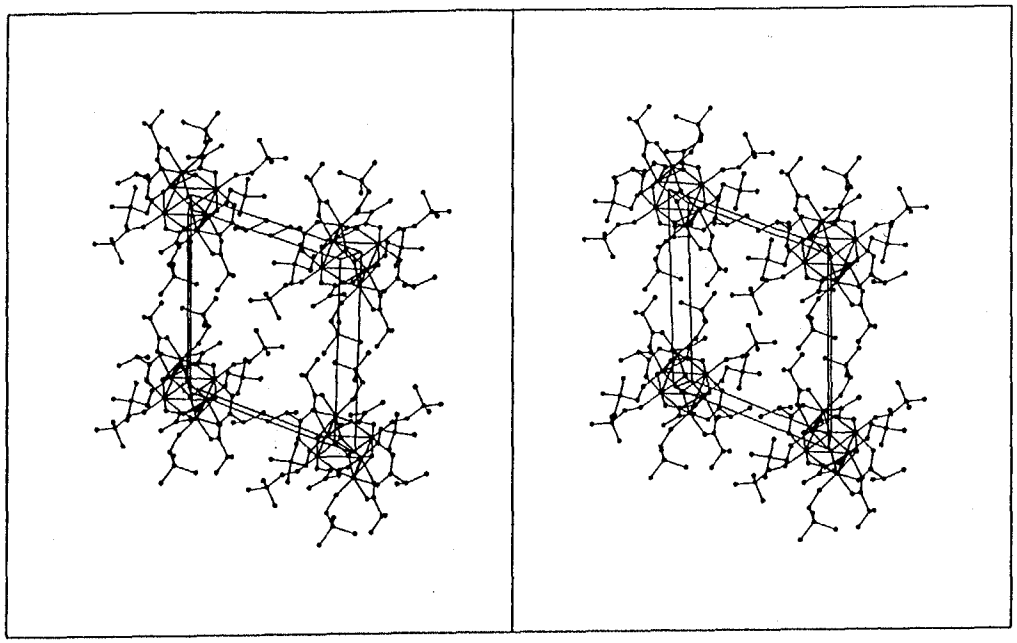
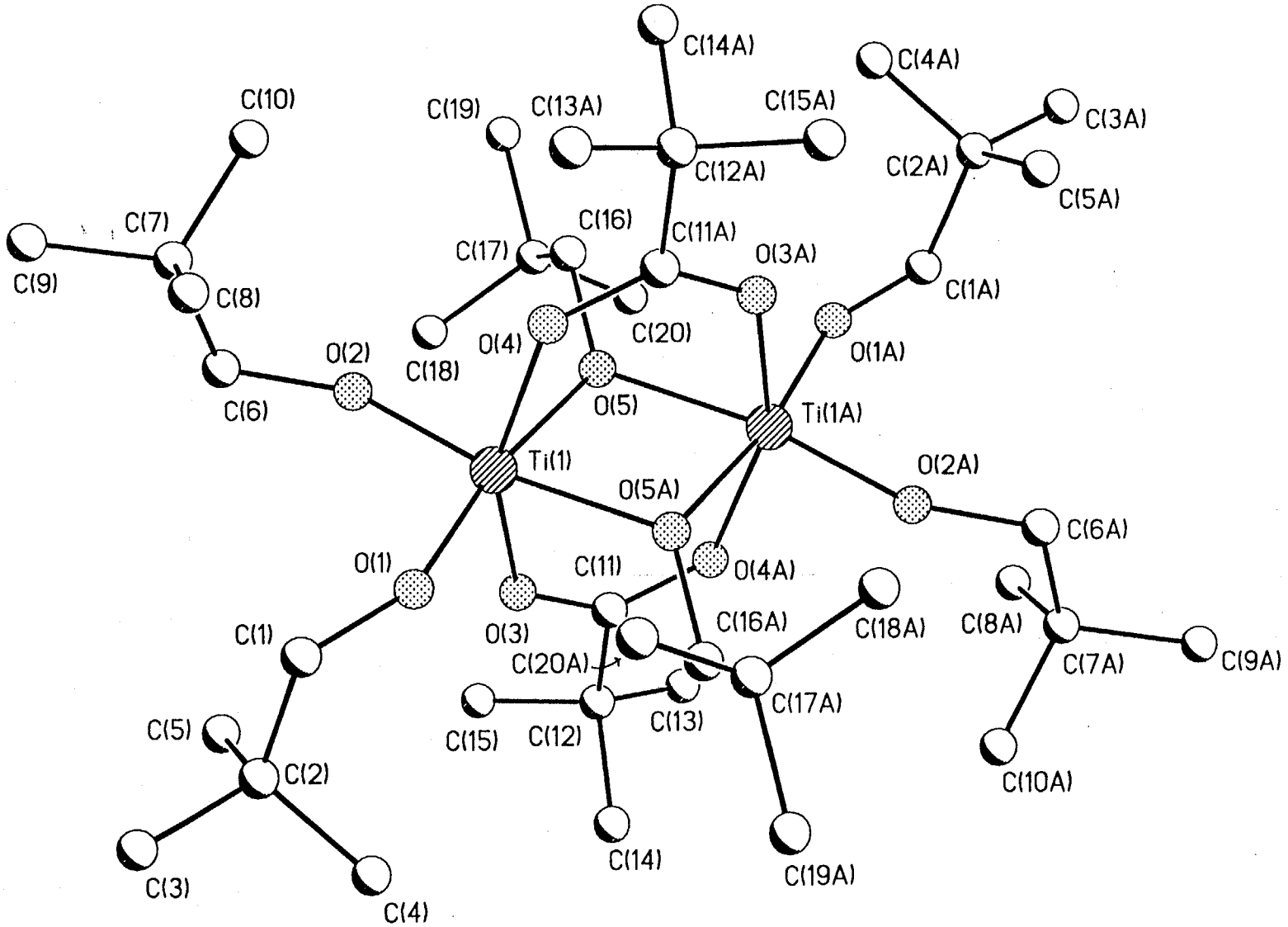
O(2)
O(12A)
O(5)
O(9A)



view down c-axis

Compound 5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C(7)
C(16)
C(11A)
C(17)
O(3A)
C(9)
C(8)
C(1A)
C(20)
O(4)
O(2)
C(18)
O(1A)
C(6)
O(5)
Ti(1A)
Ti(1)
O(2A)
O(5A)
C(6A)
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O(3)
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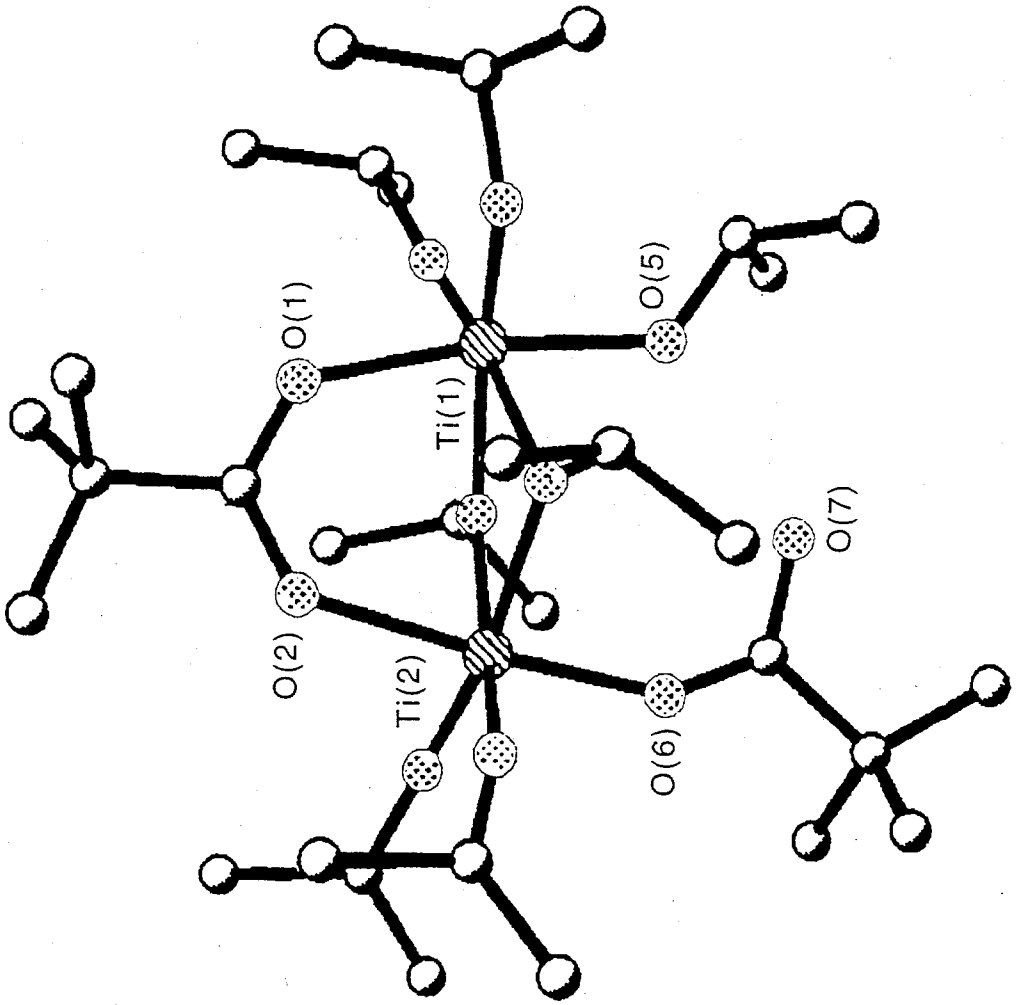
O(1)
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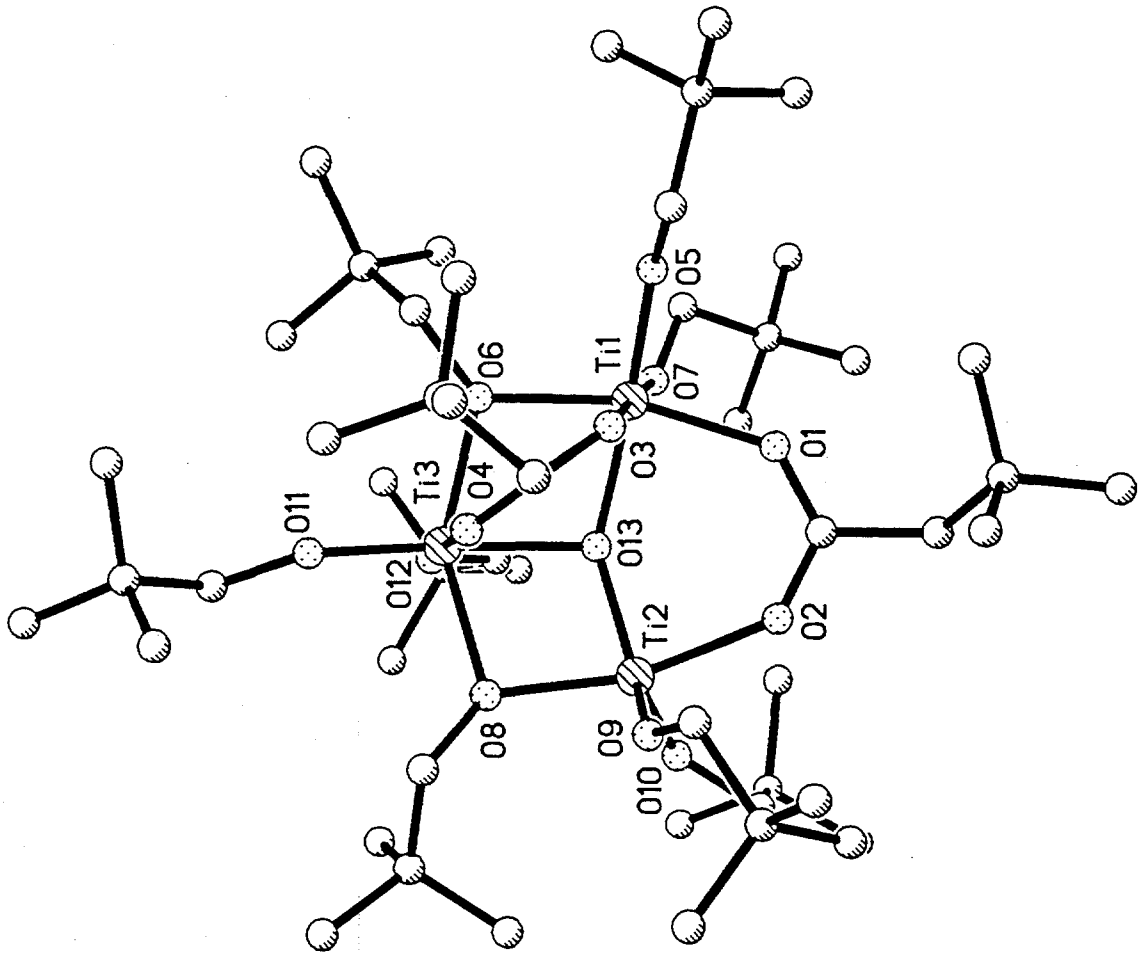
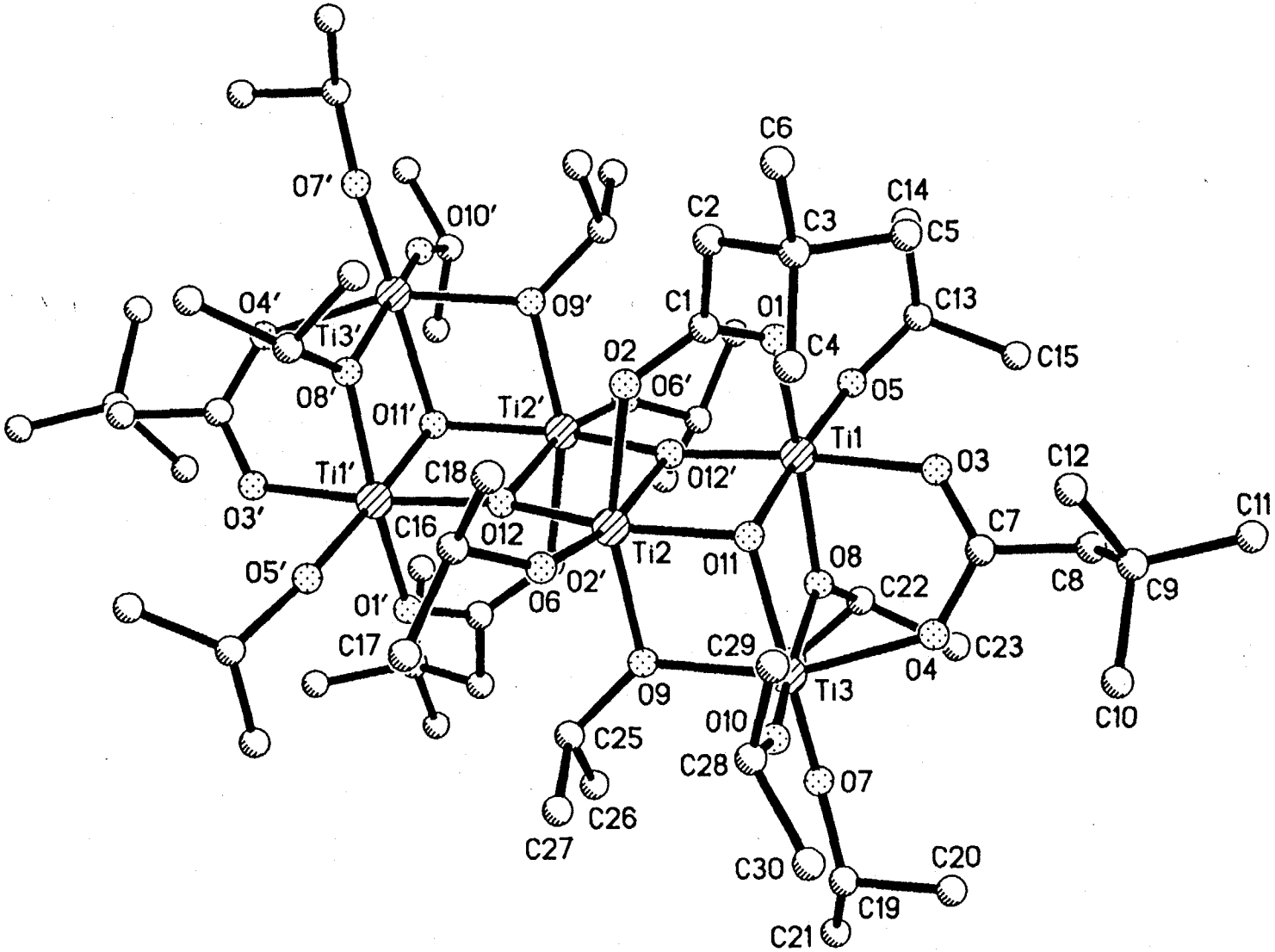
Ti(1)
O(7)
O(2)
Ti(2)
O(6)


Ti1
Ti2
Ti3
O1
O2
O3
O4
O5
O6
O7
O8
O9
O10
O11
O12
O13

Compound 6a


C6
O7′
O10′
C2
C3
C14
C5
O4′
O9′
C1
O1
C13
Ti3′
O2
C4
C15
O8′
O6′
O5
O11′
Ti2′
Ti1
Ti1′
C18
O12′
O3
C12
O3′
C16
O12
C7
C11
Ti2
O11
O8
O5′
O2′
C22
C8
C9
O1′
O6
C17
C29
O4
C23
O9
Ti3
C10
O10
C25
C28
O7
C26
C27
C30
C20
C19
C21