

# Mechanistic aspects of the hydrolysis and condensation of titanium alkoxides complexed by tripodal ligands †

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Titanium alkoxides  $Ti(OR)_4$  ( $R = Et, Pr^i$  and  $Bu^n$ ) react with tris(hydroxymethyl)nitromethane (THMNM- $H_3$ ) with retention of their basic tetrameric structural unit even after hydrolysis and condensation. The chemical reactivity of these molecular precursors are analyzed using a model based on a point charge approximation of density functional equations. Based on these theoretical results plausible reaction pathways can be anticipated, providing a deep insight into the mechanism of formation of these new molecular structures. Consequences for the sol-gel processing of titania-based material and for the rational design of novel solid-state materials are also briefly addressed.

## Introduction

Transition metal alkoxides  $M(OR)_n$  are widely used as molecular precursors of metal oxides  $MO_{n/2}$  in sol-gel chemistry.<sup>1</sup> Among them titanium(IV) alkoxides have been attracting much attention owing to their widespread occurrence in conventional (e.g. paints, inks, plastics, cosmetics, ceramics) as well as high-tech materials (e.g. coatings, membranes, photoanodes, capacitors). Moreover, the non-toxicity of titania,  $TiO_2$ , appears to be rather appealing for biological applications requiring either inert supports such as for enzyme immobilization or hybrid organic-inorganic networks for biomineralization. Titanium alkoxides are easily hydrolyzed affording oligomeric oxoalkoxide species displaying a wide range of nuclearity: trimers,<sup>2</sup> heptamers,<sup>3</sup> decamers,<sup>4</sup> undecamers,<sup>5</sup> dodecamers<sup>5</sup> and hexadecamers.<sup>3</sup> In all cases mentioned above, the basic tetrameric unit of these compounds<sup>6,7</sup> is either lost ( $R = Pr^i$ ) or is deeply engaged in compact edge-sharing assemblies ( $R = Et$ ). From a mechanistic point of view, the formation of a  $[Ti(OR)_4]_4$  oligomer from tetrahedral  $Ti(OR)_4$  monomers may be rationalized by noticing that direct addition of two  $Ti(OR)_4$  tetrahedra leads to a dimer  $[(RO)_4Ti(OR)_2Ti(OR)_4]$  displaying edge-sharing between a  $Ti(OR)_6$  octahedron and a  $Ti(OR)_4$  tetrahedron (Fig. 1).

Repetition of this process may lead either to a tetramer  $Ti_4(OR)_{16}$  (smallest cyclic species containing only sixfold-coordinated titanium atoms) or to an infinite edge-sharing octahedral chain  $[(RO)_2Ti(OR)_{4 \times 1/2}] \equiv Ti(OR)_4$ . Although for  $R = Me$ , both structures have been characterized in the solid state,<sup>8</sup> only in the case of the tetrameric unit was its structure elucidated by a single-crystal X-ray diffraction study.<sup>6</sup> As shown in Fig. 2, the existence of three kinds of OR groups (ten terminal OR positions, four  $\mu_2$ -OR bridges and two  $\mu_3$ -OR bridges) in this tetrameric structure raises the question of their relative reactivity towards hydrolysis or substitution upon reaction with X-OH molecules. Another interesting point concerns the possibility of molecular control of the oxolation process by using such oligomers as building blocks for a rational design of novel solid-state materials<sup>9</sup> or of porous metal-organic frame-

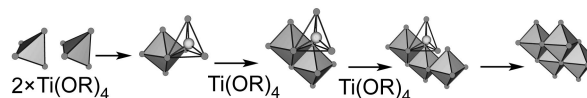


Fig. 1 Formation of a planar  $[Ti_4(OR)_{16}]$  tetramer through successive addition of  $Ti(OR)_4$  tetrahedra.

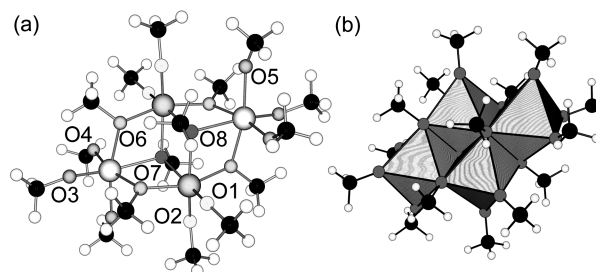


Fig. 2 (a) Molecular structure of  $Ti(OMe)_4$  according to Wright and Williams.<sup>6</sup> Partial charges on oxygen atoms are  $-0.740$  (O8),  $-0.665$  (O6),  $-0.663$  (O7),  $-0.581$  (O1),  $-0.580$  (O2),  $-0.527$  (O3),  $-0.497$  (O4) and  $-0.484$  (O5). (b) Polyhedral view of the  $[Ti_4(OMe)_{16}]$  tetramer.

works.<sup>10</sup> This paper is an attempt to provide some experimental and theoretical answers to these fundamental questions which appears to be relevant both to supramolecular and sol-gel chemistry.

## Theory

Within the frame of the partial charge model,<sup>11</sup> any chemical compound can be characterized by four global mean values, symbolized hereafter as  $\langle EN \rangle$ ,  $\langle GH \rangle$ ,  $\langle EB \rangle$  and  $\langle GI \rangle$ .  $\langle EN \rangle$  corresponds to the mean electronegativity of the system and may be identified to the energy situated halfway between the HOMO and the LUMO.  $e^2\langle GH \rangle$  measures the global hardness which should scale like the HOMO-LUMO gap.  $\langle EB \rangle$  reflects the energetic balance between all attractive ( $\delta^+ \cdots \delta^-$ ) and repulsive ( $\delta^+ \cdots \delta^+$  or  $\delta^- \cdots \delta^-$ ) interactions between atomic pairs. Finally,  $\langle GI \rangle$  is a global ionicity index ranging from 0 to 100% which helps to decide whether a given compound should be considered as ionic ( $\langle GI \rangle > 50\%$ ) or covalent ( $\langle GI \rangle < 50\%$ ). Partial charges  $\delta$  have been evaluated using the Allen electronegativity

† Electronic supplementary information (ESI) available: Partial charge calculations and spectroscopic data of reagents. See <http://www.rsc.org/suppdata/dt/b1/b103398k/>

scale<sup>12,13</sup> and atomic orbital radii<sup>14</sup> for approximating the chemical hardness. Detailed reports of all partial charge calculations made for this paper (charge distribution, frontier and retrosynthetic indexes for each atom in the asymmetric unit cell) are available as ESI. †

Applying this partial charge model to the Ti(OMe)<sub>4</sub> molecular network leads to  $\langle EN \rangle = 12.37$  V,  $e^2\langle GH \rangle = 5.7$  eV and  $\langle GI \rangle = 31.3\%$ . A comparison between the electrostatic balances (EB) of the network ( $\langle EB \rangle_{\text{net}} = -139.3$  eV for  $Z = 1$ ) and of the isolated tetramer ( $\langle EB \rangle_{\text{mol}} = -139.2$  eV) shows that crystal packing forces are rather weak ( $-4.1$  kJ mol<sup>-1</sup>). Retrosynthetic indexes<sup>11</sup> reveal that these van der Waals interactions are mainly concentrated on bridging groups ( $\mu_3$ -OR and  $\mu_2$ -OR). However, NMR studies on these oligomeric titanium alkoxides at room temperature reveal that bridging and terminal OR groups are indistinguishable on the NMR time-scale. Since the proton transfer from an incoming water molecule is considerably faster than the OR exchange process, this particular geometry raises the problem of the relative reactivity of bridging and terminal OR groups. Fig. 2 shows the charge distribution derived from our partial charge model. It may be convenient to convert the negative charges found on oxygen atoms into approximate  $pK_a$  values<sup>15</sup> ( $\pm 1$  unit) using the following relationship adapted to the Allen scale:  $-pK_a = 17.3 + 39.5 \times q(\text{O})$ . The result obtained clearly demonstrates a significantly higher basicity for bridging groups ( $pK_a$ : O8 = 11.9, O6 = 9.0 and O7 = 8.9) than for terminal groups ( $pK_a$ : O1 = 5.7, O2 = 5.6, O3 = 3.5, O4 = 2.3 and O5 = 1.8). These results indicate that bridging groups should be hydrolyzed first, thus explaining the rather compact structures found for the resulting oxo-alkoxides, and the localization of the oxo groups at the core of the architecture.

Based on these results, we have investigated the possibility of substituting all reactive bridging OR groups by a suitable multidentate ligand. The planar geometry of the tetramer and the triangular disposition of the bridging OR groups suggested the use of a tripodal ligand of the type XC(CH<sub>2</sub>OH)<sub>3</sub>. A survey of the Cambridge Structural Database showed that tris(hydroxymethyl)ethane or tris(hydroxymethyl)propane react with titanium isopropoxide to yield a tetrameric complex in the expected way,<sup>14</sup> despite the fact that titanium isopropoxide is known to be monomeric in the liquid state.<sup>16</sup> In order to elucidate the influence of the OR group, we have undertaken a structural investigation on products formed by reacting Ti(OR)<sub>4</sub> (R = Et, Pr<sup>i</sup> and Bu<sup>n</sup>) with tris(hydroxymethyl)nitromethane (THMNM-H<sub>3</sub>). It is worth noting that the presence of the nitro group allows on one hand <sup>17</sup>O- and <sup>14</sup>N-NMR studies and, on the other hand, further functionalization of the ligand.

## Experimental

All reagents were commercial products bought in their purest form and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 200 MHz on a BRUKER WP200 SY spectrometer. <sup>17</sup>O and <sup>14</sup>N NMR spectra were recorded at 400 MHz in 10 mm tubes on a BRUKER spectrometer. References for <sup>17</sup>O and <sup>14</sup>N NMR chemical shifts were tap water and aqueous nitrate ion, respectively. FT-IR spectra were recorded between 400 and 4000 cm<sup>-1</sup> on a BRUKER IF25 spectrometer. Spectroscopic data of reagents are provided as ESI. †

### Reaction of Ti(OEt)<sub>4</sub> with THMNM-H<sub>3</sub> 1

Translucid platelet-like crystals with hexagonal morphology were formed after few hours from a clear yellow solution obtained by injecting 20 ml of a 0.33 M solution of THMNM-H<sub>3</sub> in ethanol into 14 ml of pure titanium ethoxide (67 mmol) under vigorous stirring.

IR (KBr, cm<sup>-1</sup>): 1534s ( $\nu_{\text{as}}\text{N-O}$ ), 1375s, 1446m, 1375s ( $\nu_{\text{s}}\text{N-O}$ ), 1343s. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (overlapping multiplets,

15 H, CH<sub>3</sub>), 1.64 (singlet, large, OH), 3.71 (quadruplet, 2 H, CH<sub>2</sub>), 4.32–4.97 (overlapping multiplets, 14 H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  18.4 (CH<sub>3</sub>), 19.3 (CH<sub>3</sub>), 19.6 (CH<sub>3</sub>), 58.4 ( $\mu_3$ -OCH<sub>2</sub>), 72.1 ( $\mu_2$ -OCH<sub>2</sub>), 73.1 (OCH<sub>2</sub>), 74.2 (OCH<sub>2</sub>), 78.4 (OCH<sub>2</sub>), 84.6 (CNO<sub>2</sub>). <sup>17</sup>O NMR (CDCl<sub>3</sub>):  $\delta$  -184.9 ( $\mu_3$ -OCH<sub>2</sub>), 116.8 ( $\mu_2$ -OCH<sub>2</sub>), 423.8 (OCH<sub>2</sub>), 840.7 (NO<sub>2</sub>). <sup>14</sup>N NMR (CDCl<sub>3</sub>):  $\delta$  250.3 (NO<sub>2</sub>).

### Reaction of Ti(OPr<sup>i</sup>)<sub>4</sub> with THMNM-H<sub>3</sub> 2

Translucid platelet-like crystals with square morphology were formed within a few days from a clear colorless solution obtained by injecting 3 ml of a 0.33 M solution of THMNM-H<sub>3</sub> in isopropanol into 40 ml of pure titanium isopropoxide (134 mmol) under vigorous stirring.

IR (KBr, cm<sup>-1</sup>): 1542s ( $\nu_{\text{as}}\text{N-O}$ ), 1453m, 1347s ( $\nu_{\text{s}}\text{N-O}$ ). <sup>1</sup>H and <sup>13</sup>C NMR (CDCl<sub>3</sub>): hydrolyzed species. <sup>17</sup>O NMR (CDCl<sub>3</sub>):  $\delta$  296 ( $\mu_3$ -OTi), 42 ( $\mu_4$ -OTi), 532 (NO<sub>2</sub>). <sup>14</sup>N NMR (CDCl<sub>3</sub>):  $\delta$  261.7 (NO<sub>2</sub>).

### Reaction of Ti(OBu<sup>n</sup>)<sub>4</sub> with THMNM-H<sub>3</sub> 3

Translucid rod-like crystals suitable for X-ray diffraction were deposited after a week from a clear yellowish solution obtained by injecting 45 ml of a 0.33 M solution of THMNM-H<sub>3</sub> in *n*-butanol into 22.5 ml of pure titanium *n*-butoxide (132 mmol) under vigorous stirring.

IR (KBr, cm<sup>-1</sup>): 1540s ( $\nu_{\text{as}}\text{N-O}$ ), 1462m, 1373m, 1342s ( $\nu_{\text{s}}\text{N-O}$ ). <sup>1</sup>H, <sup>13</sup>C, <sup>17</sup>O and <sup>14</sup>N NMR (CDCl<sub>3</sub>): hydrolyzed species.

## Crystal structure determination

X-Ray single crystal diffraction measurements were made using a Philips PW1100/16 diffractometer using graphite monochromated Cu-K $\alpha$  radiation.

It is worth noting that in contrast to **2**, crystal data for **1** and **3** show some fairly large thermal displacement parameters. Despite the fact that the data were recorded at low temperature (173 K), this shows that some terminal ethoxy, butoxy and nitro groups are still vibrating. This is well in line with NMR data showing that these compounds are indeed very labile species and highly susceptible to hydrolysis. Consequently, if the titanium oxygen cores are correct, further data recording at lower temperature under an inert atmosphere is needed to confirm the position of some of these terminal groups.

**Crystal data.** C<sub>28</sub>H<sub>62</sub>N<sub>2</sub>O<sub>20</sub>Ti<sub>4</sub>,  $M = 938.4$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 13.970(4)$ ,  $b = 11.088(3)$ ,  $c = 17.488(5)$  Å,  $\beta = 96.19(2)^\circ$ ,  $U = 2693.1$  Å<sup>3</sup>,  $T = 173$  K,  $Z = 2$ ,  $\mu(\text{Cu-K}\alpha) = 54.840$  cm<sup>-1</sup>, 3552 reflections measured, 2622 unique ( $R_{\text{int}} = 0.043$ ). The final  $wR(F^2)$  was 0.070.

**Crystal data.** C<sub>38</sub>H<sub>82</sub>N<sub>2</sub>O<sub>20</sub>Ti<sub>4</sub>,  $M = 1078.7$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 18.351(5)$ ,  $b = 13.158(4)$ ,  $c = 18.182(5)$  Å,  $\beta = 102.44(2)^\circ$ ,  $U = 4287.2$  Å<sup>3</sup>,  $T = 173$  K,  $Z = 4$ ,  $\mu(\text{Cu-K}\alpha) = 68.101$  cm<sup>-1</sup>, 2634 reflections measured, 1723 unique ( $R_{\text{int}} = 0.048$ ). The final  $wR(F^2)$  was 0.063.

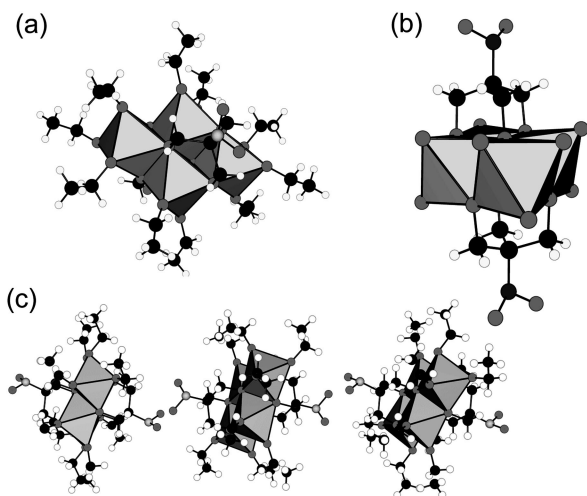
**Crystal data.** C<sub>80</sub>H<sub>168</sub>N<sub>4</sub>O<sub>38</sub>Ti<sub>8</sub>,  $M = 2177.4$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 11.057(3)$ ,  $b = 14.115(4)$ ,  $c = 18.362(5)$  Å,  $\alpha = 70.45(2)$ ,  $\beta = 81.54(2)$ ,  $\gamma = 86.30(2)^\circ$ ,  $U = 2670.8$  Å<sup>3</sup>,  $T = 173$  K,  $Z = 1$ ,  $\mu(\text{Mo-K}\alpha) = 6.358$  cm<sup>-1</sup>, 11 266 reflections measured, 5089 unique ( $R_{\text{int}} = 0.078$ ). The final  $wR(F^2)$  was 0.093.

CCDC reference numbers 158128–158130.

See <http://www.rsc.org/suppdata/dt/bl/b103398k/> for crystallographic data in CIF or other electronic format.

## Results

Compound **1** displays the same basic structural unit as Ti(OEt)<sub>4</sub><sup>7</sup> with, as expected, all six bridging OR groups substituted



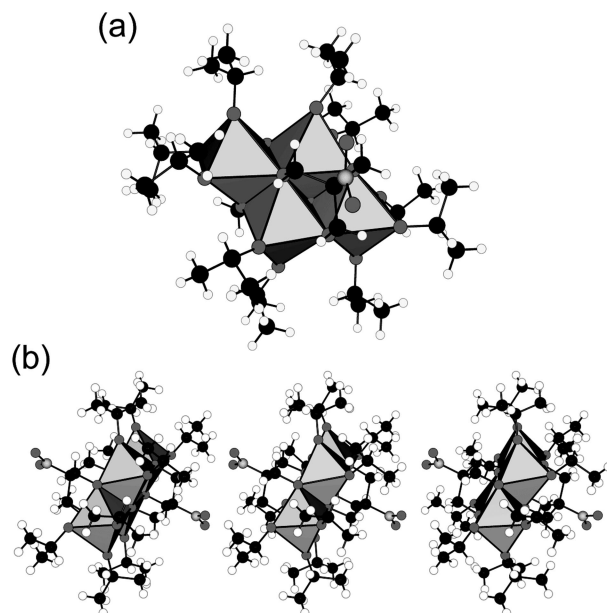
**Fig. 3** (a) Molecular structure of compound **1**. (b) Sandwich structure of **1**. (c) van der Waals chain through nitro groups based on **1**. Selected distances (Å) and angles (°): Ti–OEt 1.761(3)–1.800(3), Ti–( $\mu_2$ -OH<sub>2</sub>) 1.960(3)–2.140(3), Ti–( $\mu_3$ -OCH<sub>2</sub>) 2.170(3)–2.243(3); Ti–( $\mu_3$ -O)–Ti 97.6(1)–106.7(1), Ti–( $\mu_2$ -O)–Ti 109.0(1), Ti–O–Et 130.5(1)–164.2(1).

by two tripodal ligands. The two tripods are situated above and below the plane defined by the four titanium atoms (Fig. 3).

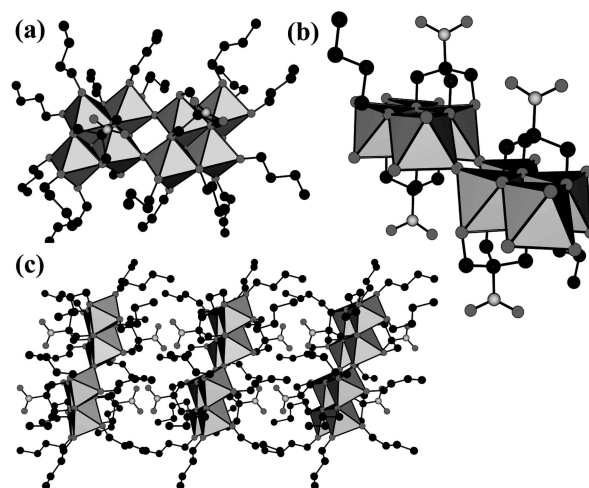
The tetrameric unit of **1** may be described as [Ti<sub>4</sub>(OEt)<sub>10</sub>–{( $\mu_2$ -OCH<sub>2</sub>)<sub>2</sub>( $\mu_3$ -OCH<sub>2</sub>)C(NO<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]. In the solid state, these units are strongly associated together through disordered nitro groups leading to a 1D van der Waals network. From an electronic point of view, this network is more electronegative ( $\langle EN \rangle = 13.03$  eV) and less ionic ( $\langle GI \rangle = 25.8\%$ ) than the one based on [Ti<sub>4</sub>(OMe)<sub>16</sub>] tetramers. Owing to some disorder around the nitro groups it is not possible to give a reliable estimation of the van der Waals energy. However, it should be fairly weak as the electrostatic balance of the whole network is found to be  $\langle EB \rangle_{\text{net}} = -153.87$  eV, a value comparable to that obtained for the free tetramer ( $\langle EB \rangle_{\text{mol}} = -153.99$  eV). More interesting are the predicted  $pK_a$  values for oxygen atoms of the ligand. These range from  $-8$  for the nitro group to  $+11.0$  for the  $\mu_3$ -OCH<sub>2</sub> moiety of the THMNM ligand. Terminal OEt groups are found to be more basic than OMe groups ( $4.7 \leq pK_a \leq 5.6$ ), whereas for the remaining  $\mu_2$ -OCH<sub>2</sub> moieties a value around 8.6 is obtained.

In a very similar way, the tetrameric unit of **2** may be described as [Ti<sub>4</sub>(OPr<sup>i</sup>)<sub>10</sub>–{( $\mu_2$ -OCH<sub>2</sub>)<sub>2</sub>( $\mu_3$ -OCH<sub>2</sub>)C(NO<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]. As before, these units are further associated in the solid state through nitro groups leading to a 1D van der Waals network (Fig. 4). From an electronic point of view, this network is more electronegative ( $\langle EN \rangle = 13.22$  eV) and less ionic ( $\langle GI \rangle = 21.77\%$ ) than the one with ethoxide-based tetramers. As nitro groups are found to be ordered in **2**, it is possible to compare the electrostatic balance of the whole network ( $\langle EB \rangle_{\text{net}} = -154.95$  eV) to that of the free tetramer ( $\langle EB \rangle_{\text{mol}} = -154.67$  eV). Van der Waals crystal packing forces are found to be 7 times stronger ( $-27.4$  kJ mol<sup>-1</sup>) for the THMNM-substituted tetramer than for the [Ti<sub>4</sub>(OMe)<sub>16</sub>] tetramers. Predicted  $pK_a$  values for oxygen atoms of the ligand range from  $-7.8$  for the nitro group up to  $+10.8$  for the  $\mu_3$ -OCH<sub>2</sub> moiety of the THMNM ligand. Terminal OPr<sup>i</sup> groups are found to be slightly less basic than OEt groups ( $4.3 \leq pK_a \leq 5.4$ ), whereas for the remaining  $\mu_2$ -OCH<sub>2</sub> moieties a  $pK_a$  value of *ca.* 8.6 is obtained. This value is almost the same as that obtained for the ethoxy-based THMNM tetramer.

In contrast with **1** or **2** compound **3** is a hydrolyzed product. Interestingly enough, it displays exactly the same basic structural unit with a butoxy group replacing the ethoxy and isopropoxy groups respectively, except that two such units are fused through two  $\mu_2$ -oxo groups (Fig. 5). The octameric unit of **3** may be described as [Ti<sub>4</sub>(OBu<sup>n</sup>)<sub>7</sub>( $\mu_2$ -OBu<sup>n</sup>)<sub>2</sub>–{( $\mu_3$ -OCH<sub>2</sub>)<sub>2</sub>( $\mu_3$ -OCH<sub>2</sub>)–



**Fig. 4** (a) Molecular structure of compound **2**. (b) van der Waals chain through nitro groups based on **2**. Selected distances (Å) and angles (°): Ti–OPr<sup>i</sup> 1.757(3)–1.819(3), Ti–( $\mu_2$ -OPr<sup>i</sup>) 1.953(3)–2.155(3), Ti–( $\mu_3$ -OPr<sup>i</sup>) 2.258(3); Ti–( $\mu_3$ -OPr<sup>i</sup>)–Ti 98.1(1)–106.2(1), Ti–( $\mu_2$ -O)–Ti 109.5(1)–111.0(1), Ti–O–Pr<sup>i</sup> 128.6(1)–164.9(1).



**Fig. 5** (a) Molecular structure of compound **3**. (b) Coordination mode of the THMNM ligand with bridging  $\mu_2$ -OBu<sup>n</sup> groups. (c) van der Waals chain through nitro groups based on **3**. Selected distances (Å) and angles (°): Ti–( $\mu_2$ -O) 1.748(6)–1.895(6), Ti–OBu 1.753(6)–1.814(6), Ti–( $\mu_2$ -OBu) 1.984(6)–2.052(6), Ti–( $\mu_1$ -OCH<sub>2</sub>) 1.803(6), Ti–( $\mu_2$ -OCH<sub>2</sub>) 1.962(6)–2.145(6), Ti–( $\mu_3$ -OCH<sub>2</sub>) 2.140(6)–2.248(6); Ti–( $\mu_2$ -O)–Ti 167.3(2), Ti–( $\mu_3$ -OCH<sub>2</sub>)–Ti 97.4(2)–108.3(2), Ti–( $\mu_2$ -OCH<sub>2</sub>)–Ti 108.8(2), Ti–( $\mu_1$ -OCH<sub>2</sub>)–Ti 130.3(2), Ti–( $\mu_2$ -OBu)–Ti 110.6(2), Ti–O–Bu 130.3(2)–170.0(2).

C(NO<sub>2</sub>)<sub>2</sub>}{(OCH<sub>2</sub>)( $\mu_2$ -OCH<sub>2</sub>)( $\mu_3$ -OCH<sub>2</sub>)C(NO<sub>2</sub>)<sub>2</sub>}O<sub>2</sub>]. As before, these units are further associated in the solid state through nitro groups leading to a 1D van der Waals network. As hydrogen coordinates are not available for this refinement, no electronic signature for this compound may be given.

## Discussion

Based on the above mentioned observations, one may propose some mechanistic conclusions concerning the hydrolysis and condensation of these THMNM-based titanium alkoxides. Although primary and secondary titanium alkoxides are known to have different molecular structures, the same tetrameric form is obtained after reacting these alkoxides with THMNM-H<sub>3</sub>

indicating a strong structuring role of the THMNM ligand. Thus, the present contribution shows that it is possible to change the OR group while maintaining the molecular structure. Moreover, the overall affinity of oxygen atoms for protons is not significantly modified after complexation. Consequently, and in agreement with other experiments,<sup>17</sup> these complexed titanium alkoxides are as reactive towards hydrolysis as uncomplexed ones. As evidenced by our NMR data, the overall susceptibility towards hydrolysis was found to be  $\text{Bu}^n \gg \text{Pr}^i > \text{Et}$ , and one may ask for a simple explanation for such a behavior. On purely electronic grounds, partial charge calculations made on these  $\text{Ti}_4(\text{OR})_{10}(\text{THMNM})_2$  tetramers ( $\text{R} = \text{Et}, \text{Pr}^i$ ) show that the two compounds are virtually indistinguishable:  $q[\text{Ti}(\text{OR})_3] = +2.512$  ( $\text{R} = \text{Et}$ ),  $+2.497$  ( $\text{R} = \text{Pr}^i$ ) and  $q[\text{Ti}(\text{OR})_2] = +2.397$  ( $\text{R} = \text{Et}$ ),  $+2.396$  ( $\text{R} = \text{Pr}^i$ ). Very similar values are also found for the terminal OR groups:  $\langle q(\text{OEt}) \rangle = -0.572$  and  $\langle q(\text{OPr}^i) \rangle = -0.562$ . Consequently, solvation effects are expected to play a major role to explain the different hydrolytic behavior of the two tetramers. A possible explanation would then be that hydrogen bonding interactions between the ethoxy-based tetramer and ethanol should be more important than hydrogen bonding between the isopropoxy-based tetramer and isopropanol. Further calculations including interactions with solvent molecules are thus needed to clarify further this point.

Nevertheless, our results also show that there is a clear benefit for substituting bridging OR groups with a multidentate ligand. This substitution, obviously, does not alter the affinity of oxygen for water, but does prevent the rapid elimination of the THMNM ligand. Accordingly, the removal of such a ligand would require the simultaneous attack of three water molecules upon a single tetramer, a rather unlikely process for entropic reasons. Finally, the fact that the THMNM ligand is effectively attacked by water molecules is demonstrated by the butoxide-based structure. The observed octamer is obviously made after partial hydrolysis and further oxolation of four terminal butoxy groups between two complexed tetramers. If the THMNM ligand was significantly inert in this process, the octamer would have displayed only terminal butoxy groups. As shown in Fig. 4 this is not the case as two butoxy ligands are found in bridging positions. The occurrence of these  $\mu_2\text{-O}^n\text{Bu}$  groups may be explained by assuming that the  $\mu_3\text{-OCH}_2$  moiety have been first hydrolyzed as suggested by our predicted  $\text{p}K_a$  values. Since the THMNM ligand is still linked by its remaining two arms to the tetramer, it is not eliminated and the uncomplexed arm is able to react with a neighbouring terminal butoxy group to form a new link between the  $\text{OCH}_2$  moiety and titanium. A fast cyclic permutation between three neighbouring  $\mu_2\text{-OCH}_2 \rightarrow \mu_3\text{-OH} \rightarrow \mu_1\text{-O}^n\text{Bu}$  groups should then lead to a hydroxo group in the terminal position ( $\mu_1\text{-OH}$ ), ideally placed for undergoing the final oxolation reaction and to the final observed structure:  $\mu_2\text{-O}^n\text{Bu}$  and  $\mu_3\text{-OCH}_2$ .

## Conclusion

These results are highly relevant with respect to the sol-gel processing of titania-based materials. Accordingly, we consider

we have demonstrated that bridging positions for OR groups are sites of preferential attack for substitution by OH and/or OX groups. We also have demonstrated that the basic structure of the  $\text{Ti}_4\text{O}_{16}$  core can be conserved upon hydrolysis and can be used as a building block for building complexes of higher nuclearity. These findings are then in deep contrast with previous results concerning the hydrolysis and condensation of unsubstituted titanium alkoxides,<sup>2-5</sup> where no evident structural relationship is found after partial hydrolysis of OR groups. Obviously, these preliminary results call for the search for new ligands that provide a better protection of titanium atoms against hydrolysis. For example, we have recently been able to show that the  $\text{Ti}_4\text{O}_{16}$  core can be fully preserved even after a complete substitution of OR groups by 2,6-bis(hydroxymethyl)-*p*-cresol (BHMPC) molecules.<sup>18</sup> In contrast with the compounds reported here, this new  $\text{Ti}_4\text{O}_{16}$  core was found to be completely inert towards hydrolysis, allowing its possible use as a building block in various supramolecular architectures. Work along these lines is currently under progress, in particular using other types of structuring organic ligands.

## Acknowledgements

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## Supplementary materials

*Spectroscopic data of reagents:* THMNM-H<sub>3</sub>: IR (neat)  $\nu/\text{cm}^{-1}$  1545s ( $\nu_{\text{as}}$  N-O), 1455s, 1364s ( $\nu_{\text{s}}$  N-O), 1270m; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  4.01 (6H, CH<sub>2</sub>), 4.36 (3H, OH); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  60.9 (CH<sub>2</sub>), 95.7 (CNO<sub>2</sub>); <sup>17</sup>O NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  -13.6 (OH), 597.4 (NO<sub>2</sub>); <sup>14</sup>N NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  1.97 (NO<sub>2</sub>).

Ti(OEt)<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.25 (triplet, *J* 6.7 Hz, 3H, CH<sub>3</sub>), 4.38 (quadruplet, *J* 6.7 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  26.5 (CH<sub>3</sub>), 70.3 (OCH<sub>2</sub>); <sup>17</sup>O NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  350 (wide) (OCH<sub>2</sub>CH<sub>3</sub>).

Ti(OPr<sup>i</sup>)<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.24 (doublet, *J* 6.1 Hz, 6H, CH<sub>3</sub>), 4.48 (septuplet, *J* 6.1 Hz, 1H, CH); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  26.47 (CH<sub>3</sub>), 75.94 (OCH); <sup>17</sup>O NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  293 (OCH(CH<sub>3</sub>)<sub>2</sub>).

Ti(OBu<sup>n</sup>)<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  0.93 (triplet, *J* 7.3 Hz, 3H, CH<sub>3</sub>), 1.35 (sextuplet, *J* 7.2 Hz, 2H, CH<sub>2</sub>), 1.59 (quintuplet, *J* 6.9 Hz, 2H, CH<sub>2</sub>), 1.35 (triplet, *J* 6.7 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  14.13 (CH<sub>3</sub>), 19.29 (CH<sub>2</sub>), 35.84 (CH<sub>2</sub>), 74.40 (OCH<sub>2</sub>); <sup>17</sup>O NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  350 (wide) (OCH<sub>2</sub>CH<sub>3</sub>).

X-ray experimental data for compound 1

Formula : C<sub>28</sub>H<sub>62</sub>N<sub>2</sub>O<sub>20</sub>Ti<sub>4</sub>  
Molecular weight : 938.4  
Color : without  
Crystal system : monoclinic  
a (Å) : 18.351 (5)  
b (Å) : 13.158 (4)  
c (Å) : 18.182 (5)  
β (deg) : 102.44 (2)  
Volume (Å<sup>3</sup>) : 4287.2  
Z : 4  
D<sub>calc</sub> (gcm<sup>-3</sup>) : 1.454  
Wavelength (Å) : 1.5418  
μ (cm<sup>-1</sup>) : 68.101  
Space group : C2/c  
Diffractometer : Philips PW1100/16  
Crystal dim. (mm) : 0.40\*0.20\*0.20  
Temperature : -100°C  
Radiation : CuKα graphite monochromated  
Mode : θ/2θ flying step-scan  
Scan speed (deg s<sup>-1</sup>) : 0.020  
Step width (deg) : 0.04  
Scan width (deg) : 0.90 + 0.14\*tg(θ)  
Octants : ±h+k+l  
θ min/max (deg) : 3/52  
Number of data collected : 2634  
Number of data with I>3σ(I) : 1723  
Number of variables : 253  
Abs min/max : 0.82/1.17  
R(F) : 0.048  
Rw(F) : 0.070  
p : 0.08  
Largest peak in final diff. (eÅ<sup>-3</sup>) : 0.03  
GOF : 1.439

Table of Positional Parameters and Their E.S.D.

Atom	x	y	z	B(Å <sup>2</sup> )
----	-	-	-	-----
TI1	0.60998 (6)	0.27999 (9)	0.53987 (6)	4.95 (3)
TI2	0.73303 (5)	0.11918 (8)	0.49251 (5)	4.23 (2)
O1	0.5180 (2)	0.3036 (4)	0.4851 (2)	7.2 (1)
C1	0.4547 (4)	0.3605 (7)	0.4693 (5)	9.8 (3)
C2	0.4101 (4)	0.3603 (7)	0.5263 (5)	11.5 (3)
O2	0.5911 (2)	0.1729 (3)	0.5945 (2)	5.9 (1)
C3	0.5385 (4)	0.0951 (6)	0.5764 (5)	9.3 (2)
C4	0.5097 (5)	0.0602 (9)	0.6394 (6)	16.2 (3)
O3	0.6217 (2)	0.3732 (3)	0.6135 (2)	6.7 (1)
C5	0.6043 (6)	0.3962 (9)	0.6808 (5)	14.5 (3)
C6	0.6000 (9)	0.359 (1)	0.7317 (6)	24.2 (6)
O4	0.6325 (2)	0.1750 (3)	0.4577 (2)	4.12 (8)
C7	0.6052 (3)	0.1915 (5)	0.3804 (3)	5.2 (2)
C8	0.6443 (3)	0.2809 (5)	0.3522 (3)	5.1 (1)
C9	0.7278 (3)	0.2626 (4)	0.3579 (3)	4.4 (1)
O5	0.7669 (2)	0.2508 (2)	0.4341 (2)	3.80 (8)
N1	0.6125 (3)	0.2975 (5)	0.2694 (3)	7.4 (2)
O6	0.5592 (6)	0.3640 (8)	0.2512 (6)	10.1 (3)
O7	0.5926 (5)	0.2255 (5)	0.2337 (3)	15.0 (3)
O6'	0.3609 (5)	0.3467 (8)	0.2701 (4)	9.0 (3)
C10	0.6275 (3)	0.3783 (5)	0.3897 (3)	5.5 (2)
O8	0.6579 (2)	0.3752 (3)	0.4688 (2)	4.61 (9)
O9	0.7175 (2)	0.0325 (3)	0.5619 (2)	5.8 (1)
C11	0.7085 (6)	-0.0522 (8)	0.5979 (8)	23.2 (4)
C12	0.7032 (9)	-0.1283 (8)	0.600 (1)	21.2 (6)
O10	0.7299 (2)	0.0396 (3)	0.4140 (2)	5.7 (1)

C13 0.7363(6) -0.0404(8) 0.3684(6) 16.1(3)

C14 0.6950(7) -0.0951(9) 0.3292(7) 19.3(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$(4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$$

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
TI1	0.0514 (5)	0.0830 (7)	0.0563 (6)	0.0004 (6)	0.0178 (4)	0.0030 (6)
TI2	0.0601 (6)	0.0482 (5)	0.0526 (5)	0.0040 (5)	0.0124 (5)	0.0024 (5)
O1	0.056 (2)	0.132 (4)	0.087 (3)	0.022 (3)	0.018 (2)	0.006 (3)
C1	0.075 (5)	0.169 (8)	0.128 (6)	0.032 (5)	0.019 (4)	0.008 (6)
C2	0.099 (5)	0.176 (8)	0.178 (7)	0.047 (5)	0.066 (4)	0.001 (7)
O2	0.066 (2)	0.091 (3)	0.070 (2)	0.023 (2)	0.023 (2)	0.002 (2)
C3	0.103 (5)	0.100 (6)	0.154 (7)	0.012 (5)	0.037 (5)	0.004 (5)
C4	0.229 (7)	0.189 (9)	0.245 (8)	0.096 (6)	0.155 (5)	0.006 (7)
O3	0.097 (3)	0.091 (3)	0.079 (2)	0.001 (2)	0.048 (2)	0.020 (2)
C5	0.218 (8)	0.24 (1)	0.121 (5)	0.082 (8)	0.101 (5)	0.080 (6)
C6	0.46 (2)	0.37 (2)	0.137 (7)	0.18 (1)	0.158 (8)	0.09 (1)
O4	0.049 (2)	0.065 (2)	0.041 (2)	0.008 (2)	0.005 (2)	0.001 (2)
C7	0.053 (3)	0.083 (4)	0.059 (3)	0.008 (3)	0.007 (3)	0.006 (3)
C8	0.063 (3)	0.080 (4)	0.045 (3)	0.002 (3)	0.002 (3)	0.009 (3)
C9	0.050 (3)	0.071 (4)	0.046 (3)	0.008 (3)	0.005 (2)	0.001 (3)
O5	0.052 (2)	0.054 (2)	0.037 (2)	0.004 (2)	0.006 (2)	0.001 (2)
N1	0.071 (3)	0.136 (5)	0.057 (3)	0.012 (4)	0.021 (3)	0.013 (3)
O6	0.135 (9)	0.150 (9)	0.080 (6)	0.034 (7)	0.021 (7)	0.036 (6)
O7	0.273 (8)	0.201 (6)	0.069 (4)	0.041 (6)	0.022 (5)	0.009 (4)
O6'	0.120 (7)	0.173 (8)	0.042 (4)	0.066 (6)	0.001 (4)	0.044 (5)
C10	0.054 (3)	0.087 (4)	0.063 (4)	0.008 (3)	0.001 (3)	0.021 (3)
O8	0.058 (2)	0.060 (2)	0.058 (2)	0.010 (2)	0.014 (2)	0.006 (2)
O9	0.088 (3)	0.057 (2)	0.075 (2)	0.008 (2)	0.018 (2)	0.016 (2)
C11	0.172 (9)	0.167 (7)	0.57 (1)	0.046 (7)	0.144 (9)	0.239 (7)
C12	0.33 (2)	0.126 (9)	0.35 (2)	0.050 (9)	0.07 (1)	0.07 (1)
O10	0.086 (3)	0.061 (2)	0.070 (2)	0.002 (2)	0.016 (2)	0.019 (2)

C13 0.157(8) 0.190(8) 0.277(9) 0.043(7) 0.070(7) 0.162(6)  
C14 0.20(1) 0.26(1) 0.27(1) 0.054(9) 0.044(9) 0.194(7)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2 [h^2 a^2 U(1,1) + k^2 b^2 U(2,2) + l^2 c^2 U(3,3) \\ + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)]]$$

where a, b, and c are reciprocal lattice constants.

Table of Positional Parameters and Their E.S.D.

Atom	x	y	z	B (Å <sup>2</sup> )
----	-	-	-	-----
H1	0.4244	0.3354	0.4237	12*
H2	0.4686	0.4287	0.4622	12*
H3	0.3673	0.4019	0.5101	14*
H4	0.3947	0.2928	0.5338	14*
H5	0.4389	0.3860	0.5722	14*
H6	0.5613	0.0392	0.5570	12*
H7	0.4980	0.1194	0.5387	12*
H8	0.4743	0.0075	0.6235	21*
H9	0.5494	0.0349	0.6773	21*
H10	0.4861	0.1150	0.6591	21*
H11	0.5559	0.4247	0.6650	18*
H12	0.6391	0.4486	0.6989	18*
H13	0.5855	0.4067	0.7649	31*
H14	0.5636	0.3065	0.7207	31*
H15	0.6469	0.3304	0.7546	31*
H16	0.5532	0.2053	0.3717	6*
H17	0.6132	0.1320	0.3536	6*
H18	0.7480	0.3189	0.3365	5*
H19	0.7339	0.2027	0.3307	5*
H20	0.5750	0.3869	0.3812	7*
H21	0.6487	0.4338	0.3683	7*
H22	0.6636	-0.0341	0.6127	30*
H23	0.7494	-0.0443	0.6394	30*
H24	0.6972	-0.1470	0.6492	27*
H25	0.6608	-0.1496	0.5639	27*
H26	0.7467	-0.1598	0.5906	27*

H27	0.7670	-0.0861	0.4017	20*
H28	0.7640	-0.0120	0.3348	20*
H29	0.7224	-0.1422	0.3063	25*
H30	0.6660	-0.1307	0.3582	25*
H31	0.6629	-0.0566	0.2912	25*

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
=====	=====	=====	=====	=====	=====
TI1	O1	1.792 (3)	O4	C7	1.402 (5)
TI1	O2	1.800 (3)	C7	C8	1.525 (6)
TI1	O3	1.794 (3)	C8	C9	1.531 (6)
TI1	O4	2.140 (3)	C8	N1	1.508 (6)
TI1	O5	2.243 (3)	C8	C10	1.513 (6)
TI1	O8	2.122 (3)	C9	O5	1.424 (5)
TI2	O4	1.960 (3)	N1	O6	1.302 (9)
TI2	O5	2.191 (2)	N1	O7	1.161 (7)
TI2	O5	2.170 (3)	N1	O6'	1.151 (7)
TI2	O8	1.974 (3)	O6	O7	1.97 (1)
TI2	O9	1.768 (3)	O6	O6'	1.61 (1)
TI2	O10	1.761 (3)	O7	O6'	1.82 (1)
O1	C1	1.359 (6)	C10	O8	1.428 (5)
C1	C2	1.454 (9)	O9	C11	1.321 (9)
O2	C3	1.397 (7)	C11	C12	1.01 (1)
C3	C4	1.438 (9)	O10	C13	1.361 (8)
O3	C5	1.362 (8)	C13	C14	1.17 (1)
C5	C6	1.07 (1)			

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 Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
O1	TI1	O2	99.9 (2)	O5	TI2	O8	76.8 (1)
O1	TI1	O3	104.1 (2)	O5	TI2	O9	164.1 (1)
O1	TI1	O4	91.4 (1)	O5	TI2	O10	92.3 (1)
O1	TI1	O5	159.0 (1)	O5	TI2	O8	83.4 (1)
O1	TI1	O8	91.3 (1)	O5	TI2	O9	92.8 (1)
O2	TI1	O3	97.4 (2)	O5	TI2	O10	164.4 (1)
O2	TI1	O4	88.2 (1)	O8	TI2	O9	94.4 (1)
O2	TI1	O5	92.7 (1)	O8	TI2	O10	99.4 (1)
O2	TI1	O8	162.3 (1)	O9	TI2	O10	102.3 (1)
O3	TI1	O4	162.2 (1)	O1	C1	C2	115.8 (6)
O3	TI1	O5	90.7 (1)	O2	C3	C4	113.6 (6)
O3	TI1	O8	93.0 (1)	O3	C5	C6	139. (2)
O4	TI1	O5	72.17 (9)	O4	C7	C8	111.4 (3)
O4	TI1	O8	77.8 (1)	C7	C8	C9	113.1 (4)
O5	TI1	O8	72.8 (1)	C7	C8	N1	109.8 (4)
O4	TI2	O5	83.8 (1)	C7	C8	C10	110.2 (4)
O4	TI2	O5	77.2 (1)	C9	C8	N1	104.9 (4)
O4	TI2	O8	155.9 (1)	C9	C8	C10	113.6 (4)
O4	TI2	O9	100.8 (1)	N1	C8	C10	104.8 (4)
O4	TI2	O10	95.6 (1)	C8	C9	O5	111.8 (3)
O5	TI2	O5	73.3 (1)	C8	N1	O6	117.3 (6)

C8	N1	O7	116.6 (6)	N1	O7	O6'	38.0 (4)
C8	N1	O6'	125.4 (6)	O6	O7	O6'	50.2 (5)
O6	N1	O7	106.1 (6)	N1	O6'	O6	53.1 (5)
O6	N1	O6'	81.9 (8)	N1	O6'	O7	38.4 (4)
O7	N1	O6'	103.6 (7)	O6	O6'	O7	69.8 (5)
N1	O6	O7	34.5 (4)	C8	C10	O8	110.9 (3)
N1	O6	O6'	45.0 (5)	O9	C11	C12	152. (2)
O7	O6	O6'	60.0 (5)	O10	C13	C14	136. (1)
N1	O7	O6	39.4 (4)				

-----  
 Numbers in parentheses are estimated standard deviations in the least significant digits.

X-ray experimental data for compound 2

Formula : C<sub>38</sub>H<sub>82</sub>N<sub>2</sub>O<sub>20</sub>Ti<sub>4</sub>  
Molecular weight : 1078.7  
Color : without  
Crystal system : monoclinic  
a (Å) : 13.970 (4)  
b (Å) : 11.088 (3)  
c (Å) : 17.488 (5)  
β (deg) : 96.19 (2)  
Volume (Å<sup>3</sup>) : 2693.1  
Z : 2  
D<sub>calc</sub> (gcm<sup>-3</sup>) : 1.330  
Wavelength (Å) : 1.5418  
μ (cm<sup>-1</sup>) : 54.840  
Space group : P2<sub>1</sub>/n  
Diffractometer : Philips PW1100/16  
Crystal dim. (mm) : 0.25\*0.20\*0.20  
Temperature : -100°C  
Radiation : CuKα graphite monochromated  
Mode : θ/2θ flying step-scan  
Scan speed (deg s<sup>-1</sup>) : 0.020  
Step width (deg) : 0.03  
Scan width (deg) : 0.80 + 0.14\*tg(θ)  
Octants : ±h+k+l  
θ min/max (deg) : 3/54  
Number of data collected : 3552  
Number of data with I > 3σ(I) : 2622  
Number of variables : 289  
Abs min/max : 0.81/1.37  
R(F) : 0.043  
Rw(F) : 0.063  
p : 0.08  
Largest peak in final diff. (eÅ<sup>-3</sup>) : 0.07  
GOF : 1.406

Table of Positional Parameters and Their E.S.D.

Atom	x	y	z	B (Å <sup>2</sup> )
----	-	-	-	-----
TI1	0.80928 (4)	-0.07990 (6)	1.02252 (4)	2.33 (1)
TI2	0.95706 (4)	0.04944 (6)	0.90746 (4)	2.32 (1)
O1	0.7227 (2)	0.0230 (2)	0.9768 (2)	3.32 (6)
C1	0.6564 (3)	0.0554 (5)	0.9138 (3)	5.7 (1)
C2	0.5886 (4)	0.1490 (6)	0.9388 (4)	8.6 (2)
C3	0.6026 (4)	-0.0527 (7)	0.8799 (4)	8.8 (2)
O2	0.7813 (2)	-0.0520 (2)	1.1202 (1)	2.95 (5)
C4	0.6915 (3)	-0.0144 (4)	1.1457 (2)	3.56 (9)
C5	0.6743 (3)	-0.0833 (5)	1.2169 (3)	5.1 (1)
C6	0.6926 (3)	0.1197 (5)	1.1581 (3)	5.4 (1)
O3	0.7513 (2)	-0.2240 (2)	1.0026 (1)	3.02 (5)
C7	0.6860 (3)	-0.3007 (4)	1.0361 (2)	3.87 (9)
C8	0.7387 (4)	-0.3682 (5)	1.1029 (3)	5.6 (1)
C9	0.6366 (5)	-0.3794 (6)	0.9771 (4)	9.1 (2)
O4	0.9286 (2)	0.0582 (2)	1.0267 (1)	2.09 (5)
C10	0.9151 (2)	0.1763 (3)	1.0562 (2)	2.70 (8)
C11	1.0068 (2)	0.2537 (3)	1.0561 (2)	2.83 (8)
C12	1.0930 (3)	0.2077 (3)	1.1082 (2)	3.11 (8)
O5	1.1230 (2)	0.0929 (2)	1.0822 (1)	2.40 (5)
N1	0.9795 (2)	0.3765 (3)	1.0857 (2)	4.42 (8)
O6	0.9141 (3)	0.4318 (3)	1.0482 (2)	7.1 (1)
O7	1.0210 (3)	0.4141 (3)	1.1441 (2)	8.0 (1)
C13	1.0351 (3)	0.2773 (3)	0.9741 (2)	2.91 (8)
O8	1.0600 (2)	0.1680 (2)	0.9397 (1)	2.32 (5)
O9	0.9968 (2)	0.0085 (2)	0.8191 (1)	3.13 (5)
C14	1.0440 (3)	-0.0023 (4)	0.7505 (2)	3.54 (9)

C15	1.0588 (3)	0.1213 (5)	0.7196 (2)	4.8 (1)
C16	0.9853 (4)	-0.0848 (5)	0.6944 (3)	5.4 (1)
O10	0.8691 (2)	0.1626 (2)	0.8796 (1)	3.26 (6)
C17	0.8490 (3)	0.2491 (4)	0.8194 (3)	4.9 (1)
C18	0.7937 (4)	0.1880 (6)	0.7498 (3)	7.5 (2)
C19	0.7969 (4)	0.3546 (5)	0.8478 (4)	7.8 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  
 $(4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
TI1	0.0250 (3)	0.0297 (3)	0.0339 (3)	0.0002 (3)	0.0025 (3)	0.0003 (3)
TI2	0.0269 (3)	0.0303 (3)	0.0302 (3)	0.0009 (3)	0.0006 (3)	0.0046 (3)
O1	0.030 (1)	0.046 (1)	0.050 (1)	0.007 (1)	0.002 (1)	0.008 (1)
C1	0.037 (2)	0.110 (4)	0.069 (3)	0.013 (3)	0.004 (2)	0.040 (3)
C2	0.066 (3)	0.099 (4)	0.158 (6)	0.036 (3)	0.006 (4)	0.040 (4)
C3	0.074 (4)	0.162 (6)	0.089 (4)	0.015 (4)	0.036 (3)	0.028 (4)
O2	0.033 (1)	0.044 (1)	0.035 (1)	0.004 (1)	0.006 (1)	0.004 (1)
C4	0.032 (2)	0.058 (3)	0.046 (2)	0.002 (2)	0.008 (2)	0.011 (2)
C5	0.051 (2)	0.091 (4)	0.057 (3)	0.002 (3)	0.025 (2)	0.009 (3)
C6	0.057 (3)	0.060 (3)	0.093 (3)	0.010 (2)	0.023 (2)	0.028 (3)
O3	0.035 (1)	0.038 (1)	0.042 (1)	0.011 (1)	0.008 (1)	0.001 (1)
C7	0.044 (2)	0.051 (2)	0.054 (2)	0.014 (2)	0.013 (2)	0.003 (2)
C8	0.067 (3)	0.065 (3)	0.086 (3)	0.007 (3)	0.025 (2)	0.025 (3)
C9	0.135 (4)	0.125 (4)	0.090 (4)	0.094 (3)	0.025 (3)	0.034 (3)
O4	0.027 (1)	0.019 (1)	0.034 (1)	0.003 (1)	0.005 (1)	0.000 (1)
C10	0.032 (2)	0.028 (2)	0.043 (2)	0.001 (2)	0.009 (2)	0.003 (2)
C11	0.029 (2)	0.024 (2)	0.056 (2)	0.001 (2)	0.011 (2)	0.009 (2)
C12	0.045 (2)	0.037 (2)	0.038 (2)	0.013 (2)	0.011 (2)	0.012 (2)
O5	0.027 (1)	0.033 (1)	0.031 (1)	0.006 (1)	0.003 (1)	0.000 (1)
N1	0.052 (2)	0.035 (2)	0.086 (2)	0.012 (2)	0.029 (2)	0.020 (2)
O6	0.085 (2)	0.042 (2)	0.146 (3)	0.019 (2)	0.032 (2)	0.012 (2)
O7	0.107 (3)	0.069 (2)	0.129 (3)	0.004 (2)	0.017 (2)	0.060 (2)
C13	0.033 (2)	0.021 (2)	0.056 (2)	0.001 (2)	0.004 (2)	0.004 (2)
O8	0.028 (1)	0.025 (1)	0.036 (1)	0.002 (1)	0.005 (1)	0.003 (1)
O9	0.041 (1)	0.048 (2)	0.029 (1)	0.010 (1)	0.004 (1)	0.001 (1)
C14	0.042 (2)	0.059 (3)	0.035 (2)	0.011 (2)	0.011 (2)	0.003 (2)

C15	0.069(3)	0.073(3)	0.041(2)	0.017(3)	0.012(2)	0.009(2)
C16	0.068(3)	0.093(4)	0.044(2)	0.027(3)	0.013(2)	0.016(2)
O10	0.031(1)	0.045(1)	0.048(1)	0.001(1)	0.000(1)	0.015(1)
C17	0.039(2)	0.067(3)	0.080(3)	0.005(2)	0.000(2)	0.049(2)
C18	0.064(3)	0.153(5)	0.062(3)	0.009(4)	0.021(3)	0.047(3)
C19	0.061(3)	0.076(3)	0.157(5)	0.020(3)	0.002(3)	0.063(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2 [h^2 a^2 U(1,1) + k^2 b^2 U(2,2) + l^2 c^2 U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)]]$$

where a, b, and c are reciprocal lattice constants.

Table of Positional Parameters and Their E.S.D.

Atom	x	y	z	B (Å <sup>2</sup> )
----	-	-	-	-----
H1	0.6905	0.0883	0.8745	7*
H2	0.5437	0.1709	0.8963	11*
H3	0.5550	0.1170	0.9786	11*
H4	0.6241	0.2181	0.9571	11*
H5	0.5584	-0.0281	0.8375	11*
H6	0.6469	-0.1089	0.8627	11*
H7	0.5683	-0.0893	0.9178	11*
H8	0.6394	-0.0317	1.1077	4*
H9	0.6149	-0.0585	1.2338	6*
H10	0.6718	-0.1671	1.2057	6*
H11	0.7252	-0.0677	1.2562	6*
H12	0.6332	0.1443	1.1749	7*
H13	0.7439	0.1402	1.1959	7*
H14	0.7013	0.1592	1.1111	7*
H15	0.6371	-0.2547	1.0563	5*
H16	0.6948	-0.4194	1.1252	7*
H17	0.7885	-0.4153	1.0851	7*
H18	0.7657	-0.3121	1.1403	7*
H19	0.5930	-0.4304	0.9999	11*
H20	0.6020	-0.3316	0.9383	11*
H21	0.6827	-0.4272	0.9548	11*
H22	0.8990	0.1697	1.1074	3*
H23	0.8639	0.2146	1.0251	3*
H24	1.0759	0.1999	1.1590	4*
H25	1.1445	0.2635	1.1077	4*
H26	1.0886	0.3305	0.9772	3*

H27	0.9822	0.3129	0.9435	3*
H28	1.1058	-0.0380	0.7603	4*
H29	1.0899	0.1154	0.6740	6*
H30	0.9981	0.1598	0.7081	6*
H31	1.0975	0.1672	0.7569	6*
H32	1.0161	-0.0923	0.6488	6*
H33	0.9801	-0.1620	0.7171	6*
H34	0.9227	-0.0517	0.6821	6*
H35	0.9072	0.2793	0.8033	6*
H36	0.7802	0.2453	0.7096	9*
H37	0.8314	0.1243	0.7323	9*
H38	0.7349	0.1562	0.7639	9*
H39	0.7839	0.4114	0.8074	10*
H40	0.7380	0.3282	0.8647	10*
H41	0.8356	0.3912	0.8894	10*

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
=====	=====	=====	=====	=====	=====
TI1	O1	1.788 (2)	C7	C8	1.511 (5)
TI1	O2	1.819 (2)	C7	C9	1.466 (5)
TI1	O3	1.808 (2)	O4	C10	1.428 (3)
TI1	O4	2.258 (2)	C10	C11	1.542 (4)
TI1	O5	2.155 (2)	C11	C12	1.518 (4)
TI1	O8	2.113 (2)	C11	N1	1.520 (4)
TI2	O4	2.167 (2)	C11	C13	1.550 (4)
TI2	O4	2.215 (2)	C12	O5	1.430 (3)
TI2	O5	1.953 (2)	N1	O6	1.231 (4)
TI2	O8	1.984 (2)	N1	O7	1.192 (4)
TI2	O9	1.757 (2)	O6	O7	2.131 (5)
TI2	O10	1.786 (2)	C13	O8	1.413 (3)
O1	C1	1.407 (4)	O9	C14	1.435 (3)
C1	C2	1.501 (6)	C14	C15	1.496 (5)
C1	C3	1.502 (6)	C14	C16	1.515 (5)
O2	C4	1.439 (3)	O10	C17	1.430 (3)
C4	C5	1.502 (5)	C17	C18	1.528 (6)
C4	C6	1.502 (5)	C17	C19	1.491 (6)
O3	C7	1.419 (3)			

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 Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
=====	=====	=====	=====	=====	=====	=====	=====
O1	TI1	O2	96.21 (9)	O4	TI2	O8	75.46 (6)
O1	TI1	O3	102.10 (9)	O4	TI2	O9	92.27 (8)

O1	TI1	O4	92.49 (8) O4	TI2	O10	163.02 (8)
O1	TI1	O5	90.02 (8) O5	TI2	O8	155.91 (7)
O1	TI1	O8	162.76 (8) O5	TI2	O9	96.36 (8)
O2	TI1	O3	101.22 (8) O5	TI2	O10	102.05 (8)
O2	TI1	O4	94.97 (8) O8	TI2	O9	97.68 (8)
O2	TI1	O5	165.37 (8) O8	TI2	O10	93.92 (8)
O2	TI1	O8	92.94 (7) O9	TI2	O10	102.40 (9)
O3	TI1	O4	156.77 (7) TI1	O1	C1	150.4 (2)
O3	TI1	O5	90.33 (7) O1	C1	C2	109.4 (4)
O3	TI1	O8	90.36 (8) O1	C1	C3	111.4 (3)
O4	TI1	O5	71.48 (6) C2	C1	C3	111.2 (4)
O4	TI1	O8	72.13 (6) TI1	O2	C4	128.6 (2)
O5	TI1	O8	77.90 (6) O2	C4	C5	109.5 (3)
O4	TI2	O4	73.79 (7) O2	C4	C6	109.5 (3)
O4	TI2	O5	77.32 (7) C5	C4	C6	112.6 (3)
O4	TI2	O8	84.22 (6) TI1	O3	C7	138.1 (2)
O4	TI2	O9	165.06 (8) O3	C7	C8	109.6 (3)
O4	TI2	O10	92.22 (7) O3	C7	C9	110.0 (3)
O4	TI2	O5	84.52 (7) C8	C7	C9	113.7 (4)
TI1	O4	TI2	98.64 (7) C11	N1	O6	117.6 (3)
TI1	O4	TI2	98.05 (6) C11	N1	O7	119.3 (3)
TI1	O4	C10	120.5 (1) O6	N1	O7	123.1 (3)
TI2	O4	TI2	106.21 (7) N1	O6	O7	28.0 (2)
TI2	O4	C10	115.7 (1) N1	O7	O6	28.9 (2)
TI2	O4	C10	115.0 (1) C11	C13	O8	110.3 (2)
O4	C10	C11	111.6 (2) TI1	O8	TI2	110.99 (8)
C10	C11	C12	114.7 (2) TI1	O8	C13	120.5 (2)
C10	C11	N1	105.0 (2) TI2	O8	C13	119.1 (1)
C10	C11	C13	113.0 (2) TI2	O9	C14	166.9 (2)

C12	C11	N1	107.9 (2)	O9	C14	C15	108.6 (3)
C12	C11	C13	110.3 (2)	O9	C14	C16	109.0 (2)
N1	C11	C13	105.2 (2)	C15	C14	C16	113.9 (3)
C11	C12	O5	110.4 (2)	TI2	O10	C17	138.3 (2)
TI1	O5	TI2	109.45 (8)	O10	C17	C18	109.4 (3)
TI1	O5	C12	120.0 (1)	O10	C17	C19	110.1 (3)
TI2	O5	C12	120.0 (1)	C18	C17	C19	113.0 (3)

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Numbers in parentheses are estimated standard deviations in  
the least significant digits.

X-ray experimental data for compound 3

Formula : C<sub>80</sub>H<sub>168</sub>N<sub>4</sub>O<sub>38</sub>Ti<sub>8</sub>  
Molecular weight : 2177.4  
Color : without  
Crystal system : triclinic  
a (Å) : 11.057 (3)  
b (Å) : 14.115 (4)  
c (Å) : 18.362 (5)  
α (deg) : 70.45 (2)  
β (deg) : 81.54 (2)  
γ (deg) : 86.30 (2)  
Volume (Å<sup>3</sup>) : 2670.8  
Z : 1  
Dcalc (gcm<sup>-3</sup>) : 1.354  
Wavelength (Å) : 0.7107  
μ (cm<sup>-1</sup>) : 6.358  
Space group : P-1  
Diffractometer : Enraf-Nonius CAD4-F  
Crystal dim. (mm) : 0.40\*0.35\*0.10  
Temperature : -100°C  
Radiation : MoKα graphite monochromated  
Mode : θ/2θ  
Scan speed : Variable  
Scan width (deg) : 1.38 + 0.34\*tg(θ)  
Octants : +h+k+l  
θ min/max (deg) : 2/26  
Number of data : 11266  
collected  
Number of data : 5089  
with I > 3σ(I)  
Number of variables : 525  
Abs min/max : 0.90/1.00  
R(F) : 0.078  
Rw(F) : 0.093  
p : 0.08  
Largest peak in : 0.11  
final diff. (eÅ<sup>-3</sup>)  
GOF : 1.181

Table of Positional Parameters and Their E.S.D.

Atom	x	y	z	B(Å <sup>2</sup> )
----	-	-	-	-----
TI1	0.4793 (1)	0.0337 (1)	1.23996 (9)	3.22 (4)
TI2	0.5943 (1)	-0.0856 (1)	1.10518 (8)	2.43 (3)
TI3	0.5724 (1)	-0.2047 (1)	1.29730 (9)	3.38 (4)
TI4	0.4937 (1)	-0.1541 (1)	0.95078 (8)	2.78 (3)
O1	0.4486 (5)	-0.1519 (4)	0.8457 (3)	3.6 (1)
C1	0.455 (1)	-0.2487 (7)	0.8299 (6)	4.8 (2)
C2	0.325 (1)	-0.2832 (9)	0.8383 (7)	6.9 (3)
C3	0.337 (1)	-0.3935 (9)	0.8265 (9)	10.1 (4)
C4	0.216 (2)	-0.427 (2)	0.835 (2)	16.7 (9) *
O2	0.5467 (6)	0.0527 (5)	1.3145 (4)	4.8 (2)
C5	0.610 (1)	0.051 (1)	1.3768 (7)	8.9 (4)
C6	0.591 (1)	0.142 (1)	1.3982 (7)	8.3 (4)
C7	0.656 (2)	0.134 (1)	1.4701 (8)	11.5 (4)
C8	0.654 (2)	0.223 (2)	1.485 (1)	14.9 (6)
O3	0.3324 (6)	0.0878 (4)	1.2529 (3)	4.6 (2)
C9	0.254	0.146	1.290	16*
C10	0.133	0.104	1.339	15*
C11	0.081	0.218	1.303	15*
C12	-0.049	0.229	1.327	15*
O4	0.4215 (5)	-0.1059 (4)	1.2926 (3)	3.3 (1)
C13	0.3019 (8)	-0.1316 (7)	1.2850 (5)	3.7 (2)
C14	0.3040 (7)	-0.1350 (7)	1.2013 (5)	3.1 (2)
C15	0.3881 (7)	-0.2190 (6)	1.1873 (5)	2.9 (2)
O5	0.5126 (5)	-0.1976 (4)	1.1896 (3)	2.8 (1)
N1	0.1762 (6)	-0.1639 (6)	1.1951 (4)	3.9 (2)
O6	0.0961 (7)	-0.162 (1)	1.2453 (5)	11.4 (4)

O7	0.1576 (6)	-0.1778 (6)	1.1379 (4)	6.5 (2)
C16	0.3235 (7)	-0.0320 (6)	1.1378 (5)	3.1 (2)
O8	0.4457 (5)	0.0047 (4)	1.1359 (3)	2.6 (1)
O9	0.6322 (5)	-0.0586 (4)	1.2125 (3)	2.7 (1)
C17	0.7510 (8)	-0.0205 (7)	1.2115 (5)	3.7 (2)
C18	0.8274 (7)	-0.0025 (7)	1.1314 (5)	3.4 (2)
C19	0.7770 (7)	0.0786 (6)	1.0628 (5)	3.3 (2)
O10	0.6553 (5)	0.0539 (4)	1.0568 (3)	2.5 (1)
N2	0.9499 (7)	0.0400 (6)	1.1356 (4)	4.2 (2)
O11	1.0322 (6)	0.0391 (6)	1.0866 (4)	6.2 (2)
O12	0.9570 (7)	0.0735 (7)	1.1865 (5)	9.9 (2)
C20	0.8583 (8)	-0.1011 (7)	1.1128 (6)	3.8 (2)
O13	0.7486 (5)	-0.1346 (4)	1.0977 (3)	3.1 (1)
O14	0.4745 (6)	-0.3107 (5)	1.3485 (4)	4.7 (2)
C21	0.460 (1)	-0.400 (1)	1.4119 (7)	7.6 (4)
C22	0.369 (2)	-0.468 (1)	1.401 (1)	11.5 (6)
C23	0.428 (2)	-0.516 (2)	1.344 (1)	12.3 (7)
C24	0.346 (2)	-0.598 (1)	1.335 (1)	11.0 (5)
O15	0.6253 (6)	-0.1734 (5)	1.3753 (3)	4.4 (2)
C25	0.6942 (9)	-0.227 (1)	1.4370 (6)	5.7 (3)
C26	0.828 (1)	-0.197 (1)	1.4115 (7)	7.5 (4)
C27	0.901 (1)	-0.259 (2)	1.4775 (9)	12.0 (7)
C28	1.037 (2)	-0.226 (2)	1.453 (1)	17 (1)
O16	0.7095 (6)	-0.2701 (5)	1.2734 (4)	4.4 (2)
C29	0.745 (1)	-0.3484 (8)	1.2427 (6)	5.2 (3)
C30	0.866 (2)	-0.398 (1)	1.2741 (9)	10.7 (5)
C31	0.842 (2)	-0.454 (2)	1.353 (1)	13.7 (7) *
C32	0.977 (3)	-0.493 (2)	1.382 (2)	18 (1) *
O17	0.5336 (5)	-0.1071 (4)	1.0295 (3)	2.6 (1)

O18	0.4070 (5)	-0.2647 (4)	1.0078 (3)	3.6 (1)
C33	0.449 (1)	-0.3663 (8)	1.0464 (8)	5.9 (3)
C34	0.351 (1)	-0.4402 (9)	1.0694 (8)	6.9 (4)
C35	0.255 (1)	-0.427 (1)	1.1330 (8)	7.4 (4)
C36	0.159 (1)	-0.513 (1)	1.158 (1)	9.4 (5)
O19	0.6389 (6)	-0.2114 (5)	0.9357 (4)	4.0 (2)
C37	0.7659 (9)	-0.2211 (9)	0.9428 (8)	5.9 (3)
C38	0.790 (1)	-0.3266 (9)	0.9958 (8)	11.6 (6)
C39	0.9046	-0.3407	1.0193	22 (1) *
C40	1.0208	-0.2961	1.0054	19 (1) *

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  
 $(4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
TI1	0.0370 (8)	0.0510 (8)	0.0393 (7)	0.0066 (7)	0.0056 (6)	0.0200 (6)
TI2	0.0262 (6)	0.0344 (7)	0.0315 (6)	0.0020 (6)	0.0099 (5)	0.0078 (5)
TI3	0.0378 (8)	0.0525 (9)	0.0343 (7)	0.0045 (7)	0.0125 (6)	0.0054 (7)
TI4	0.0354 (7)	0.0326 (7)	0.0407 (7)	0.0045 (6)	0.0116 (6)	0.0129 (5)
O1	0.050 (3)	0.041 (3)	0.053 (3)	0.003 (3)	0.015 (3)	0.022 (2)
C1	0.066 (6)	0.061 (5)	0.073 (5)	0.010 (5)	0.015 (5)	0.038 (4)
C2	0.083 (8)	0.080 (6)	0.122 (8)	0.026 (5)	0.007 (6)	0.060 (5)
C3	0.097 (9)	0.135 (7)	0.208 (9)	0.049 (6)	0.000 (7)	0.128 (5)
O2	0.063 (4)	0.076 (4)	0.050 (3)	0.013 (3)	0.009 (3)	0.029 (3)
C5	0.15 (1)	0.13 (1)	0.084 (6)	0.001 (8)	0.059 (6)	0.058 (5)
C6	0.12 (1)	0.140 (8)	0.095 (6)	0.001 (7)	0.033 (6)	0.087 (4)
C7	0.15 (1)	0.200 (9)	0.155 (7)	0.036 (8)	0.025 (7)	0.142 (5)
C8	0.10 (1)	0.34 (2)	0.21 (1)	0.01 (1)	0.036 (9)	0.188 (9)
O3	0.052 (4)	0.063 (4)	0.067 (4)	0.002 (3)	0.000 (3)	0.033 (3)
O4	0.033 (3)	0.056 (3)	0.038 (3)	0.007 (3)	0.006 (2)	0.013 (2)
C13	0.029 (4)	0.074 (6)	0.041 (4)	0.014 (4)	0.004 (3)	0.018 (4)
C14	0.024 (4)	0.048 (5)	0.044 (4)	0.011 (3)	0.011 (3)	0.008 (3)
C15	0.026 (4)	0.042 (4)	0.045 (4)	0.007 (3)	0.009 (3)	0.013 (3)
O5	0.030 (3)	0.037 (3)	0.036 (3)	0.002 (2)	0.012 (2)	0.006 (2)
N1	0.025 (3)	0.071 (5)	0.046 (4)	0.018 (3)	0.004 (3)	0.008 (3)
O6	0.056 (4)	0.30 (1)	0.074 (5)	0.073 (5)	0.003 (4)	0.058 (6)
O7	0.048 (4)	0.126 (5)	0.089 (4)	0.022 (4)	0.017 (3)	0.052 (3)
C16	0.023 (4)	0.043 (4)	0.051 (4)	0.007 (3)	0.014 (3)	0.008 (4)
O8	0.026 (3)	0.038 (3)	0.035 (3)	0.005 (2)	0.006 (2)	0.011 (2)
O9	0.025 (3)	0.048 (3)	0.030 (2)	0.005 (2)	0.007 (2)	0.011 (2)
C17	0.033 (4)	0.065 (5)	0.046 (4)	0.019 (4)	0.012 (3)	0.016 (4)

C18	0.027 (4)	0.060 (5)	0.045 (4)	0.010 (4)	0.015 (3)	0.013 (4)
C19	0.035 (4)	0.040 (4)	0.047 (4)	0.012 (3)	0.023 (3)	0.000 (3)
O10	0.025 (3)	0.033 (3)	0.037 (3)	0.004 (2)	0.008 (2)	0.009 (2)
N2	0.036 (4)	0.075 (5)	0.048 (4)	0.017 (3)	0.016 (3)	0.013 (3)
O11	0.042 (4)	0.117 (5)	0.080 (4)	0.033 (4)	0.009 (3)	0.040 (4)
O12	0.057 (4)	0.253 (7)	0.114 (4)	0.069 (4)	0.010 (3)	0.119 (4)
C20	0.029 (4)	0.054 (5)	0.069 (5)	0.001 (4)	0.019 (4)	0.023 (4)
O13	0.027 (3)	0.049 (3)	0.041 (3)	0.000 (2)	0.011 (2)	0.013 (2)
O14	0.059 (4)	0.055 (4)	0.053 (4)	0.011 (3)	0.020 (3)	0.006 (3)
C21	0.13 (1)	0.089 (8)	0.060 (7)	0.049 (7)	0.020 (7)	0.004 (6)
C22	0.22 (2)	0.09 (1)	0.10 (1)	0.07 (1)	0.02 (1)	0.017 (9)
C23	0.17 (2)	0.16 (1)	0.15 (1)	0.02 (1)	0.05 (1)	0.05 (1)
C24	0.17 (1)	0.11 (1)	0.14 (1)	0.074 (8)	0.043 (9)	0.012 (9)
O15	0.046 (3)	0.084 (4)	0.036 (3)	0.000 (3)	0.013 (3)	0.014 (3)
C25	0.054 (5)	0.104 (9)	0.052 (5)	0.007 (6)	0.029 (4)	0.006 (5)
C26	0.058 (6)	0.15 (1)	0.065 (7)	0.004 (7)	0.031 (5)	0.003 (7)
C27	0.069 (8)	0.28 (2)	0.087 (9)	0.01 (1)	0.036 (7)	0.02 (1)
C28	0.071 (9)	0.40 (3)	0.12 (1)	0.06 (1)	0.024 (9)	0.02 (2)
O16	0.051 (3)	0.061 (4)	0.055 (3)	0.009 (3)	0.026 (3)	0.012 (3)
C29	0.067 (6)	0.068 (6)	0.068 (6)	0.031 (5)	0.029 (5)	0.029 (4)
C30	0.17 (1)	0.13 (1)	0.10 (1)	0.096 (9)	0.04 (1)	0.040 (8)
O17	0.032 (3)	0.032 (3)	0.036 (2)	0.003 (2)	0.013 (2)	0.008 (2)
O18	0.045 (3)	0.043 (3)	0.053 (3)	0.008 (3)	0.008 (3)	0.018 (2)
C33	0.077 (7)	0.034 (5)	0.098 (8)	0.011 (5)	0.001 (7)	0.007 (5)
C34	0.085 (9)	0.064 (7)	0.105 (9)	0.013 (7)	0.007 (8)	0.024 (6)
C35	0.077 (8)	0.095 (9)	0.104 (9)	0.019 (7)	0.011 (8)	0.032 (7)
C36	0.10 (1)	0.10 (1)	0.14 (1)	0.040 (8)	0.00 (1)	0.026 (9)
O19	0.044 (3)	0.048 (3)	0.068 (3)	0.005 (3)	0.015 (3)	0.027 (2)
C37	0.039 (5)	0.059 (7)	0.111 (9)	0.014 (5)	0.009 (6)	0.008 (6)

C38 0.062(7) 0.09(1) 0.26(2) 0.008(8) 0.071(9) 0.00(1)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2 [h^2 a^2 U(1,1) + k^2 b^2 U(2,2) + l^2 c^2 U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)]]$$

where a, b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1 =====	Atom 2 =====	Distance =====	Atom 1 =====	Atom 2 =====	Distance =====
TI1	O1	1.984 (6)	TI4	O17	1.896 (5)
TI1	O2	1.753 (6)	TI4	O18	1.804 (6)
TI1	O3	1.768 (6)	TI4	O19	1.778 (6)
TI1	O4	1.983 (6)	O1	C1	1.48 (1)
TI1	O8	2.170 (5)	C1	C2	1.52 (1)
TI1	O9	2.171 (5)	C2	C3	1.64 (2)
TI2	O5	1.962 (5)	C3	C4	1.41 (3)
TI2	O8	2.140 (5)	O2	C5	1.42 (1)
TI2	O9	2.231 (5)	C5	C6	1.45 (2)
TI2	O10	1.987 (5)	C6	C7	1.56 (2)
TI2	O13	1.803 (5)	C7	C8	1.37 (2)
TI2	O17	1.748 (5)	O3	C9	1.419 (6)
TI3	O4	2.098 (6)	C9	C10	1.529 (0)
TI3	O5	2.145 (5)	C9	C11	2.124 (0)
TI3	O9	2.200 (5)	C10	C11	1.617 (0)
TI3	O14	1.806 (6)	C11	C12	1.454 (0)
TI3	O15	1.814 (6)	O4	C13	1.431 (8)
TI3	O16	1.799 (6)	C13	C14	1.55 (1)
TI4	O1	2.052 (5)	C14	C15	1.53 (1)
TI4	O8	2.249 (5)	C14	N1	1.526 (9)
TI4	O10	2.090 (5)	C14	C16	1.53 (1)
C15	O5	1.438 (8)	C23	C24	1.58 (2)
N1	O6	1.19 (1)	O15	C25	1.43 (1)
N1	O7	1.179 (9)	C25	C26	1.53 (1)
O6	O7	2.07 (1)	C26	C27	1.54 (2)
C16	O8	1.470 (8)	C27	C28	1.55 (2)

O9	C17	1.446 (8)	O16	C29	1.41 (1)
C17	C18	1.53 (1)	C29	C30	1.57 (2)
C18	C19	1.54 (1)	C30	C31	1.40 (2)
C18	N2	1.538 (9)	C31	C32	1.66 (3)
C18	C20	1.55 (1)	O18	C33	1.45 (1)
C19	O10	1.440 (8)	C33	C34	1.47 (1)
N2	O11	1.185 (9)	C34	C35	1.51 (2)
N2	O12	1.19 (1)	C35	C36	1.58 (2)
O11	O12	2.09 (1)	O19	C37	1.42 (1)
C20	O13	1.426 (8)	C37	C38	1.51 (1)
O14	C21	1.40 (1)	C38	C39	1.38 (1)
C21	C22	1.52 (2)	C39	C40	1.418 (0)
C22	C23	1.48 (2)			

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Numbers in parentheses are estimated standard deviations in  
the least significant digits.

Table of Bond Angles in Degrees

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
O1	TI1	O2	96.7 (3)	O8	TI2	O10	76.2 (2)
O1	TI1	O3	96.5 (3)	O8	TI2	O13	157.4 (2)
O1	TI1	O4	158.0 (2)	O8	TI2	O17	97.1 (2)
O1	TI1	O8	76.9 (2)	O9	TI2	O10	81.2 (2)
O1	TI1	O9	89.5 (2)	O9	TI2	O13	86.9 (2)
O2	TI1	O3	101.2 (3)	O9	TI2	O17	168.4 (2)
O2	TI1	O4	100.4 (3)	O10	TI2	O13	90.4 (2)
O2	TI1	O8	164.8 (3)	O10	TI2	O17	103.2 (2)
O2	TI1	O9	92.5 (3)	O13	TI2	O17	103.7 (2)
O3	TI1	O4	93.7 (2)	O4	TI3	O5	78.3 (2)
O3	TI1	O8	93.2 (2)	O4	TI3	O9	73.2 (2)
O3	TI1	O9	164.2 (2)	O4	TI3	O14	90.5 (3)
O4	TI1	O8	83.1 (2)	O4	TI3	O15	92.7 (2)
O4	TI1	O9	76.0 (2)	O4	TI3	O16	164.3 (2)
O8	TI1	O9	73.8 (2)	O5	TI3	O9	73.9 (2)
O5	TI2	O8	85.2 (2)	O5	TI3	O14	89.9 (2)
O5	TI2	O9	76.8 (2)	O5	TI3	O15	164.1 (3)
O5	TI2	O10	154.5 (2)	O5	TI3	O16	89.7 (2)
O5	TI2	O13	101.0 (2)	O9	TI3	O14	158.8 (2)
O5	TI2	O17	96.3 (2)	O9	TI3	O15	91.0 (2)
O8	TI2	O9	73.2 (2)	O9	TI3	O16	93.9 (2)
O14	TI3	O15	103.4 (3)	O2	C5	C6	114. (1)
O14	TI3	O16	99.7 (3)	C5	C6	C7	112. (1)
O15	TI3	O16	96.5 (3)	C6	C7	C8	113. (2)
O1	TI4	O8	73.8 (2)	O3	C9	C10	120.5 (2)
O1	TI4	O10	81.3 (2)	O3	C9	C11	148.7 (2)

O1	TI4	O17	159.9 (2)	C10	C9	C11	49. (0)
O1	TI4	O18	95.1 (2)	C9	C10	C11	84. (0)
O1	TI4	O19	92.8 (3)	C9	C11	C10	45. (0)
O8	TI4	O10	71.9 (2)	C9	C11	C12	159. (0)
O8	TI4	O17	87.5 (2)	C10	C11	C12	113. (0)
O8	TI4	O18	164.1 (2)	O4	C13	C14	108.1 (6)
O8	TI4	O19	92.5 (2)	C13	C14	C15	111.6 (6)
O10	TI4	O17	86.0 (2)	C13	C14	N1	107.1 (6)
O10	TI4	O18	95.5 (2)	C13	C14	C16	113.5 (7)
O10	TI4	O19	164.3 (2)	C15	C14	N1	105.0 (6)
O17	TI4	O18	101.6 (2)	C15	C14	C16	114.8 (6)
O17	TI4	O19	95.3 (2)	N1	C14	C16	103.9 (6)
O18	TI4	O19	99.6 (3)	C14	C15	O5	109.6 (6)
O1	C1	C2	107.5 (8)	C14	N1	O6	117.9 (8)
C1	C2	C3	105.9 (9)	C14	N1	O7	119.5 (7)
C2	C3	C4	106. (2)	O6	N1	O7	122.1 (8)
N1	O6	O7	28.8 (4)	C18	C20	O13	107.6 (6)
N1	O7	O6	29.1 (4)	O14	C21	C22	111 (1)
C14	C16	O8	109.9 (6)	C21	C22	C23	109. (2)
O9	C17	C18	110.4 (6)	C22	C23	C24	113. (2)
C17	C18	C19	115.5 (7)	O15	C25	C26	108.7 (8)
C17	C18	N2	106.4 (6)	C25	C26	C27	108 (1)
C17	C18	C20	112.4 (7)	C26	C27	C28	108. (1)
C19	C18	N2	103.9 (6)	O16	C29	C30	108.3 (9)
C19	C18	C20	111.1 (7)	C29	C30	C31	110. (2)
N2	C18	C20	106.5 (6)	C30	C31	C32	106. (2)
C18	C19	O10	110.2 (6)	O18	C33	C34	112.6 (9)
C18	N2	O11	117.4 (7)	C33	C34	C35	113. (1)
C18	N2	O12	119.1 (8)	C34	C35	C36	110. (1)

O11	N2	O12	123.5 (8)	O19	C37	C38	108.0 (8)
N2	O11	O12	28.4 (4)	C37	C38	C39	114.0 (9)
N2	O12	O11	28.2 (4)	C38	C39	C40	143.3 (5)

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Numbers in parentheses are estimated standard deviations in  
the least significant digits.

WinPacha atomic charges calculations report for TI4OME16  
Titanium methoxide Ti4(OMe)16  
The crystal and molecular structure of titanium methoxide  
Acta Cryst. (1968) B24, 1107-1114  
D.A. Wright & D.A. Williams  
V= 774.87 Å<sup>3</sup> (Z = 4) -> Rval = 13.90%

\*\*\*Atomic electronegativies (eV) and radii (pm) \*\*\*

C( 15.050, 62.0)  
O( 21.360, 45.0)  
Ti( 8.170, 147.7)  
H( 13.610, 53.0)

Madelung summation with gaussian inner-charge scaling (G = 0.21 Å<sup>-1</sup>)  
Reciprocal space exploration: -2 <= (h, k, l) <= 2

Madelung constant A = 108.8922646/4 = 27.2230662 (dmin = 1.10 Å )  
min = -0.40293 Å<sup>-1</sup> < mean = 0.31156 Å<sup>-1</sup> < max = 1.73813 Å<sup>-1</sup>  
Total electrostatic balance = -1425.5 eV = -137536.2 kJ.mol<sup>-1</sup>

Mean electronegativity: <EN> = 12.4 eV  
Global hardness: <GH> = 5.66 eV (G = 0.21 Å<sup>-1</sup>)

Electronic signature: #n Label(±ox) [CN] = ±q {±f}

	Atom	Charge	Fukui
#16	O8(-2) [ 4] =	-0.74 {	-0.01}
#14	O6(-2) [ 3] =	-0.66 {	-0.00}
#15	O7(-2) [ 3] =	-0.66 {	-0.00}
#9	O1(-2) [ 2] =	-0.58 {	0.01}
#10	O2(-2) [ 2] =	-0.58 {	0.01}
#11	O3(-2) [ 2] =	-0.53 {	0.01}
#12	O4(-2) [ 2] =	-0.50 {	0.02}
#13	O5(-2) [ 2] =	-0.48 {	0.02}
#8	C8(-2) [ 4] =	-0.13 {	0.01}
#6	C6(-2) [ 4] =	-0.09 {	0.02}
#7	C7(-2) [ 4] =	-0.08 {	0.02}
#3	C3(-2) [ 4] =	-0.05 {	0.02}
#2	C2(-2) [ 4] =	-0.04 {	0.02}
#1	C1(-2) [ 4] =	-0.04 {	0.02}
#4	C4(-2) [ 4] =	-0.02 {	0.02}
#38	H81(+1) [ 1] =	-0.00 {	0.04}
#39	H82(+1) [ 1] =	+0.00 {	0.04}
#32	H61(+1) [ 1] =	+0.01 {	0.05}
#5	C5(-2) [ 4] =	+0.01 {	0.02}
#28	H40(+1) [ 1] =	+0.01 {	0.04}
#37	H80(+1) [ 1] =	+0.01 {	0.05}
#31	H60(+1) [ 1] =	+0.01 {	0.05}
#35	H71(+1) [ 1] =	+0.01 {	0.05}
#25	H30(+1) [ 1] =	+0.01 {	0.05}
#40	H50(+1) [ 1] =	+0.01 {	0.04}
#34	H70(+1) [ 1] =	+0.01 {	0.05}
#22	H20(+1) [ 1] =	+0.01 {	0.06}
#19	H10(+1) [ 1] =	+0.02 {	0.05}
#42	H52(+1) [ 1] =	+0.02 {	0.06}
#41	H51(+1) [ 1] =	+0.02 {	0.05}
#36	H72(+1) [ 1] =	+0.03 {	0.05}
#26	H31(+1) [ 1] =	+0.03 {	0.06}
#29	H41(+1) [ 1] =	+0.03 {	0.06}
#30	H42(+1) [ 1] =	+0.03 {	0.05}
#24	H22(+1) [ 1] =	+0.03 {	0.05}

#20	H11(+1) [ 1] =	+0.03 {	0.05}
#21	H12(+1) [ 1] =	+0.03 {	0.05}
#23	H21(+1) [ 1] =	+0.03 {	0.06}
#33	H62(+1) [ 1] =	+0.03 {	0.05}
#27	H32(+1) [ 1] =	+0.04 {	0.05}
#17	Ti1(+4) [ 6] =	+2.25 {	0.30}
#18	Ti2(+4) [ 6] =	+2.49 {	0.28}

Partial electrostatic balance: <EB> = -139.2 eV = -13435.0 kJ.mol<sup>-1</sup>

Reduced electrostatic balance: <EB/4> = -34.8 eV = -3358.8 kJ.mol<sup>-1</sup>

Global ionicity: <GI> = 31.3 %

Statistical report: <Atom>[num] = mean ± 3xstdev (stdev) <avdev>

<q(H)>[24] = 0.02 ± 0.04 (0.01) <0.01>

<f(H)>[24] = 0.05 ± 0.01 (0.00) <0.00>

<q(C)>[8] = -0.06 ± 0.13 (0.04) <0.03>

<f(C)>[8] = 0.02 ± 0.01 (0.00) <0.00>

<q(O)>[8] = -0.59 ± 0.27 (0.09) <0.07>

<f(O)>[8] = 0.01 ± 0.04 (0.01) <0.01>

<q(Ti)>[2] = 2.37 ± 0.50 (0.17) <0.12>

<f(Ti)>[2] = 0.29 ± 0.05 (0.02) <0.01>

WinPacha retrosynthetic report for TI4OME16  
Titanium methoxide Ti4(OMe)16  
The crystal and molecular structure of titanium methoxide  
Acta Cryst. (1968) B24, 1107-1114  
D.A. Wright & D.A. Williams  
V= 774.87 Å<sup>3</sup> (Z = 4) -> Rval = 13.90%

Current molecular fragment is: [H12C4O4Ti]\*4 = 688.16 g.mol<sup>-1</sup>

\*\*\* Total electrical charge on molecular fragment = 0 \*\*\*  
Partial electrostatic balance: <EB> = -139.203 eV = -13430.9 kJ.mol<sup>-1</sup>

#n Mol symb <=> Net symb = fragment PC => Retrosynthetic index(%)

#1	O10 <=>	O7 = -0.663 =>	0%
#2	O4 <=>	O7 = -0.663 =>	0%
#3	O5 <=>	O8 = -0.740 =>	0%
#4	O6 <=>	O8 = -0.740 =>	0%
#5	O3 <=>	O6 = -0.665 =>	0%
#6	O14 <=>	O6 = -0.665 =>	0%
#7	O1 <=>	O1 = -0.584 =>	0%
#8	O15 <=>	O1 = -0.584 =>	0%
#9	Ti3 <=>	Ti1 = +2.251 =>	0%
#10	Ti2 <=>	Ti1 = +2.251 =>	0%
#11	Ti4 <=>	Ti2 = +2.484 =>	0%
#12	Ti1 <=>	Ti2 = +2.484 =>	0%
#13	O2 <=>	O2 = -0.580 =>	0%
#14	O16 <=>	O2 = -0.580 =>	0%
#15	O9 <=>	O5 = -0.483 =>	0%
#16	O13 <=>	O5 = -0.483 =>	0%
#17	O8 <=>	O4 = -0.495 =>	0%
#18	O12 <=>	O4 = -0.495 =>	0%
#19	O7 <=>	O3 = -0.526 =>	0%
#20	O11 <=>	O3 = -0.526 =>	0%
#21	C4 <=>	C7 = -0.082 =>	0%
#22	C10 <=>	C7 = -0.082 =>	0%
#23	C2 <=>	C2 = -0.042 =>	0%
#24	C16 <=>	C2 = -0.042 =>	0%
#25	C5 <=>	C8 = -0.127 =>	0%
#26	C6 <=>	C8 = -0.127 =>	0%
#27	C11 <=>	C3 = -0.048 =>	0%
#28	C7 <=>	C3 = -0.048 =>	0%
#29	C12 <=>	C4 = -0.021 =>	1%
#30	C8 <=>	C4 = -0.021 =>	1%
#31	H6 <=>	H22 = +0.031 =>	1%
#32	H48 <=>	H22 = +0.031 =>	1%
#33	H12 <=>	H72 = +0.025 =>	1%
#34	H30 <=>	H72 = +0.025 =>	1%
#35	C15 <=>	C1 = -0.041 =>	1%
#36	C1 <=>	C1 = -0.041 =>	1%
#37	C14 <=>	C6 = -0.086 =>	2%
#38	C3 <=>	C6 = -0.086 =>	2%
#39	H2 <=>	H11 = +0.030 =>	2%
#40	H44 <=>	H11 = +0.030 =>	2%
#41	H3 <=>	H12 = +0.033 =>	2%
#42	H45 <=>	H12 = +0.033 =>	2%
#43	H36 <=>	H42 = +0.028 =>	2%
#44	H24 <=>	H42 = +0.028 =>	2%
#45	H4 <=>	H20 = +0.014 =>	3%
#46	H46 <=>	H20 = +0.014 =>	3%
#47	H21 <=>	H32 = +0.039 =>	3%

#48	H33 <=>	H32 = +0.039 =>	3%
#49	H32 <=>	H31 = +0.027 =>	5%
#50	H20 <=>	H31 = +0.027 =>	5%
#51	H28 <=>	H70 = +0.011 =>	5%
#52	H10 <=>	H70 = +0.011 =>	5%
#53	H47 <=>	H21 = +0.032 =>	6%
#54	H5 <=>	H21 = +0.032 =>	6%
#55	C13 <=>	C5 = +0.006 =>	7%
#56	C9 <=>	C5 = +0.006 =>	7%
#57	H37 <=>	H50 = +0.009 =>	7%
#58	H25 <=>	H50 = +0.009 =>	7%
#59	H27 <=>	H52 = +0.022 =>	8%
#60	H39 <=>	H52 = +0.022 =>	8%
#61	H38 <=>	H51 = +0.026 =>	8%
#62	H26 <=>	H51 = +0.026 =>	8%
#63	H29 <=>	H71 = +0.009 =>	8%
#64	H11 <=>	H71 = +0.009 =>	8%
#65	H23 <=>	H41 = +0.030 =>	8%
#66	H35 <=>	H41 = +0.030 =>	8%
#67	H43 <=>	H10 = +0.018 =>	10%
#68	H1 <=>	H10 = +0.018 =>	10%
#69	H13 <=>	H80 = +0.006 =>	10%
#70	H16 <=>	H80 = +0.006 =>	10%
#71	H18 <=>	H82 = +0.004 =>	15%
#72	H15 <=>	H82 = +0.004 =>	15%
#73	H34 <=>	H40 = +0.005 =>	20%
#74	H22 <=>	H40 = +0.005 =>	20%
#75	H42 <=>	H62 = +0.027 =>	20%
#76	H9 <=>	H62 = +0.027 =>	20%
#77	H19 <=>	H30 = +0.010 =>	30%
#78	H31 <=>	H30 = +0.010 =>	30%
#79	H40 <=>	H60 = +0.004 =>	39%
#80	H7 <=>	H60 = +0.004 =>	39%
#81	H8 <=>	H61 = +0.007 =>	43%
#82	H41 <=>	H61 = +0.007 =>	43%
#83	H17 <=>	H81 = -0.005 =>	47%
#84	H14 <=>	H81 = -0.005 =>	47%

WinPacha atomic charges calculations report for compound 1  
V= 4287.20 Å<sup>3</sup> (Z = 8) -> No R-value

\*\*\*Atomic electronegativies (eV) and radii (pm) \*\*\*

Ti( 8.170, 147.7)  
O( 21.360, 45.0)  
C( 15.050, 62.0)  
N( 18.130, 52.1)  
H( 13.610, 53.0)

Madelung summation with gaussian inner-charge scaling (G = 0.12 Å<sup>-1</sup>)  
Reciprocal space exploration: -2 <= (h, k, l) <= 2

Madelung constant A = 609.6443472/8 = 76.2055434 (dmin = 0.950 Å )  
min = 0.47703 Å<sup>-1</sup> < mean = 3.15327 Å<sup>-1</sup> < max = 9.91144 Å<sup>-1</sup>  
Total electrostatic balance = -9242.49 eV = -891756.9 kJ.mol<sup>-1</sup>

Mean electronegativity: <EN> = 13.03 eV  
Global hardness: <GH> = 6.09 eV (G = 0.12 Å<sup>-1</sup>)

Electronic signature: #n Label(±ox) [CN] = ±q {±f}

	Atom	Charge	Fukui
#7	O5(-2) [ 4] =	-0.717 {	-0.005 }
#10	O8(-2) [ 3] =	-0.658 {	-0.001 }
#6	O4(-2) [ 3] =	-0.654 {	-0.000 }
#5	O3(-2) [ 2] =	-0.581 {	0.004 }
#11	O9(-2) [ 2] =	-0.579 {	0.005 }
#12	O10(-2) [ 2] =	-0.578 {	0.005 }
#4	O2(-2) [ 2] =	-0.568 {	0.005 }
#3	O1(-2) [ 2] =	-0.556 {	0.005 }
#9	O7(-2) [ 1] =	-0.227 {	0.021 }
#8	O6(-2) [ 1] =	-0.210 {	0.020 }
#24	C12(-3) [ 4] =	-0.190 {	-0.010 }
#18	C6(-3) [ 4] =	-0.175 {	-0.007 }
#26	C14(-3) [ 4] =	-0.171 {	-0.006 }
#14	C2(-3) [ 4] =	-0.159 {	-0.002 }
#16	C4(-3) [ 4] =	-0.158 {	-0.002 }
#21	C9(-1) [ 4] =	-0.103 {	0.002 }
#22	C10(-1) [ 4] =	-0.089 {	0.003 }
#19	C7(-1) [ 4] =	-0.088 {	0.002 }
#15	C3(-1) [ 4] =	-0.034 {	0.008 }
#27	N1(+3) [ 3] =	-0.028 {	0.017 }
#13	C1(-1) [ 4] =	-0.027 {	0.007 }
#17	C5(-1) [ 4] =	-0.009 {	0.006 }
#20	C8(+1) [ 4] =	-0.001 {	0.015 }
#25	C13(-1) [ 4] =	+0.001 {	0.008 }
#34	H7(+1) [ 1] =	+0.008 {	0.019 }
#23	C11(-1) [ 4] =	+0.020 {	0.008 }
#33	H6(+1) [ 1] =	+0.025 {	0.018 }
#29	H2(+1) [ 1] =	+0.027 {	0.018 }
#54	H27(+1) [ 1] =	+0.027 {	0.020 }
#45	H18(+1) [ 1] =	+0.032 {	0.019 }
#30	H3(+1) [ 1] =	+0.037 {	0.022 }
#46	H19(+1) [ 1] =	+0.037 {	0.018 }
#50	H23(+1) [ 1] =	+0.041 {	0.018 }
#32	H5(+1) [ 1] =	+0.043 {	0.022 }
#38	H11(+1) [ 1] =	+0.044 {	0.019 }
#49	H22(+1) [ 1] =	+0.047 {	0.018 }
#55	H28(+1) [ 1] =	+0.048 {	0.019 }
#41	H14(+1) [ 1] =	+0.048 {	0.024 }

#31	H4 (+1) [ 1] =	+0.052 {	0.025}
#57	H30 (+1) [ 1] =	+0.054 {	0.026}
#48	H21 (+1) [ 1] =	+0.054 {	0.019}
#53	H26 (+1) [ 1] =	+0.055 {	0.026}
#42	H15 (+1) [ 1] =	+0.055 {	0.024}
#35	H8 (+1) [ 1] =	+0.056 {	0.024}
#37	H10 (+1) [ 1] =	+0.056 {	0.025}
#44	H17 (+1) [ 1] =	+0.060 {	0.020}
#56	H29 (+1) [ 1] =	+0.061 {	0.025}
#39	H12 (+1) [ 1] =	+0.062 {	0.020}
#52	H25 (+1) [ 1] =	+0.064 {	0.026}
#58	H31 (+1) [ 1] =	+0.068 {	0.025}
#40	H13 (+1) [ 1] =	+0.069 {	0.024}
#36	H9 (+1) [ 1] =	+0.075 {	0.026}
#28	H1 (+1) [ 1] =	+0.075 {	0.023}
#51	H24 (+1) [ 1] =	+0.076 {	0.025}
#47	H20 (+1) [ 1] =	+0.082 {	0.019}
#43	H16 (+1) [ 1] =	+0.088 {	0.021}
#2	Ti2 (+4) [ 6] =	+2.397 {	0.102}
#1	Ti1 (+4) [ 6] =	+2.512 {	0.112}

Partial electrostatic balance: <EB> = -615.46 eV = -59382.4 kJ.mol<sup>-1</sup>  
 Reduced electrostatic balance: <EB/4> = -153.87 eV = -14845.6 kJ.mol<sup>-1</sup>  
 Global ionicity: <GI> = 25.81 %

Statistical report: <Atom>[num] = mean ± 3×stdev (stdev) <avdev>

<q(H)>[31] = 0.053 ± 0.054 (0.018) <0.014>  
 <f(H)>[31] = 0.022 ± 0.009 (0.003) <0.003>  
 <q(C)>[14] = -0.084 ± 0.228 (0.076) <0.065>  
 <f(C)>[14] = 0.002 ± 0.021 (0.007) <0.006>  
 <q(N)>[1] = -0.028 ± 0.000 (0.000) <0.000>  
 <f(N)>[1] = 0.017 ± 0.000 (0.000) <0.000>  
 <q(O)>[10] = -0.533 ± 0.520 (0.173) <0.126>  
 <f(O)>[10] = 0.006 ± 0.025 (0.008) <0.006>  
 <q(Ti)>[2] = 2.455 ± 0.243 (0.081) <0.057>  
 <f(Ti)>[2] = 0.107 ± 0.021 (0.007) <0.005>

WinPacha retrosynthetic report for compound 1

V= 4287.20 Å<sup>3</sup> (Z = 8) -> No R-value

Current molecular fragment is: [H31C14NO10Ti2]\*2 = 938.44 g.mol<sup>-1</sup>

\*\*\* Total electrical charge on molecular fragment = 0 \*\*\*

Partial electrostatic balance: <EB> = -153.987 eV = -14857.4 kJ.mol<sup>-1</sup>

#n Mol symb <=> Net symb = fragment PC => Retrosynthetic index(%)

#1	O6 <=>	O5 = -0.717 =>	0%
#2	O9 <=>	O5 = -0.717 =>	0%
#3	O11 <=>	O4 = -0.654 =>	0%
#4	O4 <=>	O4 = -0.654 =>	0%
#5	Ti4 <=>	Ti1 = +2.511 =>	0%
#6	Ti1 <=>	Ti1 = +2.511 =>	0%
#7	O5 <=>	O8 = -0.658 =>	0%
#8	O10 <=>	O8 = -0.658 =>	0%
#9	C7 <=>	C4 = -0.158 =>	0%
#10	C27 <=>	C4 = -0.158 =>	0%
#11	O8 <=>	O10 = -0.577 =>	0%
#12	O13 <=>	O10 = -0.577 =>	0%
#13	Ti3 <=>	Ti2 = +2.400 =>	0%
#14	Ti2 <=>	Ti2 = +2.400 =>	0%
#15	O3 <=>	O3 = -0.581 =>	0%
#16	O16 <=>	O3 = -0.581 =>	0%
#17	O7 <=>	O9 = -0.578 =>	0%
#18	O12 <=>	O9 = -0.578 =>	0%
#19	O2 <=>	O2 = -0.567 =>	0%
#20	O15 <=>	O2 = -0.567 =>	0%
#21	O1 <=>	O1 = -0.558 =>	0%
#22	O14 <=>	O1 = -0.558 =>	0%
#23	C14 <=>	C10 = -0.088 =>	1%
#24	C5 <=>	C10 = -0.088 =>	1%
#25	C2 <=>	C3 = -0.033 =>	1%
#26	C24 <=>	C3 = -0.033 =>	1%
#27	C28 <=>	C6 = -0.177 =>	1%
#28	C8 <=>	C6 = -0.177 =>	1%
#29	C13 <=>	C9 = -0.104 =>	1%
#30	C10 <=>	C9 = -0.104 =>	1%
#31	C22 <=>	C14 = -0.173 =>	2%
#32	C19 <=>	C14 = -0.173 =>	2%
#33	H50 <=>	H6 = +0.026 =>	2%
#34	H3 <=>	H6 = +0.026 =>	2%
#35	C21 <=>	C12 = -0.187 =>	2%
#36	C18 <=>	C12 = -0.187 =>	2%
#37	H31 <=>	H17 = +0.062 =>	2%
#38	H8 <=>	H17 = +0.062 =>	2%
#39	O20 <=>	O7 = -0.221 =>	3%
#40	O18 <=>	O7 = -0.221 =>	3%
#41	C11 <=>	C11 = +0.019 =>	3%
#42	C16 <=>	C11 = +0.019 =>	3%
#43	H45 <=>	H29 = +0.059 =>	3%
#44	H39 <=>	H29 = +0.059 =>	3%
#45	C15 <=>	C7 = -0.085 =>	3%
#46	C4 <=>	C7 = -0.085 =>	3%
#47	H14 <=>	H8 = +0.058 =>	3%
#48	H57 <=>	H8 = +0.058 =>	3%
#49	C6 <=>	C2 = -0.165 =>	4%
#50	C26 <=>	C2 = -0.165 =>	4%
#51	O17 <=>	O6 = -0.222 =>	6%

#52	O19 <=>	O6 = -0.222 =>	6%
#53	H32 <=>	H22 = +0.043 =>	8%
#54	H22 <=>	H22 = +0.043 =>	8%
#55	H37 <=>	H25 = +0.059 =>	8%
#56	H43 <=>	H25 = +0.059 =>	8%
#57	H58 <=>	H9 = +0.069 =>	8%
#58	H15 <=>	H9 = +0.069 =>	8%
#59	H35 <=>	H28 = +0.044 =>	8%
#60	H25 <=>	H28 = +0.044 =>	8%
#61	H13 <=>	H5 = +0.047 =>	8%
#62	H56 <=>	H5 = +0.047 =>	8%
#63	C1 <=>	C1 = -0.025 =>	9%
#64	C23 <=>	C1 = -0.025 =>	9%
#65	H59 <=>	H10 = +0.061 =>	9%
#66	H16 <=>	H10 = +0.061 =>	9%
#67	H44 <=>	H26 = +0.061 =>	10%
#68	H38 <=>	H26 = +0.061 =>	10%
#69	H10 <=>	H21 = +0.060 =>	10%
#70	H29 <=>	H21 = +0.060 =>	10%
#71	H28 <=>	H20 = +0.073 =>	11%
#72	H9 <=>	H20 = +0.073 =>	11%
#73	N1 <=>	N1 = -0.025 =>	11%
#74	N2 <=>	N1 = -0.025 =>	11%
#75	H61 <=>	H14 = +0.054 =>	11%
#76	H18 <=>	H14 = +0.054 =>	11%
#77	H47 <=>	H31 = +0.076 =>	13%
#78	H41 <=>	H31 = +0.076 =>	13%
#79	H24 <=>	H27 = +0.023 =>	13%
#80	H34 <=>	H27 = +0.023 =>	13%
#81	H17 <=>	H13 = +0.059 =>	13%
#82	H60 <=>	H13 = +0.059 =>	13%
#83	H40 <=>	H30 = +0.062 =>	14%
#84	H46 <=>	H30 = +0.062 =>	14%
#85	H23 <=>	H23 = +0.048 =>	15%
#86	H33 <=>	H23 = +0.048 =>	15%
#87	H21 <=>	H19 = +0.043 =>	15%
#88	H27 <=>	H19 = +0.043 =>	15%
#89	H12 <=>	H4 = +0.061 =>	17%
#90	H55 <=>	H4 = +0.061 =>	17%
#91	H1 <=>	H1 = +0.061 =>	19%
#92	H48 <=>	H1 = +0.061 =>	19%
#93	H36 <=>	H24 = +0.061 =>	20%
#94	H42 <=>	H24 = +0.061 =>	20%
#95	H30 <=>	H16 = +0.071 =>	20%
#96	H7 <=>	H16 = +0.071 =>	20%
#97	H62 <=>	H15 = +0.067 =>	20%
#98	H19 <=>	H15 = +0.067 =>	20%
#99	H26 <=>	H18 = +0.039 =>	21%
#100	H20 <=>	H18 = +0.039 =>	21%
#101	H49 <=>	H2 = +0.032 =>	22%
#102	H2 <=>	H2 = +0.032 =>	22%
#103	H53 <=>	H12 = +0.048 =>	23%
#104	H6 <=>	H12 = +0.048 =>	23%
#105	H52 <=>	H11 = +0.028 =>	37%
#106	H5 <=>	H11 = +0.028 =>	37%
#107	H4 <=>	H7 = +0.013 =>	56%
#108	H51 <=>	H7 = +0.013 =>	56%
#109	C25 <=>	C5 = -0.003 =>	64%
#110	C3 <=>	C5 = -0.003 =>	64%
#111	H54 <=>	H3 = +0.061 =>	66%
#112	H11 <=>	H3 = +0.061 =>	66%

#113	C17 <=>	C13 = +0.003 =>	274%
#114	C12 <=>	C13 = +0.003 =>	275%
#115	C9 <=>	C8 = -0.002 =>	291%
#116	C20 <=>	C8 = -0.002 =>	291%

WinPacha atomic charges calculations report for compound 2  
V= 2693.09 Å<sup>3</sup> (Z = 4) -> No R-value

\*\*\*Atomic electronegativies (eV) and radii (pm) \*\*\*

Ti( 8.170, 147.7)  
O( 21.360, 45.0)  
N( 18.130, 52.1)  
C( 15.050, 62.0)  
H( 13.610, 53.0)

Madelung summation with gaussian inner-charge scaling (G = 0.14 Å<sup>-1</sup>)  
Reciprocal space exploration: -2 <= (h, k, l) <= 2

Madelung constant A = 431.4783740/4 = 107.8695935 (dmin = 0.950 Å )  
min = -0.35767 Å<sup>-1</sup> < mean = 0.90968 Å<sup>-1</sup> < max = 4.20121 Å<sup>-1</sup>  
Total electrostatic balance = -6541.00 eV = -631104.9 kJ.mol<sup>-1</sup>

Mean electronegativity: <EN> = 13.22 eV  
Global hardness: <GH> = 3.62 eV (G = 0.14 Å<sup>-1</sup>)

Electronic signature: #n Label(±ox) [CN] = ±q {±f}

	Atom	Charge	Fukui
#6	O4(-2) [ 4] =	-0.712 {	-0.003 }
#7	O5(-2) [ 3] =	-0.655 {	0.000 }
#10	O8(-2) [ 3] =	-0.653 {	-0.000 }
#3	O1(-2) [ 2] =	-0.575 {	0.003 }
#11	O9(-2) [ 2] =	-0.574 {	0.003 }
#4	O2(-2) [ 2] =	-0.559 {	0.003 }
#12	O10(-2) [ 2] =	-0.558 {	0.004 }
#5	O3(-2) [ 2] =	-0.548 {	0.004 }
#9	O7(-2) [ 1] =	-0.242 {	0.018 }
#8	O6(-2) [ 1] =	-0.236 {	0.017 }
#21	C8(-3) [ 4] =	-0.173 {	-0.002 }
#16	C3(-3) [ 4] =	-0.168 {	-0.002 }
#32	C19(-3) [ 4] =	-0.166 {	-0.002 }
#31	C18(-3) [ 4] =	-0.166 {	-0.001 }
#18	C5(-3) [ 4] =	-0.165 {	-0.002 }
#19	C6(-3) [ 4] =	-0.163 {	-0.002 }
#28	C15(-3) [ 4] =	-0.162 {	-0.003 }
#29	C16(-3) [ 4] =	-0.162 {	-0.002 }
#22	C9(-3) [ 4] =	-0.159 {	-0.003 }
#15	C2(-3) [ 4] =	-0.158 {	-0.002 }
#23	C10(-1) [ 4] =	-0.104 {	0.002 }
#26	C13(-1) [ 4] =	-0.092 {	0.003 }
#25	C12(-1) [ 4] =	-0.088 {	0.002 }
#13	N1(+3) [ 3] =	-0.020 {	0.013 }
#24	C11(+1) [ 4] =	-0.005 {	0.012 }
#17	C4(+0) [ 4] =	+0.003 {	0.011 }
#40	H8(+1) [ 1] =	+0.007 {	0.012 }
#30	C17(+0) [ 4] =	+0.009 {	0.011 }
#14	C1(+0) [ 4] =	+0.012 {	0.011 }
#27	C14(+0) [ 4] =	+0.013 {	0.011 }
#20	C7(+0) [ 4] =	+0.013 {	0.011 }
#47	H15(+1) [ 1] =	+0.014 {	0.013 }
#67	H35(+1) [ 1] =	+0.024 {	0.015 }
#33	H1(+1) [ 1] =	+0.029 {	0.013 }
#54	H22(+1) [ 1] =	+0.036 {	0.015 }
#60	H28(+1) [ 1] =	+0.037 {	0.013 }
#38	H6(+1) [ 1] =	+0.042 {	0.017 }
#69	H37(+1) [ 1] =	+0.046 {	0.016 }

#50	H18 (+1) [ 1 ] =	+0.047 {	0.017 }
#55	H23 (+1) [ 1 ] =	+0.047 {	0.015 }
#63	H31 (+1) [ 1 ] =	+0.048 {	0.017 }
#46	H14 (+1) [ 1 ] =	+0.051 {	0.019 }
#39	H7 (+1) [ 1 ] =	+0.053 {	0.017 }
#56	H24 (+1) [ 1 ] =	+0.053 {	0.015 }
#51	H19 (+1) [ 1 ] =	+0.054 {	0.022 }
#62	H30 (+1) [ 1 ] =	+0.054 {	0.018 }
#64	H32 (+1) [ 1 ] =	+0.054 {	0.019 }
#61	H29 (+1) [ 1 ] =	+0.056 {	0.020 }
#34	H2 (+1) [ 1 ] =	+0.056 {	0.019 }
#68	H36 (+1) [ 1 ] =	+0.057 {	0.017 }
#44	H12 (+1) [ 1 ] =	+0.057 {	0.019 }
#52	H20 (+1) [ 1 ] =	+0.058 {	0.019 }
#66	H34 (+1) [ 1 ] =	+0.058 {	0.018 }
#35	H3 (+1) [ 1 ] =	+0.059 {	0.018 }
#42	H10 (+1) [ 1 ] =	+0.061 {	0.018 }
#36	H4 (+1) [ 1 ] =	+0.062 {	0.021 }
#48	H16 (+1) [ 1 ] =	+0.062 {	0.019 }
#71	H39 (+1) [ 1 ] =	+0.063 {	0.019 }
#45	H13 (+1) [ 1 ] =	+0.064 {	0.018 }
#57	H25 (+1) [ 1 ] =	+0.065 {	0.016 }
#65	H33 (+1) [ 1 ] =	+0.065 {	0.019 }
#37	H5 (+1) [ 1 ] =	+0.066 {	0.020 }
#70	H38 (+1) [ 1 ] =	+0.067 {	0.018 }
#72	H40 (+1) [ 1 ] =	+0.070 {	0.019 }
#43	H11 (+1) [ 1 ] =	+0.074 {	0.019 }
#53	H21 (+1) [ 1 ] =	+0.074 {	0.021 }
#41	H9 (+1) [ 1 ] =	+0.078 {	0.021 }
#59	H27 (+1) [ 1 ] =	+0.078 {	0.015 }
#58	H26 (+1) [ 1 ] =	+0.083 {	0.015 }
#49	H17 (+1) [ 1 ] =	+0.094 {	0.020 }
#73	H41 (+1) [ 1 ] =	+0.098 {	0.020 }
#2	Ti2 (+4) [ 6 ] =	+2.396 {	0.079 }
#1	Ti1 (+4) [ 6 ] =	+2.497 {	0.086 }

Partial electrostatic balance: <EB> = -309.90 eV = -29900.4 kJ.mol<sup>-1</sup>  
 Reduced electrostatic balance: <EB/2> = -154.95 eV = -14950.2 kJ.mol<sup>-1</sup>  
 Global ionicity: <GI> = 21.77 %

Statistical report: <Atom>[num] = mean ± 3×stdev (stdev) <avdev>  
 <q(H)>[41] = 0.057 ± 0.055 (0.018) <0.013>  
 <f(H)>[41] = 0.018 ± 0.007 (0.002) <0.002>  
 <q(C)>[19] = -0.099 ± 0.236 (0.079) <0.069>  
 <f(C)>[19] = 0.003 ± 0.019 (0.006) <0.005>  
 <q(N)>[1] = -0.020 ± 0.000 (0.000) <0.000>  
 <f(N)>[1] = 0.013 ± 0.000 (0.000) <0.000>  
 <q(O)>[10] = -0.531 ± 0.489 (0.163) <0.117>  
 <f(O)>[10] = 0.005 ± 0.021 (0.007) <0.005>  
 <q(Ti)>[2] = 2.446 ± 0.215 (0.072) <0.051>  
 <f(Ti)>[2] = 0.083 ± 0.015 (0.005) <0.003>

## WinPacha retrosynthetic report for compound 2

V= 2693.09 Å<sup>3</sup> (Z = 4) -> No R-valueCurrent molecular fragment is: [H41C19NO10Ti2]\*2 = 1078.74 g.mol<sup>-1</sup>

\*\*\* Total electrical charge on molecular fragment = 0 \*\*\*

Partial electrostatic balance: <EB> = -154.665 eV = -14922.8 kJ.mol<sup>-1</sup>

#n Mol symb &lt;=&gt; Net symb = fragment PC =&gt; Retrosynthetic index(%)

#1	O15 <=>	O2 = -0.559 =>	0%
#2	O2 <=>	O2 = -0.559 =>	0%
#3	O16 <=>	O3 = -0.548 =>	0%
#4	O3 <=>	O3 = -0.548 =>	0%
#5	Ti4 <=>	Ti1 = +2.497 =>	0%
#6	Ti1 <=>	Ti1 = +2.497 =>	0%
#7	O4 <=>	O4 = -0.712 =>	0%
#8	O10 <=>	O4 = -0.712 =>	0%
#9	Ti3 <=>	Ti2 = +2.395 =>	0%
#10	Ti2 <=>	Ti2 = +2.395 =>	0%
#11	O12 <=>	O9 = -0.574 =>	0%
#12	O8 <=>	O9 = -0.574 =>	0%
#13	O9 <=>	O10 = -0.558 =>	0%
#14	O13 <=>	O10 = -0.558 =>	0%
#15	O11 <=>	O5 = -0.654 =>	0%
#16	O5 <=>	O5 = -0.654 =>	0%
#17	O1 <=>	O1 = -0.574 =>	0%
#18	O14 <=>	O1 = -0.574 =>	0%
#19	C34 <=>	C3 = -0.168 =>	0%
#20	C8 <=>	C3 = -0.168 =>	0%
#21	C25 <=>	C19 = -0.167 =>	0%
#22	C29 <=>	C19 = -0.167 =>	0%
#23	C26 <=>	C15 = -0.163 =>	0%
#24	C22 <=>	C15 = -0.163 =>	0%
#25	O7 <=>	O8 = -0.654 =>	0%
#26	O6 <=>	O8 = -0.654 =>	0%
#27	C24 <=>	C18 = -0.165 =>	0%
#28	C28 <=>	C18 = -0.165 =>	0%
#29	C18 <=>	C10 = -0.104 =>	1%
#30	C4 <=>	C10 = -0.104 =>	1%
#31	C2 <=>	C4 = +0.003 =>	1%
#32	H47 <=>	H39 = +0.064 =>	1%
#33	H59 <=>	H39 = +0.064 =>	1%
#34	C31 <=>	C4 = +0.003 =>	1%
#35	C5 <=>	C12 = -0.089 =>	1%
#36	C19 <=>	C12 = -0.089 =>	1%
#37	H57 <=>	H37 = +0.045 =>	2%
#38	H45 <=>	H37 = +0.045 =>	2%
#39	C1 <=>	C1 = +0.012 =>	2%
#40	C30 <=>	C1 = +0.012 =>	2%
#41	C7 <=>	C2 = -0.161 =>	2%
#42	C33 <=>	C2 = -0.161 =>	2%
#43	C12 <=>	C9 = -0.162 =>	2%
#44	C38 <=>	C9 = -0.162 =>	2%
#45	C27 <=>	C16 = -0.165 =>	2%
#46	C23 <=>	C16 = -0.165 =>	2%
#47	C36 <=>	C6 = -0.167 =>	2%
#48	C10 <=>	C6 = -0.167 =>	2%
#49	O19 <=>	O6 = -0.231 =>	2%
#50	O17 <=>	O6 = -0.231 =>	2%
#51	H52 <=>	H31 = +0.047 =>	2%

#52	H40 <=>	H31 = +0.047 =>	2%
#53	H77 <=>	H16 = +0.061 =>	3%
#54	H22 <=>	H16 = +0.061 =>	3%
#55	C9 <=>	C5 = -0.159 =>	3%
#56	C35 <=>	C5 = -0.159 =>	3%
#57	H14 <=>	H6 = +0.043 =>	3%
#58	H69 <=>	H6 = +0.043 =>	3%
#59	H39 <=>	H30 = +0.056 =>	4%
#60	H51 <=>	H30 = +0.056 =>	4%
#61	C11 <=>	C8 = -0.166 =>	4%
#62	C37 <=>	C8 = -0.166 =>	4%
#63	C20 <=>	C14 = +0.013 =>	4%
#64	C16 <=>	C14 = +0.013 =>	4%
#65	N1 <=>	N1 = -0.019 =>	5%
#66	N2 <=>	N1 = -0.019 =>	5%
#67	H56 <=>	H36 = +0.059 =>	5%
#68	H44 <=>	H36 = +0.059 =>	5%
#69	H10 <=>	H2 = +0.059 =>	5%
#70	H65 <=>	H2 = +0.059 =>	5%
#71	C6 <=>	C13 = -0.087 =>	5%
#72	C15 <=>	C13 = -0.087 =>	5%
#73	H38 <=>	H29 = +0.059 =>	5%
#74	H50 <=>	H29 = +0.059 =>	5%
#75	H33 <=>	H23 = +0.050 =>	5%
#76	H5 <=>	H23 = +0.050 =>	5%
#77	O18 <=>	O7 = -0.228 =>	5%
#78	O20 <=>	O7 = -0.228 =>	5%
#79	H82 <=>	H21 = +0.079 =>	6%
#80	H27 <=>	H21 = +0.079 =>	6%
#81	H15 <=>	H7 = +0.056 =>	6%
#82	H70 <=>	H7 = +0.056 =>	6%
#83	C17 <=>	C17 = +0.010 =>	6%
#84	C21 <=>	C17 = +0.010 =>	6%
#85	H17 <=>	H10 = +0.057 =>	7%
#86	H72 <=>	H10 = +0.057 =>	7%
#87	H7 <=>	H25 = +0.070 =>	7%
#88	H35 <=>	H25 = +0.070 =>	7%
#89	H1 <=>	H1 = +0.027 =>	7%
#90	H62 <=>	H1 = +0.027 =>	7%
#91	H43 <=>	H34 = +0.062 =>	7%
#92	H55 <=>	H34 = +0.062 =>	7%
#93	H60 <=>	H40 = +0.075 =>	8%
#94	H48 <=>	H40 = +0.075 =>	8%
#95	C32 <=>	C7 = +0.012 =>	8%
#96	C3 <=>	C7 = +0.012 =>	8%
#97	H30 <=>	H28 = +0.040 =>	9%
#98	H36 <=>	H28 = +0.040 =>	9%
#99	H18 <=>	H11 = +0.067 =>	9%
#100	H73 <=>	H11 = +0.067 =>	9%
#101	H6 <=>	H24 = +0.058 =>	9%
#102	H34 <=>	H24 = +0.058 =>	9%
#103	H12 <=>	H4 = +0.068 =>	10%
#104	H67 <=>	H4 = +0.068 =>	10%
#105	H24 <=>	H18 = +0.042 =>	10%
#106	H79 <=>	H18 = +0.042 =>	10%
#107	H11 <=>	H3 = +0.065 =>	10%
#108	H66 <=>	H3 = +0.065 =>	10%
#109	H68 <=>	H5 = +0.059 =>	11%
#110	H13 <=>	H5 = +0.059 =>	11%
#111	H46 <=>	H38 = +0.060 =>	11%
#112	H58 <=>	H38 = +0.060 =>	11%

#113	H26 <=>	H20 = +0.064 =>	11%
#114	H81 <=>	H20 = +0.064 =>	11%
#115	H74 <=>	H12 = +0.064 =>	11%
#116	H19 <=>	H12 = +0.064 =>	11%
#117	H32 <=>	H22 = +0.040 =>	11%
#118	H4 <=>	H22 = +0.040 =>	11%
#119	H61 <=>	H41 = +0.086 =>	12%
#120	H49 <=>	H41 = +0.086 =>	12%
#121	H20 <=>	H13 = +0.072 =>	12%
#122	H75 <=>	H13 = +0.072 =>	12%
#123	C14 <=>	C11 = -0.006 =>	12%
#124	C13 <=>	C11 = -0.006 =>	12%
#125	H21 <=>	H14 = +0.057 =>	12%
#126	H76 <=>	H14 = +0.057 =>	12%
#127	H25 <=>	H19 = +0.060 =>	13%
#128	H80 <=>	H19 = +0.060 =>	13%
#129	H54 <=>	H33 = +0.075 =>	15%
#130	H42 <=>	H33 = +0.075 =>	15%
#131	H53 <=>	H32 = +0.063 =>	17%
#132	H41 <=>	H32 = +0.063 =>	17%
#133	H2 <=>	H8 = +0.008 =>	17%
#134	H63 <=>	H8 = +0.008 =>	17%
#135	H64 <=>	H15 = +0.016 =>	19%
#136	H3 <=>	H15 = +0.016 =>	19%
#137	H29 <=>	H27 = +0.061 =>	23%
#138	H9 <=>	H27 = +0.061 =>	23%
#139	H16 <=>	H9 = +0.059 =>	25%
#140	H71 <=>	H9 = +0.059 =>	25%
#141	H28 <=>	H26 = +0.062 =>	26%
#142	H8 <=>	H26 = +0.062 =>	26%
#143	H78 <=>	H17 = +0.069 =>	27%
#144	H23 <=>	H17 = +0.069 =>	27%
#145	H31 <=>	H35 = +0.017 =>	32%
#146	H37 <=>	H35 = +0.017 =>	32%