Titanium-Oxo Clusters with Bi- and Tridentate Organic Ligands: Gradual Evolution of the Structures from Small to Big

Ulrich Schubert*[a]

Abstract: Homometallic titanium oxo clusters are one of the most important groups of metal oxo clusters, with more than 300 examples characterized by X-ray structure analyses. Most of them are uncharged and are obtained by partial hydrolysis and condensation of titanium alkoxo derivatives. The cluster cores, ranging from 3 to >50 titanium atoms, are stabilized by organic ligands. Apart from residual OR groups, carboxylato and phosphonato ligands are most frequent. The article critically reviews and categorizes the known structures and works out basic construction principles by comparing the different cluster types.

1. Introduction

The building blocks of titanium oxo clusters (TOC) are edge- or corner-sharing [TiO$_6$] octahedra and, less often, [TiO$_5$] or [TiO$_7$] polyhedra. "Naked" TOC, that is, clusters without capping organic groups ("ligands"), are unknown. Early investigations concentrated on partially hydrolyzed titanium alkoxides, Ti$_x$O$_y$(OR)$_{4x-2y}$, where the Ti polyhedra are connected with each other via bridging oxide and/or OR ions, and with terminal OR groups capping the cluster core. Clusters of different sizes, ranging from Ti$_3$O(OR)$_6$[1] to Ti$_{42}$O$_{54}$(OH)$_{18}$(OiPr)$_{42}$[2] were isolated. More recently, TOCs have gained much attention in which part of the OR groups are replaced by organic, mostly oxygen-based ligands. Ti–O–Ti or Ti–OR–Ti units also connect the Ti atoms, as in Ti$_x$O$_y$(OR)$_{4x-2y}$, while the organic ligands are bonded to the cluster surface. Bi- and multidentate capping ligands allow a much richer structural chemistry because their coordination can easily be matched with the structural requirements of the cluster core. They also influence the structures because bridging two [TiO$_x$] polyhedra requires a certain mutual positioning of the polyhedra.

In this article, the structures of (homometallic) TOC with capping organic ligands will be critically reviewed and basic construction principles worked out. Preparation, properties and (potential) uses of such clusters were treated in earlier reviews,[3] but a comprehensive treatment and a systematization of the structural chemistry is still missing. Due to the fact that a variety of organic groups was used to control the reactivity of Ti(OR)$_4$

in sol-gel processes,[3a] TOC with a variety of organic ligands were isolated. They can be considered partially hydrolyzed/condensed species on the way to organically substituted titania. However, only carboxylato-substituted (>200 examples) and phosphonato-substituted TOC (>100 examples) are so numerous that a systematic treatment of their structures is reasonable, as well as considerations on structural blueprints for clusters of increasing size. For this very reason, only structures of carboxylato- (Section 2) and phosphonato-substituted TOC (Section 3) are discussed in this article. Clusters containing both carboxylato and phosphonato ligands will be discussed in Section 3, for the reasons given there. TOC structures with hydroxycarboxylato ligands (such as mandelate,[4] salicylate,[5] 1-hydroxy-2-naphthoate,[5c] 2,5-dihydroxybenzoate[6] or citrate[7]) will not be treated. The OH group is always deprotonated and therefore hydroxycarboxylato ligands not only have a variety of coordination possibilities[8] but also a stronger and different structure-directing role than simple carboxylato ligands; their coordination requires a specific orientation of the coordination polyhedra of neighboring metals.

TOC with other ligands are only occasionally mentioned for comparison, without a claim to completeness. Metal-organic framework structures (MOF) with TOCs as connector units[3f,9] are not included. The literature until early 2021 is covered.

Metal clusters are compounds with at least three metal atoms, where each metal atom is linked to at least two others. According to this definition, polynuclear compounds in which isolated [TiO$_x$] polyhedra and/or dimeric entities are bridged by multidentate organic ligands, are not considered clusters. This is occasionally found for dicarboxylate or phosphonate derivatives.

Heterometallic clusters will only be mentioned if their structures are related to that of their homometallic counterparts. The reason for doing so is that the presence of two (or more) metals results in a much greater variety of possible structures[10] which are therefore difficult to categorize.

The TOC discussed in this article are characterized by the R′CO$_2$/Ti or R″PO$_3$/Ti ratio ("degree of substitution", d_s) and the

[a] *Prof. Dr. U. Schubert*
Institute of Materials Chemistry
Technische Universität Wien
Getreidemarkt 9, 1060 Wien (Austria)
E-mail: Ulrich.Schubert@tuwien.ac.at

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O/Ti ratio ("degree of condensation", d_c). Both d_c and d_s are just the numerical ratio of oxo groups or carboxylato/phosphonato ligands per titanium atom; the different coordination of the oxo groups (μ_2, μ_3 or μ_4) and the different charge and coordination of the organic ligands are not taken into account. Only carboxylato and phosphonato ligands are calculated for d_s, but not the OR groups. As the maximum value of d_c in titanium oxo compounds is 2 (in TiO_2), d_c in TOC is $0 < d_c < 2$.

Capping ligands must meet two conditions: they must compensate the charge of the cluster core and allow the metal atoms to reach certain coordination numbers. This is illustrated by the following example: The $+12$ charge of the Ti_4O_2 cluster core in $Ti_4O_2(OR)_6(O_2CR')_6$ (see below) is compensated by six OR and six R'COO groups. Since all titanium atoms are octahedrally coordinated, the total number of coordination sites is 24. The two μ_3-O occupy 6 and the bridging carboxylato ligands 12 coordination sites, that is, all alkoxo groups must be terminal (μ_1) to fill the remaining six sites. Such considerations can help to analyze and understand the structure of a certain cluster and particularly the coordination mode of certain ligands. In principle, it is possible to predict which cluster types are not possible.[11]

Peripheral (capping) ligands are necessary to stabilize the cluster core by satisfying "dangling bonds" at the metal centers. They are, however, relatively mobile in most cases, as solution studies have shown.[12] In consequence, the capping ligands can easily adjust to an altered cluster core by changing their position at the cluster surface or their coordination mode (e.g., terminal/bridging), provided that the previously mentioned conditions are met. Because of this mobility, among other reasons, it is difficult to compare the solid state and solution structures of TOC. Therefore, only solid-state structures (determined by single crystal structure analyses) are discussed in this review.

Nearly nothing is known about the mechanisms by which the clusters are formed and/or grow. One of the reasons is that spectroscopic investigations in solution are difficult, because most of the clusters have no readily accessible characteristic signatures.[13] The clusters are usually obtained by crystallization

Ulrich Schubert received his Ph.D. from the Technische Universität München. After a postdoctoral stay at Stanford University, he returned to Munich where he became a Privatdozent. He held a professorship at the University of Würzburg from 1982 to 1994, and additionally served at the Fraunhofer Institute for Silicate Research from 1989 bis 1994. In 1994 he moved to the Technische Universität Wien, where he is now Professor Emeritus. He is a member of the Austrian Academy of Sciences and the German Academy Leopoldina and was President of the Austrian Chemical Society in 2001–2004 and the European Chemical Society (EuChemS) in 2011–2014.

from the reaction mixtures, and the failure to re-crystallize such clusters is an often-noted phenomenon. This indicates that a specific cluster might be in equilibrium with other species once it is dissolved. However, some structural features common to many TOC allow speculations on possible growth mechanism. This will be discussed in the remainder of this article.

2. Carboxylato-Substituted Titanium Oxo Clusters

The reason why carboxylato-substituted clusters constitute the greatest subset of TOC is that they are easily formed, just by reaction of $Ti(OR)_4$ with a carboxylic acid, often in the absence of a solvent. Spontaneous formation of clusters can be explained by the sequence of three reactions. In the first step, one or more alkoxo ligands are substituted by carboxylato groups to give $Ti(OR)_{4-x}(O_2CR')_x$ and ROH. Only a few substitution products $[Ti(OR)_3(O_2CR')]_2$ were isolated.[14] In the majority of reactions, the water generated by esterification of the liberated alcohol hydrolyzes all or part of the remaining alkoxo groups and is the source of oxo or hydroxo groups in the resulting clusters. The very slow in situ production of water allows a very controlled growth of the carboxylato-substituted metal oxo clusters. Cluster growth is self-limiting because it is based on three competing reactions, that is, two alcohol-producing reactions (substitution and hydrolysis of OR groups) and two carboxylic acid-consuming reactions (substitution and ester formation). Substitution of OR groups can of course also happen in later stages of the cluster formation. The relative rates of substitution and hydrolysis/condensation reactions are influenced by a number of parameters, such as kind of acid, steric bulk of the OR groups, $Ti(OR)_4$/carboxylic acid ratio, temperature or solvent (if any), sometimes also the time needed for crystallization. A prediction which cluster type will be formed in a specific case it is currently not possible owing to the complexity of such reactions. If, however, a particular synthesis protocol is exactly followed, the same cluster can be reliably synthesized in most cases, very often in high yields and in large quantities.

Despite some strong evidence for this sequence of events, a second route cannot be ruled out in many cases. In the so-called "nonhydrolytic" processes,[15] a M-OR group reacts directly with a carboxylic acid resulting in a M—OH (or M—O—M) moiety and an ester.

Most carboxylato-substituted TOC were obtained by the "in situ hydrolysis" routes (which includes possible nonhydrolytic processes) unless otherwise stated. In some cases, hydrolysis was due to small amounts of water (such as ambient humidity) introduced into the reaction mixture. Formation of carboxylato-substituted TOC by reaction of $Ti_xO_y(OR)_{4x-2y}$ with carboxylic acids has only been observed in rare cases.

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2.1. Ti$_3$O$_x$ clusters

The Ti$_3$(μ_3-O) unit is a central feature of the TiO$_2$ modifications rutile and anatase. It is therefore not surprising that it is also a wide-spread building block in TOC of higher nuclearity, as will be discussed later in more detail. With this in mind, it is rather surprising that far less trinuclear TOC were isolated than tetra- or hexanuclear ones.

In the C$_3$-symmetric parent compound, Ti$_3$O(OR)$_{10}$,[1] a Ti$_3$ triangle is capped by both a pyramidal μ_3-O and μ_3-OR group, and each Ti–Ti edge is bridged by a μ_2-OR. Two terminal OR groups per Ti atom complete the octahedral coordination. The Ti$_3$(μ_3-O) unit is retained in all structurally characterized carboxylato-substituted Ti$_3$O$_x$ clusters but is approximately planar or just slightly pyramidal; a μ_3-OR group is not observed. C$_3$ symmetry would require a C$_3$-symmetric arrangement of the ligands which is geometrically impossible in carboxylato-substituted Ti$_3$O$_x$ clusters: The Ti$_3$O unit has a +10 charge and 15 unoccupied coordination sites (if all Ti atoms are octahedrally coordinated). Thus, if only RO$^-$ or R'CO$_2^-$ are available, five ligands must be μ_2. This is not compatible with a C$_3$ symmetry (even if some ligands would be replaced by μ_2). For this reason, another arrangement of the three [TiO$_x$] polyhedra is found in Ti$_3$O$_x$ clusters, which can be described as "L-shaped" (Figure 1, center). The three titanium atoms form an isosceles triangle, with the two shorter Ti···Ti distances of equal length.

The majority of Ti$_3$O$_x$ clusters has the composition Ti$_3$O-(OR)$_8$(O$_2$CR')$_2$ (d_s 0.67). Ti$_3$O(OiPr)$_8$(O$_2$CPh)$_2$[16] was obtained by reaction of Ti$_3$O(OiPr)$_{10}$ with benzoic acid, all the other derivatives by the in situ hydrolysis method. Two OR groups and both carboxylato ligands of Ti$_3$O(OR)$_8$(O$_2$CR')$_2$ are bridging, the remaining OR groups are terminal. This renders one Ti atom five-coordinate and the Ti$_3$ triangle inequilateral. Two types of Ti$_3$O(OR)$_8$(O$_2$CR')$_2$ were found (Figure 1). In both types, one carboxylato ligand is approximately coplanar with the Ti$_3$O unit and the second perpendicular to this plane. The second carboxylato ligand can, however, bridge different Ti atoms.

Type 1: The two R'COO ligands bridge different Ti–Ti edges of the Ti$_3$O triangle, the long and one of the short edges (Figure 1, left and center). The carboxylato ligand perpendicular to the Ti$_3$O plane bridges two octahedrally coordinated Ti atoms, which are additionally bridged by a μ_2-OR, and the coplanar carboxylato ligand one octahedrally and the trigonal-bipyramidally coordinated Ti atom. This means that each Ti atom has a different coordination sphere. This cluster type is
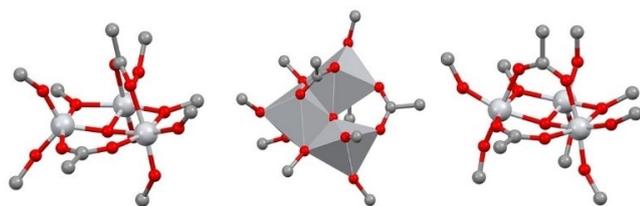
more often observed, viz. for Ti$_3$O(OCH$_2$$t$Bu)$_8$(O$_2$CR')$_2$ (R'=H, CH$_2$$t$Bu[14]) and Ti$_3$O(O$i$Pr)$_8$(O$_2$CR')$_2$ (R'=CPh$_3$,[17] Ph,[16] p-C$_6$H$_4$Cl, m-C$_6$H$_4$NO$_2$,[18] 3-thienyl[19]).

Type 2: Both R'COO ligands bridge the long edge of the Ti$_3$O triangle (Figure 1, right). The five-coordinate titanium atom is not bonded to a carboxylato ligand. Such clusters thus have an approximate mirror plane passing through the five-coordinate Ti and the μ_3-O atom. Examples are Ti$_3$O(OCH$_2$$t$Bu)$_8$(O$_2$CMe)$_2$[14] and Ti$_3$O(O$i$Pr)$_8$[O$_2$C–C(CN)=CH–C$_6H_4$-NR$_2$]$_2$ [R=Ph, Et].[20]

A variation of type 1 clusters was found for Ti$_3$O-(OiPr)$_6$(O$_2$C$_6$H$_4$)(O$_2$C-ferrocenyl)$_2$,[21] where a catecholato ligand replaces the two terminal OR groups perpendicular to the in-plane carboxylato ligand. Owing to the fact that one of the catecholato oxygen atoms is chelating-bridging, all Ti atoms in this compound are octahedrally coordinated.

In the cyclic oligomers [Ti$_3$O(OiPr)$_8$(O$_2$C–X–CO$_2$)]$_n$ (n=2: X= 1,4-cyclohexane; n=3: 2-nitro-1,4-benzene; n=4: 5-nitro-1,3-benzene, 1,4-benzene)[22] and [Ti$_3$O(OiPr)$_6$(O$_2$C$_6$H$_4$)-(O$_2$C–CMe$_2$–CO$_2$)]$_2$,[23] two, three or four Ti$_3$O(OiPr)$_8$ units are clamped together by dicarboxylato groups. The arrangement of the ligands is the same as in the parent Ti$_3$O(OR)$_8$(O$_2$CR')$_2$ clusters of type 1.

Only few Ti$_3$ clusters with a higher degree of substitution were structurally characterized, viz. Ti$_3$O(OiPr)$_7$(O$_2$CR')$_3$ (R'= CCl$_3$,[24] 4-C$_5$H$_4$N[25]) (d_s 1.0) and Ti$_3$O(OiPr)$_6$(O$_2$C-adamantyl)$_4$ (d_s 1.33). The structure of Ti$_3$O(OiPr)$_7$(O$_2$CR')$_3$ is related to type 1 Ti$_3$O(OR)$_8$(O$_2$CR')$_2$ in a way that the third edge of the Ti$_3$O triangle is also bridged by a carboxylato ligand in addition to the μ_2-OR group. Since a terminal OR group was formally substituted by a bridging R'COO ligand, all titanium atoms are six-coordinate. In the adamantyl derivative each edge of the Ti$_3$O triangle is bridged by a carboxylato ligand; the fourth adamantyl ligand replaces a terminal OR group at the formerly five-coordinate Ti atom as a *chelating* ligand. This is a very rare example of a chelating carboxylato group in TOCs. In Ti$_3$O$_2$X$_3$-(O$_2$CR')$_5$ (X=Cl, R'=Et,[26] p-C$_6$H$_4$Me;[27] X=OiPr, R'=CPh$_3$[28]) (d_c 0.66, d_s 1.66), two edges of the Ti$_3$O triangle are bridged by *two* carboxylato ligands each, and the third edge by a carboxylato ligand and a μ_2-O.

2.2. Ti$_4$O$_x$ clusters

The structure types of Ti$_4$O$_x$ clusters (Scheme 1) differ by the combination of d_c and d_s. With the exception of the rather special Ti$_4$O$_3$(OiPr)$_6$(O$_2$CR')$_4$ and Ti$_4$O$_4$(O$_2$CR')$_{12}$, the structures highlight the different possibilities of expanding the Ti$_3$O core by an additional [TiO$_6$] unit.

2.2.1. Ti$_4$O$_2$ clusters

The four Ti atoms in the clusters Ti$_4$O$_2$(OEt)$_{10}$(O$_2$C–C$_5$H$_4$N)$_2$,[25] Ti$_4$O$_2$(OiPr)$_{10}$(O$_2$CR')$_2$ (R'=H,[29] OiPr,[30] Ph, naphthyl,[31] dimethylthio-tetrathiafulvalenyl[19]) and Ti$_4$O$_2$(OiBu)$_{10}$(O$_2$CR')$_2$ (R'= C$_6$H$_4$NH$_2$,[32] C$_{13}$H$_9$, C$_6$H$_4$Cl, C$_6$H$_4$NO$_2$;[33] Figure 2) form a distorted tetrahedron around a central oxygen. The isopropyl carbonato

Figure 1. The two types of Ti$_3$O(OR)$_8$(O$_2$CR')$_2$ (left and center: type 1, right: type 2).*) – *) In all figures, the organic substituents R, R' and R'' are not drawn for simplicity.

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Ti₄O₂(OR')₁₀(OOCR')₂
$d_s = 0.5$
$d_c = 0.5$

Ti₄O₂(OR)₄(OR'')₆(OOCR')₂
$d_s = 0.5$
$d_c = 0.5$

Ti₄O₂(OR)₆(OOCR')₆
$d_s = 1.5$
$d_c = 0.5$

Ti₄O₃(OR)₆(OOCR')₄
$d_s = 1$
$d_c = 0.75$

Ti₄O₄(OR)₄(OOCR')₄
$d_s = 1$
$d_c = 1$

Ti₄O₄(OOCR')₁₂
$d_s = 3$
$d_c = 1$

Scheme 1. Schematic drawing of Ti_4O_x cluster cores. Only bridging oxo and OR groups are drawn which link the titanium polyhedra via shared corners and edges. See text for the explanation of OR''.
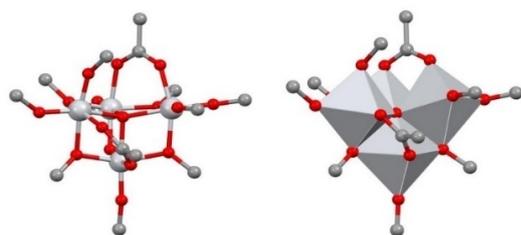
Figure 2. The structure of $Ti_4O_2(OR)_{10}(O_2CR')_2$ in ball-and-stick (left) and polyhedral representation (right).

cluster was synthesized by insertion of CO_2 into Ti–OiPr bonds in the presence of water. Ti₄O units, that is, μ_4-O ions, are relatively uncommon in the structural chemistry of carboxylato-substituted TOC. Four OR groups are bridging, which means that the four $[TiO_6]$ octahedra share four edges. When comparing the polyhedral representations of $Ti_3O(OR)_8(O_2CR')_2$ (Figure 1) and $Ti_4O_2(OR)_{10}(O_2CR')_2$ (Figure 2), a structural relationship is noticed in such a way that in the latter compound an additional $[TiO_6]$ octahedron (the bottom octahedron in Figure 2) is attached to the cluster core of L-shaped Ti₃O via the μ_4-O ion.

The heterometallic cluster $Ti_2Pb_2O(OiPr)_8(O_2CMe)_2$ has a related structure: two $[TiO_6]$ octahedra are replaced by two $[PbO_5]$ square pyramids; the acetato ligands bridge the two Ti and the two Pb atoms.[34]

A special case is the cluster type labeled $Ti_4O_2(OR)_4(OR'')_6$-$(O_2CR')_2$ in Scheme 1. The cluster has the composition Ti_4O_2-$(OiPr)_4[OCMe_2CHC(O)CH_2CMe_2O]_2(O_2CR')_2$ (R' = 7-diethylamino-2-oxochromane, $CH=CH–C_6H_4NR_2$ [R = Ph, Et])[35] where the central oxygen atom of the triolato ligand (labeled OR'' in Scheme 1) bridges two titanium atoms, and the outer (2,6) oxygen atoms are coordinated to only one Ti atom each (structurally equivalent to terminal OR groups). The carboxylato ligands bridge the same Ti atoms as the triolato ligands. The clusters were synthesized from $Ti(OiPr)_4$ and the carboxylic acids in acetone, the oxo groups were thus generated by condensation of the eliminated iso-propanol with acetone (also giving 2,6-dihydroxy-2,6-dimethylheptan-4-one). In this cluster, the triolato ligands influence the cluster core structure to a much higher degree than the carboxylato ligands. This is indicated by

the fact that $Ti_4O_2(OiPr)_8[OC(Ph)CHC(O)CHC(Ph)O]_2$[36] has the same structure, with four terminal OiPr groups in place of the two bridging carboxylato ligands (the triketonato ligand is only a di-anion).

Only few examples of a third Ti₄O₂ cluster type were isolated, namely $Ti_4O_2(OiPr)_6(O_2CR')_6$ (Figure 3) with R' = ferrocenyl,[37] $CH=CH_2$ and $CMe=CH_2$,[38] $Ti_4O_2Cl_6(O_2CPh)_6$ (obtained by reaction of $TiCl_4$ with benzoic acid)[39] and $Ti_4O_2(OiPr)_6[O_2P(OiPr)_2]_2(OC_6H_4–C_6H_4O)_2$.[40] The latter compound contains two di-iso-propyl-phosphato and two chelating-bridging 2,2'-biphenolato ligands instead of the carboxylato ligands. Comparison of the structure of $Ti_4O_2(OR)_6(O_2CR')_6$ with that of $Ti_4O_2(OR)_{10}(O_2CR')_2$ shows how a higher d_s, at a given d_c, leads to more open structures. The structures can formally be derived by condensation of a $[TiO_6]$ octahedron to a Ti₃O unit via a μ_3-O. Contrary to the "L-shaped" Ti₃O units discussed before, the Ti₃O unit is "T-shaped", that is, one $[TiO_6]$ octahedron is linked to a pair of edge-sharing octahedra via a μ_3-O. This "T-shaped" arrangement of the three titanium atoms resembles the smallest section of the rutile structure. The four μ_2-OR groups in $Ti_4O_2(OR)_{10}(O_2CR')_2$ are formally replaced by four carboxylato bridges, retaining the total number of occupied coordination sites and charges. While the oxygen atom of a μ_2-OR group is shared by two octahedra, the bridging carboxylato ligands provide an oxygen atom to both octahedra, resulting in less compact structures.
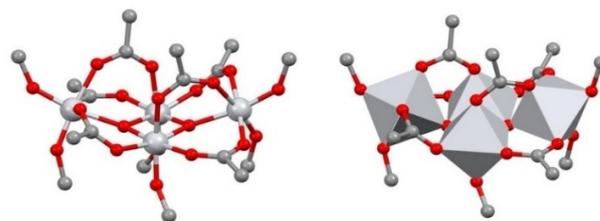
Figure 3. The structure of $Ti_4O_2(OR)_6(O_2CR')_6$ in ball-and-stick (left) and polyhedral representation (right).

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2.2.2. Ti₄O₃ clusters

Only a special example of the $Ti_4O_3(OiPr)_6(O_2CR')_4$ structure type is known, where the four R'COO groups are part of two 1,1'-ferrocenedicarboxylato ligands.[41] The cluster features a unique planar Ti_4O unit (Scheme 1) to which the ferrocenedicarboxylato ligands are coordinated on both sides. Each carboxylato group bridges the same pair of Ti atoms as the μ_2-OR groups. This results in an arrangement of four edge-sharing $[TiO_6]$ octahedra.

2.2.3. Ti₄O₄ clusters

$Ti_4O_4(OR)_4(O_2CR')_4$ clusters, with the highest d_c (1.0) among all Ti_4 clusters, are obtained with bulky OR and/or carboxylato groups, viz. $Ti_4O_4(OR)_4\{O_2CC[Co_3(CO)_9]\}_4$, (R = iPr, Bu, Ph, $C_6H_3Me_2$),[42] $Ti_4O_4(OR)_4\{O_2CC[Co_2(CO)_6-CpM(CO)_2]\}_4$ (R = iPr, Et; M=Mo, W),[43] or $Ti_4O_4(OtBu)_4(O_2CR')_4$ (R' = Et,[31] tBu, CEtMe₂, CH_2tBu[44]). Two phosphinato-substituted TOC with the same structure, viz. $Ti_4O_4(OiPr)_4(O_2PR''_2)_4$ (R'' = Ph,[45] C_6H_{11}[46]) were also isolated. The cubic Ti_4O_4 cluster core of four edge-sharing $[TiO_6]$ octahedra is the most compact among all Ti_4 clusters and minimizes the mutual interaction between the bulky R and R'

Figure 4. The structure of $Ti_4O_4(OR)_4(O_2CR')_4$ in ball-and-stick (left) and polyhedral representation (right).

substituents (Figure 4). This is also supported by the observation that $Ti_6O_6(OtBu)_6(O_2CR')_6$ clusters, with a related structure (see below), slowly transform into $Ti_4O_4(OtBu)_4(O_2CR')_4$.[44] Each R'COO ligand bridges a Ti_2O_2 face of the cubic cluster core, and all OR groups are terminal (one at each Ti atom).

A special type of Ti_4O_4 cluster are $[Ti_4O_4(C_2O_4)_8]^{8-}$ ("titanyl oxalate")[47] and $[Ti_4O_4L_4]^{n-}$ (L=nitrilotriacetato, n=4;[48] L= (pyridin-2-ylmethyl)amino diacetato, $n=0$[49]) with a square arrangement of four corner-sharing $[TiO_{6-x}N_x]$ octahedra. Two oxalato (x=0) or the tetradentate ligands L (x=1 or 2) occupy four coordination sites of each titanium atom; only one oxygen atom per COO group is bonded to the titanium center. The same arrangement of $[TiO_5N]$ octahedra was also found in $[Ti_4O_4(dpta)_2]_2^{4-}$ (dpta = 2-hydroxypropane-1,3-diamine-N,N,N',N'-tetraacetate), were the dpta ligands connect two rings of four corner-sharing $[TiO_5N]$ octahedra.[50]

2.3. Ti₆Oₓ clusters

Hexanuclear compounds have the greatest structural diversity among all TOC, with d_c ranging from 0.5 to 1.0, and d_s from 0.33 to 2.0 (Scheme 2). A possible reason for the abundance of Ti_6O_x clusters is that most of them are formed from two, mostly pyramidal Ti_3O building blocks which are connected with each other in various ways by oxo bridges and, in clusters with high d_s, additionally by bridging carboxylato ligands. Scheme 2 also shows that different cluster core geometries can be obtained for the same d_c, and that d_s also has some influence on the TOC structure.
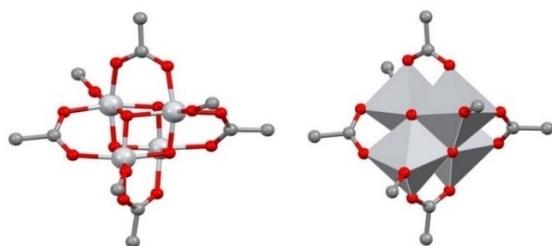
$Ti_6O_3(OR)_{14}(OOCR')_4$

$d_s = 0.67$
$d_c = 0.5$

$Ti_6O_4(OR)_{14}(OOCR')_2$

$d_s = 0.33$
$d_c = 0.67$

$Ti_6O_4(OR)_{12}(OOCR')_4$
(type 1)

$d_s = 0.67$
$d_c = 0.67$

$Ti_6O_4(OR)_{12}(OOCR')_4$
(type 2)

$d_s = 0.67$
$d_c = 0.67$

$Ti_6O_4(OR)_{10}(OOCR')_6$
(type 1)

$d_s = 1$
$d_c = 0.67$

$Ti_6O_4(OR)_8(OOCR')_8$

$d_s = 1.33$
$d_c = 0.67$

$Ti_6O_5(OR)_6(OOCR')_8$

$d_s = 1.33$
$d_c = 0.83$

$Ti_6O_6(OR)_6(OOCR')_6$

$d_s = 1$
$d_c = 1$

$Ti_6O_6(OR)_2(OOCR')_{10}$

$d_s = 1.67$
$d_c = 1$

$Ti_6O_9(OOCR')_{12}$

$d_s = 2$
$d_c = 1.5$

Scheme 2. Schematic drawing of Ti_6O_x cluster cores.

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2.3.1. Ti_6O_3 clusters

The structure of $Ti_6O_3(OR)_{14}(O_2CR')_4$ can formally be derived by a condensation reaction between two $Ti_3O(OR)_8(O_2CR')_2$ clusters, that is, by replacing two terminal OR groups (one in each Ti_3O unit) with a μ_2-O. Quite remarkably, the μ_2-O is unsymmetric, as it connects the five-coordinated Ti atom in one Ti_3O subunit with the six-coordinated Ti atom in the second Ti_3O subunit which is coordinated by two carboxylato groups.

In most Ti_6O_3 clusters, the COO groups are part of dicarboxylato ligands, viz. $Ti_6O_3(OiPr)_{14}(O_2C-X-CO_2)_2$ (X = o-C_6H_4,[51] dimethylthio-tetrathiofulvalene,[52] CH_2, CH_2CH_2,[53] CMe_2,[54] $C{\equiv}CHC_6H_4NR_2$ [R = Ph, Et],[55] $CH{=}CH$,[56] $C_6H_4-C_6H_4$;[57] Figure 5). The COO groups of the dicarboxylato ligands occupy the same positions as the monocarboxylato ligands in the type 1 $Ti_3O(OR)_8(O_2CR')_2$ clusters. One COO group of each dicarboxylato ligand is "perpendicular" in one Ti_3O subunit and the second COO group is "in-plane" in the other (as discussed for the Ti_3O clusters).

Formation of molecular clusters with dicarboxylato ligands is remarkable because use of such ligands usually gives rise to extended network (MOF) structures. A cluster with the same general structure but monocarboxylato ligands is $Ti_6O_3(OiPr)_{10}$-$(O_2CMe)_2(salicylhydroxamate)_2$.[58] The two Ti_3O subunits are not only connected by the μ_2-O, but also by two bridging acetato and two salicylhydroxamato ligands.

A variation of this structure was found for $Ti_6O_3(OiPr)_{14}(pyroglutamate)_2$.[59] The pyroglutamate ligands bridge the two Ti_3O units in a way that the carboxylate group coordinates to one Ti_3O unit and both the oxygen and nitrogen atom of the lactam unit to the other (in place of the second COO group in the dicarboxylate derivatives).
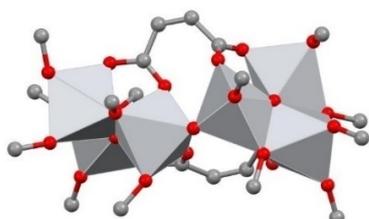
Figure 5. Polyhedral representation of $Ti_6O_3(OiPr)_{14}(O_2C-CH{=}CH-CO_2)_2$.
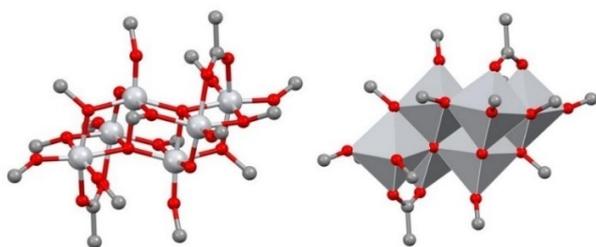
Figure 6. The structure of $Ti_6O_4(OEt)_{14}(O_2CPh)_2$ in ball-and-stick (left) and polyhedral representation (right).

2.3.2. Ti_6O_4 clusters

The clusters must have the composition $Ti_6O_4(OR)_{16-x}(O_2CR')_x$ for charge compensation of the Ti_6O_4 core. Clusters with x = 2, 4, 6 and 8 (d_s 0.33, 0.67, 1.0 and 1.33) were structurally characterized, the most frequent cluster type, however, is $Ti_6O_4(OR)_8(O_2CR')_8$.

The earliest example of the $Ti_6O_4(OR)_{14}(O_2CR')_2$ type, viz. $Ti_6O_4(OEt)_{14}(O_2CPh)_2$[60] (Figure 6), was obtained from the reaction of $Ti_7O_4(OEt)_{20}$ with benzoic acid, during which the cluster size decreases and the cluster core rearranges. Clusters $Ti_3(\mu_3$-O)$(\mu_2$-O)$(OR)_7(O_2CR')$ are not known (although their existence appears to be possible), but the structure of $Ti_6O_4(OEt)_{14}(O_2CPh)_2$ can be regarded as a dimer of such Ti_3O_2 subunits, where one Ti atom in each subunit coordinates to the μ_3-O of the second subunit. This results in a central Ti_2O_2 ring and conversion of the μ_3-O in μ_4-O atoms.

The structures of $Ti_6O_4(OiPr)_{10}(O_2C_6H_4)_2(O_2CPh)_2$[61] and Ti_6O_4-$(OiPr)_6(O_2C_6H_4)_4(O_2C$-9-anthracenyl$)_2$[62] are the same as that of $Ti_6O_4(OEt)_{14}(O_2CPh)_2$, but four or eight OR groups are exchanged against two or four doubly deprotonated catecholato ligands. Each catecholato ligand replaces a bridging OR and a neighboring terminal OR and therefore must be chelating-bridging to retain the coordination environment of each Ti atom. In the bis-catecholato derivative the terminal and bridging OR groups being trans to the μ_4-O are replaced, and in the tetrakis-catecholato derivative also the other two μ_2-OR along with a neighboring terminal OR. Both derivatives were prepared by co-reacting $Ti(OiPr)_4$, carboxylic acid and catechol.

In the clusters $Ti_6O_4(OR)_{12}(O_2CR')_4$, two $Ti_3O_2(OR)_6(O_2CR')_2$ subunits are connected with each other only by means of bridging oxygen atoms; the carboxylato ligands only bridge Ti atoms within the same subunit. Two cluster types of the same overall composition were found, both are centrosymmetric.

Type 1: In $Ti_6O_4(OiPr)_{12}(O_2CR')_4$ (R' = Me,[63] cyclohex-3-enyl[64]), the two subunits are connected via two shared corners (Figure 7). $Ti_6O_4(OiPr)_4(O_2C_6H_4)_4\{O_2CC[Co_3(CO)_9]\}_4$[42] has the same structure, but a catecholato ligand replaces two OR groups. The structure of type 1 $Ti_6O_4(OR)_{12}(O_2CR')_4$ can be formally derived from that of $Ti_6O_3(OR)_{14}(O_2CR')_4$ clusters by an inter-cluster condensation reaction, that is, by replacing two terminal OR groups (one in each Ti_3O subunit) with a μ_2-O.

Type 2: The $Ti_3O_2(OR)_6(O_2CR')_2$ subunits share a common edge (Figure 8, left), that is, all oxo groups are μ_3. This cluster type is represented by $Ti_6O_4(OEt)_{12}\{O_2CC[Co_3(CO)_9]\}_4$.[42] Two μ_3-O are planar (the ones connecting the two subunits) and two
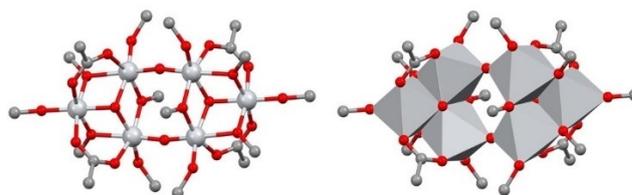
Figure 7. The structure of type 1 $Ti_6O_4(OR)_{12}(O_2CR')_4$ in ball-and-stick (left) and polyhedral representation (right).

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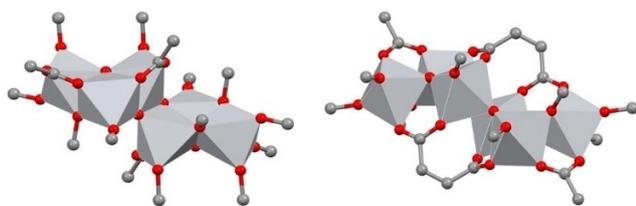
Figure 8. Polyhedral representations of the structures of type 2 $Ti_6O_4(OR)_{12}$-$(O_2CR')_4$ (left) and type 1 $Ti_6O_4(OR)_{10}(O_2CR')_6$ (right).

pyramidal (that of the Ti_3O subunits). Because of the higher coordination of the oxo groups in type 2 clusters, one μ_2-OR in each subunit is converted into a terminal OR group, compared with the type 1 clusters. In further consequence, the carboxylato ligands are differently arranged. In $Ti_6O_4(OiPr)_8$-(salicylaldoximato)$_2(O_2CPh)_4$,[23] a pair of terminal OR groups in each Ti_3O subunit is replaced by a bridging salicylaldoximato ligand.

Two types of $Ti_6O_4(OR)_{10}(O_2CR')_6$ clusters were found, both with a special set of ligands. In the first type, four carboxylato groups coordinated to the Ti atoms are part of dicarboxylato ligands and the other two are monocarboxylates. The linkage of the $[TiO_6]$ octahedra in this cluster type is approximately the same as that of type 2 $Ti_6O_4(OR)_{12}(O_2CR')_4$ (Figure 8, right), but the degree of substitution is different. In a formal sense, two μ_2-OR and two mono-carboxylato ligands are replaced by two dicarboxylato ligands which span the two Ti_3O subunits similar to $Ti_6O_3(OiPr)_{14}(O_2C—X—CO_2)_2$ (Figure 5). $Ti_6O_4(OiPr)_{10}(O_2CEt)_2(O_2C—C_6H_4—CO_2)_2$ was obtained by reacting $Ti(OiPr)_4$ with a mixture of 1,2-benzenedicarboxylic and propionic acid.[65] In the other two clusters of this type, viz. $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_2C—C_6H_4—CO_2)_2$ (R′ = C_6H_4—CO_2iPr[51] and C-(CO_2iPr)=$CHC_6H_4NPh_2$[55]), the monocarboxylato ligands was formed by esterification of one COO group of the dicarboxylic acid, as discussed before.

$Ti_6O_4(OiPr)_2(O_2C_6H_4)_4(O_2CR')_6$ (R′ = Me, Ph)[23] are the only examples of a second cluster type of the general composition $Ti_6O_4(OR)_{10}(O_2CR')_6$, where eight OR groups are replaced by four doubly deprotonated catecholato ligands. This cluster type is structurally related to type 1 $Ti_6O_4(OR)_{12}(O_2CR')_4$ (Figure 7), with the difference that the two Ti_3O subunits are not only linked by two μ_2-O, but also by two bridging carboxylato ligands. All catecholato ligands are chelating-bridging and thus replace the μ_2-OR.

The most frequent Ti_6O_4 clusters have the composition $Ti_6O_4(OR)_8(O_2CR')_8$. The centrosymmetric clusters were structurally characterized for a great variety of R/R′ combinations:
– R = Me: R′ = tBu[66]
– R = Et: R′ = Me,[67] iPr,[68] tBu,[66] C(Me)=CH_2[69]
– R = Et/iPr (1:1): R′ = Ph[66]
– R = Pr: R′ = iPr,[70] C(Me)=CH_2, CH=CH_2,[38] norbornenyl,[71] $(CH_2)_2C$≡CH)$_8$,[72] Ph[73]
– R = iPr: R′ = Me,[63b,74] CMe_2Br,[75] C(Me)=CH_2[14c,76]
– R = Bu: R′ = Me,[77] tBu,[78] $CHCl_2$,[79] CCl_3[80]

Two Ti_3O subunits are interconnected with two μ_2-O and four bridging carboxylato ligands (Figure 9). The other four carboxylato ligands bridge $[TiO_6]$ octahedra within the Ti_3O subunits. The Ti_3O subunit is "T-shaped", contrary to the other clusters discussed before, with "L-shaped" Ti_3O units.

Some heterometallic derivatives with the same general structure were obtained, showing that this structure type is very robust. In $FeTi_5O_4(OiPr)_4(O_2C—CMe$=$CH_2)_{10}$ one of the corner-sharing $[TiO_6]$ octahedra is replaced by an $[FeO_6]$ octahedron.[76] Alternatively, both lateral, edge-sharing $[TiO_6]$ octahedra can be replaced by other metal oxide polyhedra (sometimes with a different linkage of this polyhedron within the M_3O unit), such as a $[CoO_5N]$ octahedron in $Co_2Ti_4O_4$-$(O_2CPh)_{12}(MeCN)_2$,[81] a $[CdO_6]$ octahedron in $Cd_2Ti_4O_2(OH)_2(OiPr)_2(O_2CtBu)_{12}$,[82] a $[CaO_7]$ pentagonal bipyramid in $Ca_2Ti_4O_4(O_2CMe)_2(O_2C—CMe$=$CH_2)_{10}$[76] or a $[ZnO_4]$ tetrahedron in $Ti_4Zn_2O_4(OiPr)_2(O_2C—CMe$=$CH_2)_{10}$.[76]

2.3.3. Ti_6O_5 cluster

$Ti_6O_5(OiBu)_6(O_2CtBu)_8$ is the only structurally characterized example of a TOC with a Ti_6O_5 core.[83] As shown in Scheme 2, the Ti_6O_5 core can formally derived from that of $Ti_6O_4(OR)_8$-$(O_2CR')_8$ by an internal condensation reaction, which converts two terminal OR ligands (one in each Ti_3O subunit) into a third μ_2-O bridge between the Ti_3O units stretching across the central Ti_4O_4 ring, concomitant with a reorientation of the capping carboxylato and alkoxo ligands.

2.3.4. Ti_6O_6 clusters

The clusters $Ti_6O_6(OR)_6(O_2CR')_6$ and $Ti_4O_4(OR)_4(O_2CR')_4$ can be regarded oligomers of the general formula $[TiO(OR)(O_2CR')]_n$ (with $d_c = d_s = 1$). Both are characterized by dense structures in which all $[TiO_6]$ building blocks are exclusively linked via μ_3-O. All OR groups are terminal. The Ti_6O_6 core of $Ti_6O_6(OR)_6(O_2CR')_6$ is a distorted hexagonal prism with alternating Ti and O atoms (Figure 10). Three OR groups are perpendicular to each Ti_3O_3 plane, and the Ti atoms of each Ti_2O_2 square on the side of the prism are bridged by a R′COO ligand.

$Ti_6O_6(OR)_6(O_2CR')_6$ clusters with a great variety of R/R′ combinations were structurally characterized:
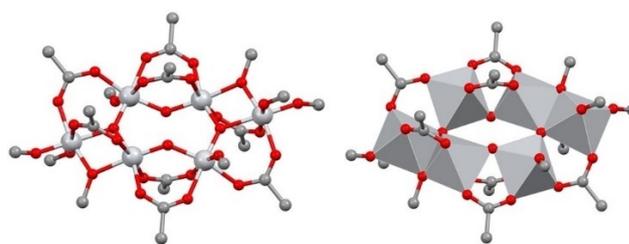
Figure 9. The structure of $Ti_6O_4(OR)_8(O_2CR')_8$ in ball-and-stick (left) and polyhedral representation (right).
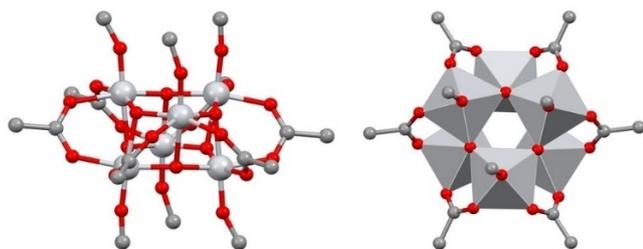
Figure 10. The structure of $Ti_6O_6(OR)_6(O_2CR')_6$ in ball-and-stick (left, side view) and polyhedral representation (right, top view).

- R = Et: R' = C_6H_4OPh[84]
- R = iPr: R' = H,[29] Me,[85,86] Et,[87] Bu,[31] iBu,[88] tBu,[89] $CHCl_2$,[24] cyclohex-3-enyl,[64] CH_2Ph,[90] CH_2-naphthyl, naphthyl,[91] C_6H_4Ph, $C_6H_4^tBu$,[92] anthracenyl,[62] adamantyl,[54] $C_6H_4COOiPr$,[14b] $C_6H_4NH_2$,[93] $C_6H_3(X)NHMe$ (X = H, F, Cl),[93b] $C_6H_4NMe_2$,[54] C_5H_4N,[25] $C_5H_3N-CO_2iPr$,[94] ferrocenyl[88,91]
- R = Bu: R' = tBu[95]
- R = iBu: R' = tBu,[95] CMe_2Et[83]
- R = tBu: R' = Et,[31] CMe_2Et, CH_2^tBu[44]
- R = CH_2^tBu: R' = iPr,[14a] Ph[73]
- R = $SiMe_3$: R' = tBu,[95] CH_2^tBu, CMe_2Et.[95a]

The same structure was observed for the ketoxime derivatives $Ti_6O_6(OiPr)_6(ON=CR_2)_6$ ($CR_2 = CMe_2$, C_5H_8),[96] thus demonstrating the robustness of this structure type. The NO group bridges two Ti atoms in the same way as the carboxylate groups.

$Ti_6O_6(OiPr)_6(O_2C-C_6H_4-CO_2iPr)_6$ was obtained from a mixture of Ti($OiPr)_4$, phthalic anhydride and acetic acid[14b] and $Ti_6O_6(OiPr)_6(O_2C-C_5H_3N-CO_2iPr)_6$ from pyridine-3,4-dicarboxylic anhydride.[94] When Ti($OiPr)_4$ is reacted with phthalic anhydride alone, the anhydride can substitute OR groups, resulting in the compound $Ti_2(OiPr)_6(O_2C-C_6H_4-CO_2iPr)_2(iPrOH)$, but there is no source for oxo groups. However, when acetic acid is added, water is produced through formation of *iso*-propyl acetate, and a cluster is obtained. $Ti_6O_6(OCH_2^tBu)_6(O_2CPh)_6$ was synthesized by reacting of $Fe_4O_2(O_2CPh)_8(py)_2$ with Ti($OPr)_4$, followed by addition of neopentanol to the reaction mixture.[73]

Another way of looking at the structures of $Ti_6O_6(OR)_6$-$(O_2CR')_6$ is to picture a distorted Ti_6 octahedron, of which six Ti_3 faces are capped by a μ_3-O, while two parallel faces (the faces perpendicular to the projection plane in Figure 10, right) are uncapped. A compound with the composition $Ti_6O_6(OiBu)_6$-$(O_2C^tBu)_6(H_2O)_2$ was formed from a solution of $Ti_6O_5(OiBu)_6$-$(O_2C^tBu)_8$,[83] where water molecules are μ_3-coordinated to the two "empty" Ti_3 faces of the Ti_6 octahedron. The Ti–O_{H_2O} distances (224–255(1) pm) clearly exclude the conceivable alternative composition $Ti_6O_4(OH)_4(OiBu)_6(O_2C^tBu)_6$, which would be analogous to the wide-spread zirconium clusters $Zr_6O_4(OH)_4(O_2CR')_{12}$.[97] However, structural "hybrids" between $Ti_6O_6(OR)_6(O_2CR')_6$ and $Zr_6O_4(OH)_4(O_2CR')_{12}$ were found, viz. $Ti_3Zr_3O_4(OH)_3(OBu)_3(O_2C^tBu)_{10}$ and $Ti_2Zr_4O_5(OH)_2(OPr)$-$(O_2C^tBu)_{11}$.[98] In the Ti_3Zr_3 cluster, one triangular face of the metal octahedron is occupied by seven- or eight-coordinate Zr

atoms and the opposite face by Ti atoms, in the Ti_2Zr_4 cluster the Ti atoms are located at one edge of the metal octahedron.

Clusters of the general composition $Ti_6O_6(OR)_2(O_2CR')_{10}$ (R' = Et, *cyclo*-C_4H_7,[56] Ph,[23] 4-$C_6H_4^tBu$, C_6H_4Ph[92]) are a second type of TOC with a Ti_6O_6 core, where the much higher d_s results in more open structures. The structures are very similar to $Ti_6O_4(OiPr)_8(O_2CR')_8$; the main difference is that the μ_2-OR are replaced by μ_2-O (Scheme 2). In consequence, a higher number of carboxylato groups must be introduced for compensation of charges and coordination numbers.

2.3.5. Ti_6O_9 cluster

The only cluster with a Ti_6O_9 core, $[Ti_6O_8(OH)\{NH-(CH_2COO)\}_6]^{5-}$,[99] is rather special because the iminodiacetato ligands are tridentate and coordinate through the nitrogen atom and one oxygen atom of each COO group to the same titanium atom, that is, the carboxylato groups do not bridge two titanium atoms as in the other TOC. The [TiO_5N] octahedra are corner-sharing and form a trigonal prism (see also Figure 12, below). The cluster was synthesized by hydrolysis of $TiCl_4$ in the presence of iminodiacetic acid.

2.4. Clusters with higher nuclearities (≥ 7)

With the exception of more frequent $Ti_8O_8(O_2CR')_{16}$ compounds, many types of carboxylato-substituted TOC with nuclearities ≥ 7 are only represented by one example. Analyzing general features is therefore not straightforward. Nonetheless, a few construction principles can be highlighted. One might expect that the structures develop more and more towards that of the TiO_2 modifications as the clusters become bigger, implying that the proportion of edge-sharing polyhedra should increase. This is, however, only the case in relatively few cluster structures.

2.4.1. Cyclic structures of corner-sharing [TiO_6] octahedra

"Titanyl carboxylates" $Ti_8O_8(O_2CR')_{16}$ ($= [TiO(O_2CR')_2]_n$) were not only obtained from Ti($OR)_4$ and carboxylic acids, but also from other TiX_4, such as $TiCl_4$ or Ti($O_2CNEt_2)_4$, in the presence of water (R' = CH_2^tBu,[100] tBu,[101] $CMe=CH_2$,[14c,102] Ph,[101b,103] C_6F_5,[104] NEt_2[105]). Contrary to most clusters with lower nuclearity, the structures of $Ti_8O_8(O_2CR')_{16}$ cannot be broken down into Ti_3O subunits. Rings of eight corner-sharing [TiO_6] octahedra are formed instead (Figure 11, left), where each titanium is linked to both neighboring $TiO(O_2CR')_2$ units via a μ_2-O and two carboxylate bridges each.

$Ti_8O_8(O_2CR')_{16}$ has crown ether-like properties, as other metals can occupy the central cavity of the Ti_8O_8 ring having an inner diameter of about 685 pm. In $Ti_8Sr_2O_8X_2(O_2CMe)_2$-$(O_2C-CMe=CH_2)_{16}$ (X = O_2CMe or $OiPr$) and $Ti_8Pb_2O_8(OBu)_2X_2$-$(O_2C-CMe=CH_2)_{16}(BuOH)_2$ (X = O_2CMe or $O_2C-CMe=CH_2$) two Sr and Pb ions are incorporated.[102] In addition to the crown-ether-like coordination of the ring oxygen atoms to the M^{2+}

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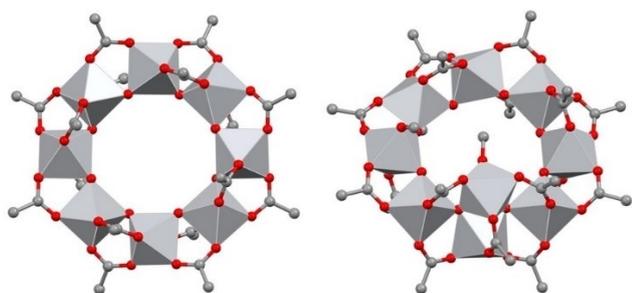
Figure 11. Polyhedral representation of the structures of $Ti_8O_8(O_2CR')_{16}$ (left) and $Ti_9O_8(OR)_4(O_2CR')_{16}$ (right).
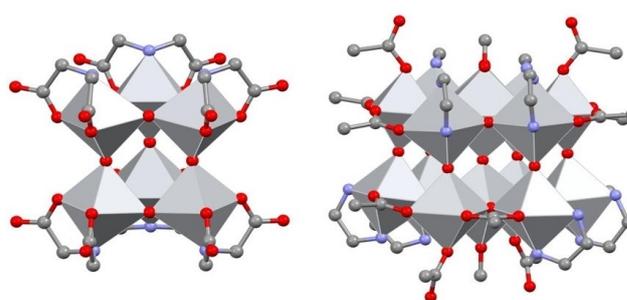
Figure 12. Polyhedral representation of the structures of $[Ti_6O_8(OH)\{NH-(CH_2COO)_2\}_6]^{5-}$ (left) and $[Ti_{14}O_{19}(OiPr)_2(OAc)_{12}(phen)_8]^{4+}$ (right).

ions, bridging carboxylato ligands support the coordination of the latter. In $[Ag_6Ti_{16}O_{22}(O_2CPh)_{26}(CH_3CN)_2]^{2-}$ and $Ag_6Ti_{16}O_{20}$-$(O_2CPh)_{24}(OAc)_4(CH_3CN)_2$ two parallel $Ti_8O_8(O_2CR')_{16}$ rings are condensed via μ_2-O and bridging carboxylato ligands and a Ag_6 cluster is incorporated in the cavity of this double-ring structure.[106]

An interesting variation of the $Ti_8O_8(O_2CR')_{16}$ structure was found for $Ti_9O_8(OPr)_4(O_2C–CMe=CH_2)_{16}$ (Figure 11, right).[14c] It has a similar ring structure, but one octahedral $[TiO_6]$ unit is replaced by an edge-sharing pair of two octahedra. From a formal point of view, this is an addition of $Ti(OPr)_4$ to the $Ti_8O_8(O_2CPr)_{16}$ ring, but the OPr groups and, concomitantly, the RCOO ligands were re-aligned.

Analogous rings with a smaller and higher number of TiO$(O_2CR')_2$ units should be possible, but have not been observed until present. However, a ring of only six corner-sharing $[TiO_6]$ octahedra was found with phosphinato instead of carboxylato ligands. Two neighboring titanium atoms in $Ti_6O_6(OH)_3(O_2P$-$cyclo$-$C_3Me_5)_9$ are alternatively bridged by two pentamethyltrimethylene phosphinato ligands and one μ_2-OH, or one phosphinato ligand and two μ_2-O.[107] Bridging phosphinato ligands are more flexible than carboxylato ligands and can therefore possibly adjust easier to varying Ti–Ti distances. Rings of only four corner-sharing $[TiO_{6-x}N_x]$ octahedra were observed in $[Ti_4O_4(C_2O_4)_8]^{8-}$ and $[Ti_4O_4(nitrilotriacetato)_4]^{4-}$ (see above).

Smaller rings can, however, be part of *double-ring structures*, where two parallel, aligned rings are condensed via shared corners. The $[TiO_5N]$ octahedra in $[Ti_6O_8(OH)\{NH(CH_2COO)_2\}_6]^{5-}$[99] (Figure 12, left) form a trigonal prism (two three-membered rings), as discussed above. In the structures of the clusters $[Ti_{12}O_{18}(AA)_6(H_2O)_{20}]^{6+}$ (AA = serine, proline)[108] the corner-sharing $[TiO_6]$ octahedra form a hexagonal prism (two planar rings of six octahedra each). This leaves a cavity with an inner diameter of about 540 pm in the center of the double-ring structure which can accommodate exchangeable guest species. The clusters were synthesized by hydrolysis of $TiCl_4$ in the presence of the amino acids. In $[Ti_{14}O_{19}(OiPr)_2(OAc)_{12}(phen)_8]^{4+}$ (Figure 12, right),[109] the center of each ring of six $[TiO_6]$ octahedra is occupied by a seventh $[TiO_6]$ unit. This results in an extended cluster core with capping phenanthroline (phen), OiPr and acetate ligands (some of them monodentate).

A similar double-layer structure was also observed in one isomer of $Ti_{20}O_{28}(8$-hydroxyquinoline$)_{10}(O_2CEt)_{14}$,[110] with ten interconnected Ti polyhedra in each layer (in the structure of a second isomer, each layer consists of eight polyhedra, and the additional four polyhedra are condensed in between the double layer at one side).

The construction principle of corner-sharing polyhedra was also found for $Ti_8O_8(OH)_4[O_2P(H)CPh_3]_{12}$,[107] with a cubic arrangement of eight $[TiO_6]$ octahedra (= two rings of four $[TiO_6]$ octahedra), each edge of the cube being bridged by a phosphinato ligand.

2.4.2. Condensation of smaller clusters via shared edges

Many structures of higher-nuclearity TOC can formally be regarded as condensation products of two or more smaller units (Scheme 3). Note that this construction principle of larger clusters by (formal) condensation of two identical smaller cluster units is the same as the buildup of $Ti_6O_4(OR)_{12}(O_2CR')_4$ from of two $Ti_3O(OR)_8(O_2CR')_2$ units.

In one group of clusters, the lower-nuclearity units exist as such:

- In $Ti_8O_{10}(O_2CR)_{12}$ (R = iPr, CCl_3,[111] $C_6H_4NH_2$;[93] Figure 13, left, and Scheme 3) two $Ti_4O_2(OR)_6(O_2CR')_6$ units are condensed (compare with Figure 3). The linkage of the $[TiO_6]$ octahedra resembles that in anatase. While the iPr and $C_6H_4NH_2$ derivative was obtained by in situ hydrolysis, the CCl_3 derivative was synthesized by treating $Ti_8O_8(O_2CtBu)_{16}$ or $Ti_8O_{10}(O_2CiPr)_{12}$ with trichloroacetic acid. In the structurally related heterometallic cluster $Ti_8Ag_2O_{10}(O_2C–C_6H_4R)_{14}(PR'_3)_2$ (R = H, R' = Ph, tolyl; R = Me, tBu, OMe: R' = Ph) two tetrahedrally coordinated Ag^+ additionally link the two Ti_4O_2 layers.[112]

- The cluster $Ti_{12}O_{12}(OPr)_{18}(OAc)_6$[86] (Figure 13, center) can formally be derived by condensation of two (slightly modified) $Ti_6O_4(OR)_{14}(O_2CR')_2$ units (compare with Figure 6).

- The structures of $Ti_{28}O_{40}(OtBu)_{20}(OAc)_{12}$[113] and $Ti_{34}O_{50}(OiPr)_{30}$-$(O_2C–C_6H_4NMe_2)_2$[114] can likewise be regarded as a condensation product of two identical halves, which exist as separate clusters, viz. $Ti_{14}O_{19}(OH)(OtBu)_{13}(OAc)_4$[113] and $Ti_{17}O_{24}$-$(OiPr)_{18}(O_2C–C_6H_4NMe_2)_2$ (R' = CH=CHPh, CH=CH–C_6H_4NMe_2,

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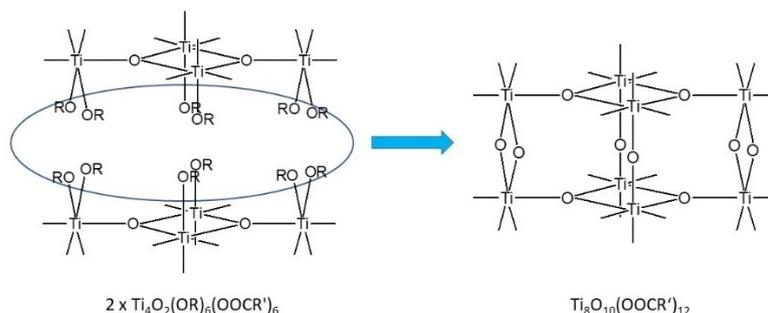
Scheme 3. Formation of a bigger cluster ($Ti_8O_{10}(O_2CR)_{12}$ as an example) by (formal) condensation of two smaller clusters ($Ti_4O_2(OR)_6(O_2CR')_6$).
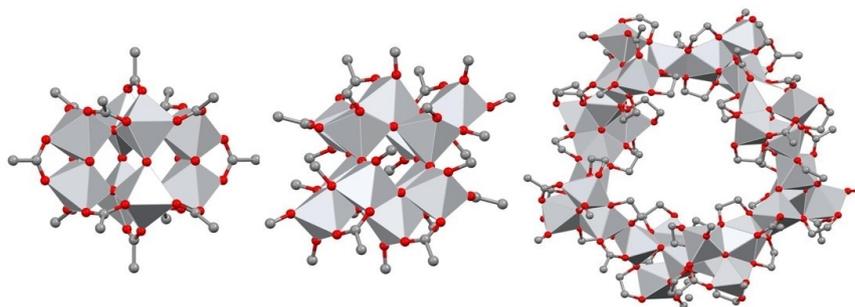
Figure 13. Polyhedral representation of the structures $Ti_8O_{10}(O_2CR')_{12}$ (left), $Ti_{12}O_{12}(OR)_{18}(O_2CR')_6$ (center) and $Ti_{32}O_{16}(OCH_2CH_2O)_{32}(OR)_{16}(O_2CR')_{16}$ (right).

$C_6H_4NMe_2$, C_5H_4N).[114] The structure of $Ti_{18}O_{25}(OtBu)_{12}$-$(OAc)_{10}$[113] can be derived by condensing the core of the Ti_{14} cluster with a Ti_4 unit.

- In $Ti_{32}O_{16}(OCH_2CH_2O)_{32}(OR)_{16}(O_2CR')_{16}$ ($OR=OCH_2CH_2OH$; $R'=$ Et, *iso*-allyl, *t*Bu,[115] Pr, CMe_2Et[116]) (Figure 13, right), eight tetranuclear subunits are connected with each other ($=$ $[Ti_4O_2(OCH_2CH_2O)_4(OR)_2(O_2CR')_2]_8$). The linkage of the $[TiO_x]$ polyhedra within the tetranuclear subunits is similar to that in $Ti_4O_2(OR)_{10}(O_2CR')_2$ (Figure 2). The Ti_4O_2 subunits are interconnected by two chelating-bridging OCH_2CH_2O and one carboxylato ligand. Due to this particular glycolate coordination, one Ti polyhedron is a rare $[TiO_7]$ unit. The twisted ring of this TOC has an inner diameter of >800 pm.

- The Ti/O skeleton of $Ti_7O_3(OiPr)_{11}(OH)(O_2C_6H_4)_4$-$(O_2C-C_6H_4-CO_2)$[21] can be constructed by condensing the cluster cores of $Ti_3O(OR)_8(O_2CR')_2$ and $Ti_4O_2(OR)_{10}(O_2CR')_2$. The Ti_4 and Ti_3 units are bridged by a μ_3-O (the μ_2-O in the Ti_4O_2

cluster), the oxygen of a chelating-bridging catecholato ligand and, additionally, a dicarboxylato ligand.

The giant clusters $Ti_{44}O_{62}(OH)_4(O_2CEt)_{46}$-$(HO_2CEt)_2(O_2CH)_2(HO_2CH)_2(H_2O)_2$ (Figure 14, left)[31] and $Ti_{52}O_{72}$-$(OH)_2(OiPr)_{28}(O_2CEt)_{34}$[65] consist of two identical, cigar-shaped halves, the tips of which are condensed via two μ_3-O (and additionally two μ_2-OR in the Ti_{52} cluster). In this case, however, the lower-nuclearity units do not exist as individual clusters. The same type of Ti_{44} cluster was obtained when the formato/formic acid ligands were pairwise replaced by glutarato or 3-methylglutarato ligands.

In a second group of clusters, two identical smaller clusters are bridged by some other unit:

- The assembly of $[TiO_6]$ octahedra in $Ti_{14}O_{18}(OiBu)_8$-$(O_2CCMe_2Et)_{12}(iBuOH)_2$[83] (Figure 14, right) can be broken down in two units of the $Ti_6O_6(OR)_6(O_2CR')_6$ type (compare with Figure 10) and a (OR-bridged) $Ti_2(OR)_8$ unit which are
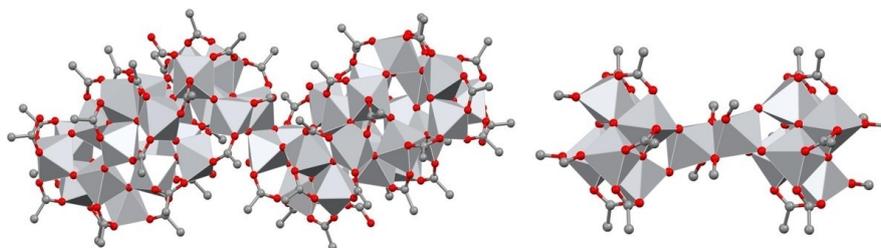
Figure 14. Polyhedral representation of the structures of $Ti_{44}O_{62}(OH)_4(O_2CR')_{48}(HO_2CR')_4(H_2O)_2$ (left) and $Ti_{14}O_{18}(OR)_8(O_2CR')_{12}(ROH)_2$ (right).

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condensed with each other. This results in a linear Ti_6–Ti_2–Ti_6 skeleton. Six μ_2-O bridges (three per Ti atom) connect the central Ti_2 unit with the Ti_6 units.

– In $Ti_8O_6(OiPr)_{14}(O_2C–C_6H_4–C_6H_4–CO_2)(dmg)_2$ (dgm = dimethylglyoxime) and in $Ti_9O_8(OiPr)_{14}(O_2C–X–CO_2)(dmg)_3$ (X = $C_6H_4–C_6H_4$, C_6H_4, C_6H_{10}), two Ti_3O units are bridged by either two $[TiO_5]$ trigonal bipyramids (and the dicarboxylato ligand) or a combination of two $[TiO_5]$ and one $[TiO_6]$ polyhedra. In the Ti_8 cluster the two $[TiO_5]$ share corners, and in the Ti_9 clusters the three polyhedra are corner-sharing.[117]

2.4.3. Other high-nuclearity clusters

One would intuitively expect that the structures of high-nuclearity clusters (including large titanium oxo/alkoxo clusters, $Ti_xO_y(OR)_{4x–2y}$) approach more and more the structures of rutile or anatase as the clusters become bigger, that is, that the proportion of μ_3-O increases. With this in mind it is quite remarkable that the number μ_2-O in such TOC is still quite high. This is possibly a consequence of the fact that in most clusters d_c is still much smaller than 2 (as in the TiO_2 modifications). Thus, many high-nuclearity-clusters have "open" structures (with a high proportion of *corner*-sharing polyhedra), many of them with elongated shapes. Examples are

– the Ti_{11} and Ti_{16} clusters $Ti_{11}O_{13}(OtBu)_4(O_2CEt)_{14}$ and $Ti_{16}O_{20}$-$(OtBu)_2(OH)_2(O_2CEt)_{20}$,[31]
– the Ti_{14} cluster $Ti_{14}O_{19}(OH)(OtBu)_{13}(O_2CMe)_4$[113] (see above),
– the Ti_{17} clusters $Ti_{17}O_{24}(OiPr)_{18}(O_2C–C_6H_4NMe_2)_2$[114] (see above) and $Ti_{17}O_{20}(OiPr)_{16}(O_2CEt)_8$[65]
– the Ti_{18} clusters $Ti_{18}O_{22}(OH)_2(OtBu)_6(OBu)_6(O_2CtBu)_{14}$,[31] $Ti_{18}O_{23}(OH)_2(OiPr)_4(O_2C$-cyclohex-3-enyl$)_{20}$[64] and $Ti_{18}O_{25}$-$(OtBu)_{12}(O_2CR')_{10}$ (R' = Me, Et)[114] (Figure 15, left)
– the two subunits of $Ti_{44}O_{62}(OH)_4(O_2CR')_{48}(HO_2CR')_4(H_2O)_2$[31] and $Ti_{52}O_{72}(OH)_2(OiPr)_{28}(O_2CEt)_{34}$[65] (see above) or
– the nearly spherical, hollow $[Ti_{22}O_{28}(OH)_3(OiPr)_{18}I(O_2CtBu)_9$-$(H_2O)]^+$ (Figure 15, center).[118]

In all cases, smaller building blocks, such as Ti_3O units, can be recognized, which, however, do not form regular superstructures.

A rare example of a higher-nuclear TOC with a symmetrical structure is $Ti_{17}O_{24}(OiPr)_{16}(O_2C–C_5H_4N)_4$ (Figure 15, right).[25] The structure consists of a central $[TiO_4]$ tetrahedron surrounded by a belt of eight edge-sharing $[TiO_6]$ octahedra. Above and below

this only slightly corrugated Ti_9 unit are two parallel rings of four $[TiO_6]$ octahedra, pairwise sharing edges and corners. Figure 15, right, is a view perpendicular to the four-membered rings and the Ti_9 unit. The cluster core of this derivative is the same as that of $Ti_{17}O_{24}(OiPr)_{16}(p$-nitrophenyl acetylacetonato$)_4$[119] with the difference that the diketonato ligands are chelating and the carboxylato ligands bridging.

In contrast, higher-nuclearity clusters with more compact structures are rare and include the unevenly-shaped Ti_9O_{12}-$(OtBu)_8(OAc)_4$[31] and $Ti_7O_4(OiPr)_8(O_2C_6H_4)_5(O_2C$-ferrocenyl$)_2$.[21] The core of the latter cluster can formally be deduced from that of type 1 $Ti_6O_4(OR)_{12}(O_2CR')_4$ (Figure 7) by coordinating a Ti-$(O_2C_6H_4)$ unit to the four oxygen atoms (two μ_2-O and two μ_3-O) and adjusting the ligand sphere, that is, by bridging the two Ti_3O units with a seventh $[TiO_6]$ octahedron.

3. Phosphonato-Substituted Titanium Oxo Clusters

Most of the *carboxylato*-substituted TOC are formed by in situ hydrolysis, due to ester formation between the employed carboxylic acid and eliminated alcohol, as discussed above. Although phosphonic acid esters were identified as a side-product in a few reactions of $Ti(OR)_4$ and $R''PO_3H$,[120,121] the main source of the oxide ions in (organo)*phosphonato*-substituted TOC appears to be moisture deliberately or accidentally introduced into the reaction mixture. Because the formation of phosphonic acid esters is sluggish, a mixture of carboxylic and organophosphonic acids is often employed (sometimes together with an organic solvent). The carboxylic acid reacts with the eliminated ROH more readily and thus produces the water needed for partial hydrolysis, whereas $R''PO_3$ groups coordinate to Ti. With this protocol, mixed carboxylato-phosphonato-substituted TOCs are often obtained, sometimes only phosphonato-substituted TOCs, but never only carboxylato-substituted TOCs. This shows that $R''PO_3$ ligands are more strongly bonded to Ti than R'COO ligands.

Trimethylsilyl esters of phosphonic acids, $R''P(O)(OSiMe_3)_2$ are sometimes used instead of the phosphonic acids due their better solubility.[122] Reactions of bis(trimethylsilyl)phosphonates with alcohols are fast and produce the corresponding phos-
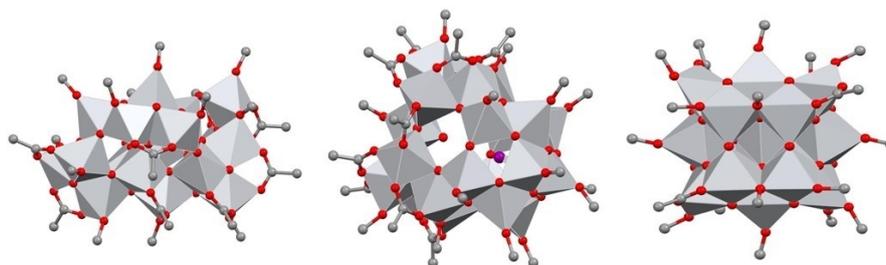
Figure 15. Polyhedral representation of the structures of $Ti_{18}O_{25}(OtBu)_{12}(O_2CR')_{10}$ (left), $[Ti_{22}O_{28}(OH)_3(OiPr)_{18}I(O_2CtBu)_9(H_2O)]^+$ (center) and $Ti_{17}O_{24}(OiPr)_{16}(O_2C–C_5H_4N)_4$ (right).

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phonic acid in situ together with Me_3SiOR. This renders the reactions often more reliable.

Phosphonic acids, $R''P(O)(OH)_2$ are diprotic and can thus form two anions, $R''PO_2(OH)^-$ and $R''PO_3^{2-}$, which can both act as ligands. $R''PO_3^{2-}$ is tripodal, while the coordination behavior of $R''PO_2(OH)^-$ is comparable to that of phosphinato ligands $R''_2PO_2^-$. A large number of coordination modes are possible for $R''PO_3^{2-}$; the most common in TOC is 3.111 (in the *w.xyz* designation, *w* denotes the number of metal atoms to which the phosphonato ligand is coordinated and *x*, *y*, *z* the number of metal atoms to which each oxygen is coordinated).[123]

3.1. Compounds with $R''PO_3$-linked Ti_3O units

One of the earliest examples of phosphonato-substituted TOC is $Cp*_3Ti_3O_2(O_3PtBu)_2[O_2P(OH) \, tBu]$ ($Cp* = \pi\text{-}C_5Me_5$)[124] where three $Cp*Ti$ units form an isosceles triangle. Two edges of the triangle are bridged by a $\mu_2\text{-}O$ each, and the third by a $\mu_2\text{-}R''P(OH)O_2$ ligand. Both faces of the triangle are capped with a $\mu_3\text{-}R''PO_3$ ligand (3.111 coordination).

There are only two phosphonato-substituted clusters with the same structure as type 1 $Ti_3O(OR)_8(O_2CR')_2$ (Figure 1). $[Ti_3O\text{-}(OiPr)_7(\text{nicotinato})(O_3PH)]_3[CuX]$ ($X = Cl$, Br)[125] is assembled from three $Ti_3O(OR)_7(O_2CR')(O_3PR'')$ units in which the HPO_3 ligand is coplanar with the Ti_3O core replacing one of the carboxylato ligands of the bis-carboxylato cluster. The third oxygen of HPO_3 coordinates to another Ti_3O unit, resulting in a ring of three Ti_3O clusters. The nicotinato ligands are perpendicular to the Ti_3O planes and point in the same direction. This allows coordination of CuX to the nitrogen atoms of the nicotinato ligands (the Cu ion is thus tetrahedrally coordinated by three nitrogen atoms and the halide anion). Formation of cyclic oligomers with Ti_3O building blocks is comparable to the cyclic oligomers $[Ti_3O(OiPr)_8(O_2C\text{–}X\text{–}CO_2)]_n$ discussed above.

The construction principle of $[Ti_6O_2(OiPr)_{14}(O_3PH)_2(O_3S\text{–}C_6H_4\text{–}C_6H_4\text{–}SO_3)]_3$[125] is the same. There are two rings of three HPO_3-linked Ti_3O units each which are connected through biphenyldisulfonato ligands. The disulfonato ligands are in place of the nicotinato ligands in the previous example.

Notwithstanding the lack of isolated $Ti_3O(OR)_7(O_2CR')(O_3PR'')$ clusters, there are several compounds based on (C_3 symmetric)

Ti_3O units, which are, however, connected to other building blocks via phosphonato ligands.

In $Ti_4O(OiPr)_8(O_3PR'')_3L$ (L = neutral ligand) a single $[TiO_6]$ octahedron is connected to the Ti_3O building block by means of three $\mu_3\text{-}R''PO_3$ ligands (3 + 1 structure, Figure 16, left). In order to render all titanium atoms octahedrally coordinated, a neutral ligand L is bonded to the fourth titanium atom. $Ti_4O(OiPr)_8\text{-}(O_3PR'')_3L$ clusters with a variety of R''/L combinations were isolated:

– $R'' = Me$, tBu: L = DMSO[126]
– $R'' = Ph$: L = THF,[127,128] DMSO,[45] imidazole[129]
– $R'' = $ naphthyl: L = THF[128]
– $R'' = $ xylyl: L = $iPrOH$[120]
– $R'' = 4\text{-}C_6H_4X$ (X = OMe, F, Cl, Br): L = $iPrOH$.[128]

The clusters $Ti_3MO(OiPr)_6(O_3PPh)_3(\text{imidazole})$ (M = Co, Zn)[129] have a very similar structure; a Zn or Co ion is coordinated to the three $\mu_3\text{-}R''PO_3$ ligands instead of a $Ti(OiPr)_2L$ unit.

With ligands L containing two basic centers, the L-bridged compounds $[Ti_4O(OiPr)_8(O_3PPh)_3]_2L$ (L = piperazine, adenine, aminopyrazine) were obtained.[130] The $Ti_4\text{-}L\text{-}Ti_6\text{-}L\text{-}Ti_4$ cluster chain with $Ti_4 = [Ti_4O(OiPr)_8(O_3PPh)_3]$, $Ti_6 = [Ti_6O_4(OiPr)_{10}(O_3PPh)_2]$ (see below) and L = 2-amino-*iso*-nicotinate[130] is based on the same construction principle (the pyridine nitrogen of L is coordinated to the Ti_4 unit, and the COO group to the Ti_6 unit).

Some other variations of the 3 + 1 structure were found. In $Ti_8O_2(OiPr)_{14}(R''PO_3)_6[R''P(OiPr)O_2]_2$ ($R'' = $ allyl, Et),[120] two 3 + 1 units are connected via two bridging $R''P(OiPr)O_2$ ligands, resulting in a 3 + 1 + 1 + 3 structure. The oxygen atoms of the $R''P(OiPr)O_2$ ligands replace the neutral ligand L and one terminal OR group of the single $[TiO_6]$ octahedron of the parent 3 + 1 structure. $Ti_8O_2(OiPr)_{14}(PO_4)_2(O_3P\text{-vinyl})_4$ also has a 3 + 1 + 1 + 3 structure. However, one of the $\mu_3\text{-}O_3PR''$ ligands of the parent 3 + 1 compound is replaced by a PO_4 group which additionally connects the single Ti atoms with each other.[131] $Ti_7O_2(OiPr)_{12}(R''PO_3)_6$ (R = $CH_2CH_2CH_2Cl$, CH_2Ph,[120] $CH_2C_6H_4Br$, C_6H_4Br[128]) has a 3 + 1 + 3 ("sandwich") structure, where a second Ti_3 unit is coordinated to the single $[TiO_6]$ octahedron. To this end, the neutral ligand L and both terminal OR groups in the 3 + 1 structure are replaced by the oxygen atoms of three 3.111 $R''PO_3$ ligands (that is, the central titanium atom is coordinated by six oxygen atoms of six $R''PO_3$ ligands).

The construction of $Ti_5O(OiPr)_{11}(O_2CR')(O_3PR'')_3$ (R' = Me, R'' = $CH_2CH_2CH_2Br$;[132] R' = CMe=CH$_2$, R'' = Et, $CH_2CH_2CH_2Br$;[133] Figure 16, center left) is based on the same principle as that of
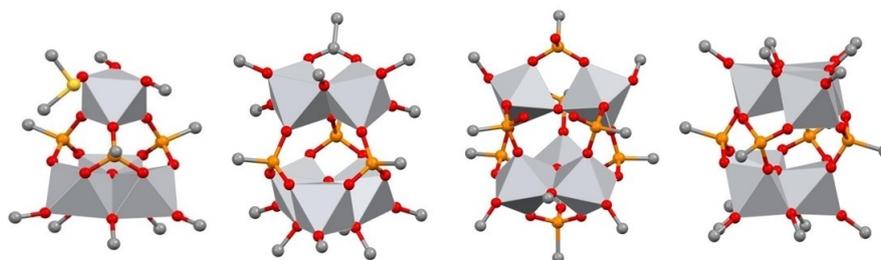
Figure 16. Polyhedral representation of the structures of $Ti_4O(OR)_8(O_3PR'')_3(DMSO)$ (3 + 1, left), $Ti_5O(OR)_{11}(O_2CR')(O_3PR'')_3$ (3 + 2, center left), $Ti_5O_2(OR)_4(O_3PR'')_5\text{-}[O_2P(OH)R'']_2$ (3 + 2, center right), and $Ti_6O_2(OR)_{12}(O_3PR'')_4$ (3 + 3 right).

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$Ti_4O(OR)_8(O_3PR'')_3L$, but the single $[TiO_6]$ octahedron is replaced by a pair of edge-sharing $[TiO_6]$ octahedra ($3+2$ structure). The titanium atoms in the Ti_2 unit are bridged by one μ_2-OR group, one oxygen atom of a $R''PO_3$ ligand, and additionally by the carboxylato ligand. Due to this arrangement, the $R''PO_3$ ligands in $Ti_5O(OR)_{11}(O_2CR')(O_3PR'')_3$ are differently coordinated: two are 3.111 (as in the Ti_4O clusters) and the third (the one in the middle in Figure 16, center left) is 4.211.

Another $3+2$ structure, with a different arrangement of the $[TiO_6]$ octahedra in the Ti_2 unit is $Ti_5O_2(OEt)_4(O_3PtBu)_5[O_2P(OH)tBu]_2$[134] (Figure 16, center right). The octahedra in the Ti_2 unit are corner-sharing (μ_2-O), and the Ti_3O and Ti_2 units are not only interlinked via three 3.111 $R''PO_3$ ligands but additionally via two $R''P(OH)O_2$ ligands.

This series is completed by $Ti_6O_2(OPh)_6(OiPr)_6(O_3PPh)_4$[135] with a $3+3$ structure. Two identical Ti_3O units are stapled together by means of four $R''PO_3$ ligands (Figure 16, right).

3.2. Ti_4O_x and Ti_5O_x clusters

Only a few examples are known with real Ti_4O_x or Ti_5O_x cores, that is, where all $[TiO_6]$ octahedra are condensed via bridging OR groups or oxygen atoms.

3.2.1. Ti_4O clusters

The cluster core of $Ti_4O(OEt)_{12}(O_3PR'')$ ($R'' = tBu$,[134,136] Ph;[137] Figure 17, left), with the lowest O/Ti ratio (d_c 0.25) among all TOC, is very similar to that of $Ti_4O_2(OR)_{10}(O_2CR')_2$ (cf. Figure 2), with the four $[TiO_6]$ octahedra centered around a μ_4-O. Compared with the carboxylato derivatives, the μ_2-O is replaced by a μ_2-OR, and the $R''PO_3$ ligand caps three octahedra (3.111 coordination; replacing a R'COO ligand and a terminal OR).

$Ti_{10}O_2(OEt)_{32}(O_3P–C_2H_4NH_2)_2$[136] consists of two such $Ti_4O(OR)_{12}(O_3PR'')$ units. The terminal amino groups of the phosphonato ligand are coordinated to a $Ti_2(OR)_8$ unit (resulting in a $4+2+4$ structure). The central $Ti_2(OR)_8(NH_2)_2$ entity has the same structure as in other amino-substituted titanium alkoxides.[138]

The core of the Ti_4O cluster cation in $[Ti_4O(OiPr)_9(O_3PPh)_2][CuBr_2]$ has a similar structure as $Ti_4O(OR)_{12}(O_3PR'')$, with a second μ_3-$R''PO_3$ ligand replacing the three terminal OR

ligands perpendicular to the projection plane in Figure 17, left (and thus introducing a positive charge).[139]

3.2.2. Ti_4O_2 clusters

The structure of $Ti_4O_2(OiPr)_6(O_3PPh)_3$(phenanthroline)[129] is a hybrid of the $Ti_4O(OR)_{12}(O_3PR'')$ and $Ti_4O(OR)_8(O_3PR'')_3L$ structures. Different to $Ti_4O(OR)_8(O_3PR'')_3L$, the single Ti octahedron, carrying a phenanthroline ligand, is linked to the Ti_3O unit by (only) two μ_3-$R''PO_3$ ligands whereas the third μ_3-$R''PO_3$ is replaced by a μ_2-O. This Ti octahedron is thus corner-sharing with one octahedron of the Ti_3O unit. The Ti_3O unit is capped by a $R''PO_3$ ligand (3.111 coordination) as in $Ti_4O(OR)_{12}(O_3PR'')$.

3.2.3. Ti_5O_3 clusters

In the clusters $Ti_5O_3(OiPr)_6(O_2CR')_4(O_3PR'')_2$ (R' = Me, R'' = xylyl;[132] R' = ferrocenyl, R'' = H,[140] CH_2Ph;[141] Figure 17, right), two dimers of edge-sharing $[TiO_6]$ octahedra are connected with a single $[TiO_6]$ octahedron via two μ_3-O, and with each other via a μ_2-O. The construction principle of $Ti_5O_3(OR)_6(O_2CR')_4(O_3PR'')_2$ is slightly reminiscent to that of $Ti_6O_4(OR)_8(O_2CR')_8$ (Figure 9).

3.3. Ti_6O_x clusters

As in the case of carboxylato-substituted TOC, hexanuclear clusters are most frequent. They are constructed from two partially condensed Ti_3O subunits. The structures can be derived from that of $Ti_6O_2(OR)_{12}(O_3PR'')_4$ (Figure 16, right) by replacing one or two of the μ_3-$R''PO_3$ ligands connecting the Ti_3O units by a μ_2-O. There is only one example for the former, viz. $Ti_6O_3(OEt)_{11}(O_3PtBu)_3[O_2P(OH)tBu]$.[134] As a 3.111 $R''PO_3$ ligand occupies three coordination sites but a μ_2-O only two, one terminal OR group is replaced by a μ_2-$R''P(OH)O_2$ ligand.

The vast majority of Ti_6O_x clusters are the mixed carboxylato-phosphonato clusters $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$ (Figure 18), where, compared with $Ti_6O_2(OR)_{12}(O_3PR'')_4$, two μ_3-$R''PO_3$ ligands are replaced by μ_2-O (Figure 18 is rotated by 90° relative to Figure 16, right). In order to compensate the coordination requirements of the titanium atoms, two terminal OR groups are replaced by bridging carboxylato ligands. One of the titanium atoms is nevertheless only five-coordinate. Note the
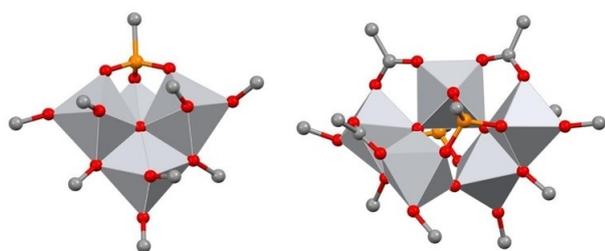
Figure 17. Polyhedral representation of the structures of $Ti_4O(OR)_{12}(O_3PR'')$ (left) and $Ti_5O_3(OR)_6(O_2CR')_4(O_3PR'')_2$ (right).
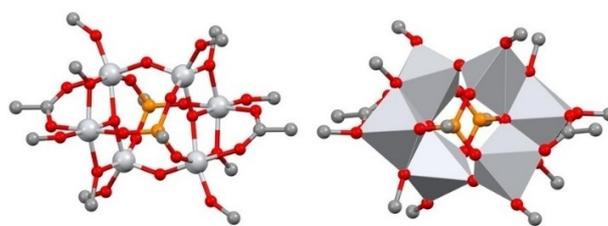
Figure 18. The structure of $Ti_6O_4(OR)_{10}(O_2CR')_2(O_3PR'')_2$ in ball-and-stick (left) and polyhedral representation (right).

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similarity of this structure with that of type 1 $Ti_6O_4(OiPr)_{12}$-$(O_2CR')_4$ (Figure 7), where the two Ti_3O subunits are also connected via two μ_2-O. In $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$, the two subunits are additionally bridged by two μ_3-$R''PO_3$ ligands.

A great number of $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$ with a huge variety of R'/R'' combinations was structurally characterized:

– R'' = H: R' = C_5H_4N,[125] ferrocenyl[140]
– R'' = Et: R' = Me,[132] $CMe{=}CH_2$[133]
– R'' = $CH{=}CH_2$, $CH_2CH{=}CH_2$: R' = Me,[132] $CMe{=}CH_2$[133]
– R'' = CH_2-naphthyl, $CH_2CH_2CH_2Cl$,[132] dodecyl:[142] R' = Me
– R'' = $CH_2CH_2CH_2Br$, CH_2CH_2CN, $CH_2C(O)Me$, $CH_2CH_2OC(O)$$C(Me){=}CH_2$): R' = $CMe{=}CH_2$[133]
– R'' = CH_2Ph: R' = ferrocenyl,[141] $CMe{=}CH_2$[133]
– R'' = Ph: R' = Me,[143,144] Et, CH_2Br, CH_2CN_4, CH_2CF_3, Ph, C_6H_4Br, C_6H_4Me, $C_6H_4NO_2$, C_6F_5, naphthyl,[144] $CMe{=}CH_2$,[133] O_2C–C_6H_4–$COOiPr$, ferrocenyl,[141] $C_6H_4NMe_2$, C_6H_4CN,[145] C_5H_4N,[144,146] C_5H_3N–NH_2,[146] C_5H_3N–Cl,[139] $C_6H_4NH_2$, $C_6H_3(NH_2)_2$, $C_6H_4N{=}CH$–$C_6H_4NR_2$, $C_6H_3(N{=}CH$–$C_6H_4NR_2)_2$ (R = Et, Ph),[147] $C_6H_4C(CN){=}CH$–$C_6H_4NR_2$ (R = Et, Ph), CH_2CN,[20] dimethylthio-tetrathiafulvalenyl, 3-thienyl.[19]

The nitrogen atom in the nicotinato- or *iso*-nicotinato derivatives was used to coordinate Cu or Co ions,[144,146] or a $Ti_4O(OiPr)_8(O_3PPh)_3$ cluster unit[130] (see above).

The great variety of functional and nonfunctional substituents in $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$ both in the carboxylato and phosphonato ligands highlights the robustness of this cluster type. This is also underlined by the fact that other negatively charged bidentate ligands can take the position of the two carboxylato ligands, such as 2-pyridinolate,[23] hydroxy benzotriazolate,[129] tolylsulfonate, $PhPO_3$,[144] or $Ph(iPrO)PO_2$.[121]

In $Ti_8O_4(OiPr)_{16}(O_3PPh)_2(adenine)_2(NO_3)_2$,[129] two adenine groups are bonded to the $Ti_6O_4(OiPr)_{10}(O_3PR'')_2$ cluster core in place of the carboxylato ligands. Additional coordination of a $Ti(OiPr)_3(NO_3)$ molecule to each adenine group results in a 1+6+1 structure.

A variation of the $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$ structure type was found in $[Ti_6O_6(OPh)_6(O_3PPh)_2L_6]^{2+}$ (L = phenanthroline, bipyridine).[135] Different to the structures of $Ti_6O_4(OiPr)_{10}(O_2CR')_2(O_3PR'')_2$, the three Ti polyhedra in the Ti_3O units do not share edges but are instead connected via two μ_2-O.

3.4. Clusters with higher nuclearities (≥ 8)

There are two examples with a true Ti_8O_4 cluster core, meaning that all titanium polyhedra are condensed, instead of being connected through phosphonato ligands only. In both $Ti_8O_4(OR)_{12}(O_3PH)_4(2,2\text{-biphenolato})_2$ (R = *i*Pr, Et;[40] Figure 19, left) and $Ti_8O_4(OiPr)_{12}(O_3PPh)_4L_2$ (L = catecholate, naphthalene-2,3-diolate)[145] two tetranuclear subunits share two corners and are additionally bridged by two phosphonato ligands. The two clusters differ how the [TiO_6] octahedra in the subunits are condensed. The structures are reminiscent of $Ti_6O_4(OR)_{10}(O_2CR')_2(O_3PR'')_2$ (Figure 18) where two trinuclear subunits are connected in the same manner.

In some other larger phosphonato-substituted TOC, two smaller subunits are either condensed with each other via μ_2-O only or connected by means of a mono- or binuclear spacer unit. This is analogous to what has been discussed before for carboxylato-substituted TOC.

In $[Ti_9O_9(OH)(OiPr)_7(O_2CEt)_8(O_3PPh)]_2$,[87] two Ti_9 clusters are dimerized via two bridging (3.111) phosphonato ligands. Each Ti_9 cluster is built from a $Ti_6O_6(OiPr)_3(O_2CEt)_6$ unit, with a core structure similar to that of $Ti_6O_4(OR)_{14}(O_2CR')_2$ (Figure 6), which is condensed to a $Ti_3O(OR)_4(O_2CR')_2(O_3PPh)$ unit via three μ_2-O/OH.

$Ti_{10}O_8(OEt)_{20}(O_3PtBu)_2(EtOH)_2$[134] can formally be derived from condensation of $Ti_2(OR)_8$ with two equivalents of Ti_4O-$(OR)_{12}(O_3PR'')$. This is analogous to $Ti_{14}O_{18}(OiBu)_8(O_2CCMe_2Et)_{12}$-$(iBuOH)_2$[83] (Figure 14, right). A $Ti_2(OR)_8$ linker is also part of the $[Ti_{26}O_{26}(OEt)_{39}(O_3PPh)_6]Br$ structure (Figure 19, right).[137] The Ti_{12} subunits condensed at both sides to the Ti_2 linker are formed from three $Ti_4O(OR)_{12}(O_3PR'')$ clusters each (*cf.* with Figure 17, left) which are condensed with each other via μ_2-O groups. In the structurally related compound $Ti_{25}O_{26}(OEt)_{36}(O_3PPh)_6$,[137] the Ti_2 unit is replaced by a single [TiO_6] octahedron.

4. Discussion and Conclusions

Some trends are conspicuous when comparing the structural chemistry of carboxylato-substituted TOC with that of phosphonato-substituted ones:

1. The structural diversity of carboxylato-substituted TOC is much greater, that is, a much larger number of cluster types is known.
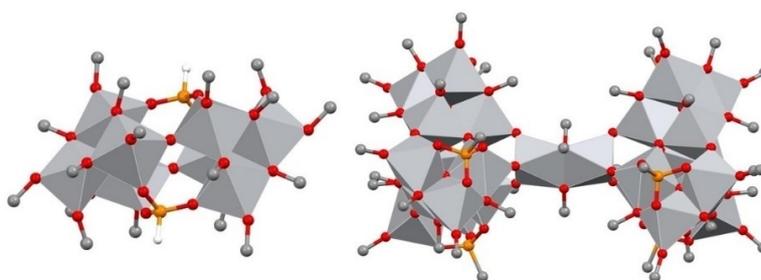
Figure 19. Polyhedral representation of the structures of $Ti_8O_4(OR)_{12}(O_3PH)_4(biphenolato)_2$ (left) and $[Ti_{26}O_{26}(OEt)_{39}(O_3PPh)_6]^+$ (right).

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2. Ti_3O or Ti_4O subunits dominate the structural chemistry of phosphonato-substituted TOC to a much greater extent than that of carboxylato-substituted clusters.
3. Very large phosphonato-substituted clusters are rare.
4. Although not especially treated in this article: there are nearly no heterometallic clusters with phosphonato ligands.

These observations may have a common origin in the coordination characteristics of $R'CO_2$ and $R''PO_3$ ligands. Carboxylato ligands are bridging and span, with very few exceptions, two corner- or edge-sharing $[TiO_6]$ octahedra (Figure 20). $Ti–O_{carboxylate}$ bond lengths are typically in the range 200–210 pm and depend on the trans ligand. In contrast, the Ti···Ti distances bridged by carboxylato ligands vary considerably (300–360 pm); they are in the upper range if the $[TiO_6]$ octahedra are corner-sharing. Since most of the fictitious five-membered Ti–O–C–O–Ti rings in TOC are more or less planar and the O···O distance is 224 pm within narrow limits, the Ti–O–C angles are the most important parameter to match with varying Ti···Ti distances. For example, the carboxylato-bridged Ti···Ti distances in $Ti_6O_4(OPr)_8(O_2C–CH=CH_2)_8$[38] (Figure 9) are 310(1) pm for the two edge-sharing octahedra, and 336(1) or 356(1) pm for the corner-sharing octahedra; the corresponding (averaged) Ti–O–C angles are 129.1° (edge-sharing octahedra) and 133.0° (corner-sharing octahedra). Since the Ti–O–C angles cannot be widened beyond a certain limit, edge-sharing $[TiO_6]$ octahedra are always tilted towards each other (Figure 20, right), and variation of the Ti–O–Ti angle in corner-sharing octahedra is limited (135.8(2)° in the Ti_6O_4 cluster). In other words, the Ti–O–C angles and the tilt or Ti–O–Ti angle mutually influence each other. Such geometrical constraints of carboxylate bridging and concomitant distortions influence the structural buildup of the cluster cores beyond the carboxylato-substituted polyhedra. This also explains that large carboxylato-substituted TOC do not have extended Ti/O cores similar to rutile or anatase: the alignment of the $[TiO_6]$ octahedra in the TiO_2 modifications is too rigid to allow bridging by carboxylato ligands (that is, the octahedra cannot be tilted and the Ti–O–Ti angles be varied sufficiently). It is often claimed that large TOC are molecular models for the TiO_2 modifications. While this may be true for some spectroscopic properties or surface reactions, this claim cannot be supported from a structural point of view.
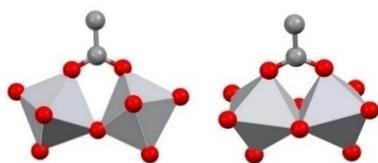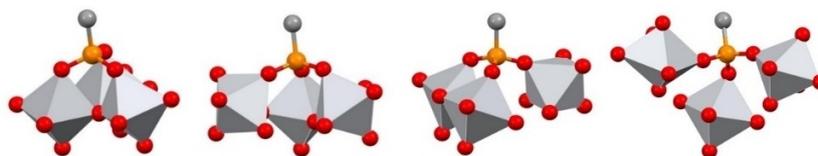
As pointed out before, the degree of condensation (d_c) and the degree of substitution (d_s) are helpful characteristics for the classification of the carboxylato-substituted TOC. As a general rule, less compact structures are formed with increasing d_s. An illustrative example is the comparison between $Ti_4O_4(OR)_4(O_2CR')_4$ (Figure 4) and $Ti_6O_6(OR)_6(O_2CR')_6$ (Figure 10), with $d_s = 1$, and $[TiO(O_2CR')_2]_8$ ($d_s = 2$, Figure 13). The three cluster types have the same d_c, but the former two (with $d_s = 1$) represent compact structures in which all oxygen atoms are μ_3, while the latter has a very open structure with only μ_2-O. The vast majority of TOC contain both μ_2- and μ_3- or μ_4-O. Nevertheless, the same trend concerning the influence of d_s can be seen, for example when comparing the structures of $Ti_4O_2(OR)_{10}(O_2CR')_2$ (Figure 2) and $Ti_4O_2(OR)_6(O_2CR')_6$ (Figure 3), both with $d_c = 0.5$, or of $Ti_6O_4(OR)_{14}(O_2CR')_2$ (Figure 6) with $Ti_6O_4(OR)_8(O_2CR')_8$ (Figure 9), both with $d_c = 0.67$.

The picture of phosphonato-substituted TOC is more complex, because such ligands have a more diverse coordination chemistry. First, phosphonato ligands can coordinate to up to three different titanium atoms. The examples in Figure 21 (extracted from real structures) show that not only pairs of edge- or corner-sharing $[TiO_6]$ octahedra can be bridged (as with carboxylato ligands), but the third octahedron can also be either connected or disconnected to this pair of octahedra. Even bridging of three independent $[TiO_6]$ octahedra is possible (Figure 21, right). The Ti···Ti distances in the latter case can be as large as 650 pm. The reason for this different coordination behavior are the larger O···O distances in $R''PO_3$ ligands (typically in the range of 250–257 pm), the non-planarity of the Ti–O–P-O–Ti grouping and more flexible Ti–O–P angles, which can be as wide as 160°. Bridging of larger Ti···Ti distances is also associated with larger Ti–O–P angles, as for carboxylato-substituted TOC. Another consequence of the more flexible phosphonato ligands is that edge-sharing $[TiO_6]$ octahedra are less tilted than in the case of carboxylato-bridged compounds.

The degree of substitution (d_s) is a less useful tool for analyzing the structures of phosphonato-substituted derivatives. The main reason is that some $[TiO_x]$ polyhedra may not be condensed to the cluster core, as shown in Figure 16, and therefore the ligand/Ti ratio is not too meaningful with regard to the cluster core structure. A second reason is that not enough cluster types are available for comparison.

No experimental studies are available on the mechanisms of cluster growth or modification, due to the difficulties mentioned in the Introduction. Although it is quite obvious that the

Figure 20. Carboxylato ligands bridging two corner-sharing (left) and edge-sharing $[TiO_6]$ octahedra (right).

Figure 21. Variations in the Ti bridging of 3.111 phosphonato ligands.

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interplay between d_s and d_c is of great importance for obtaining a particular structure type, it is currently not possible to control the ratio between both deliberately. Some general features can, however, be extracted from the comparison of the different structure types. A most striking feature is that Ti_3O units, with a μ_3-O connecting three $[TiO_x]$ polyhedra, are very frequent subunits in the various types of both carboxylato- and phosphonato-substituted TOC. One can therefore hypothesize that Ti_3O clusters are formed in early stages of the cluster syntheses which then undergo various transformations or growth reactions.

As outlined before, there are different arrangements of the three polyhedra in the Ti_3O units - one with C_3 symmetry and two with a lower symmetry, the "L-shaped" and the "T-shaped". The three titanium atoms in the latter form isosceles triangles; in the "L form" the two shorter Ti···Ti distances are of equal length and in the "T-form" the two longer. The Ti_3O units can be broken down in a pair of edge-sharing $[TiO_x]$ polyhedra to which a third $[TiO_x]$ polyhedron is connected in various ways, but always generating a μ_3-O. When the polyhedra share edges, the second corner of this edge is occupied by a μ_2-OR or a μ-O. Comparison of the structures highlights the various ways how the capping ligands (mainly RO^-, $R'CO_2^-$ and $R''PO_3^{2-}$) can be (re-)arranged to compensate charges and coordination sites in the different forms of the Ti_3O unit. This can also be extrapolated to other cluster types.

It must be emphasized again that the following considerations about cluster transformations are solely based on the comparison of structures; whether this reflects chemical reactions is an open question. The classification only considers the cluster cores since the great variability of ligand arrangement allows its easy adjustment to variations of the cluster core. Ti_3O clusters, as the basic building blocks, may serve as primary examples; one can similarly reflect about other clusters.

1. *Cluster-monomer condensation:* Formation of $Ti_4O_2(OR)_{10}(O_2CR')_2$ can be regarded as addition of a $Ti(OR)_4$ to $Ti_3O(OR)_8(O_2CR')_2$ (the two downwards pointing terminal OR groups in Figure 1 become the μ_2-OR in the Ti_4 cluster, Figure 2) followed by an internal condensation, which transforms two OR into a μ_2-O. Other examples, such as the relationship between $Ti_8O_8(O_2CR')_{16}$ and $Ti_9O_8(OR)_4(O_2CR')_{16}$ (Figure 11), were previously mentioned; this includes condensation with $Ti_2(OR)_8$, which is just the dimeric form of $Ti(OR)_4$.

2. *Cluster-cluster condensation:* Hydrolytic condensation of two $Ti_3O(OR)_8(O_2CR')_2$ clusters gives $Ti_6O_4(OR)_{12}(O_2CR')_4$. Two pairs of terminal OR groups (at the "open" edge of the Ti_3 triangle) are thus converted to two bridging oxygens connecting the two Ti_3O units, either two μ_2-O in type 1 $Ti_6O_4(OR)_{12}(O_2CR')_4$ (Figure 7) or $Ti_6O_4(OR)_{10}(O_2CR')_2(O_3PR'')_2$ (Figure 18), or two μ_3-O in type 2 $Ti_6O_4(OR)_{12}(O_2CR')_4$ (Figure 8). Many more examples of such cluster-cluster condensations were already mentioned, especially in Section 2.4 on higher-nuclearity clusters.

3. *Internal condensation:* When two terminal OR groups within a cluster undergo a condensation reaction leading to a μ_2-O, balance of charges and coordination numbers is retained.

The clusters $Ti_3O_2X_3(O_2CR')_5$ are a (not too good) example, a better example is the derivation of $Ti_6O_5(OR)_6(O_2CR')_8$ from $Ti_6O_4(OR)_8(O_2CR')_8$. Formation of an intra-cluster μ_2-O requires a certain mutual positioning of the $[TiO_x]$ polyhedra and therefore cluster-monomer or cluster-cluster condensations may be more favorable.

4. *Ligand substitution:* The cluster $Ti_3O(OR)_7(O_2CR')_3$ is formally derived from $Ti_3O(OR)_8(O_2CR')_2$ by substitution of an alkoxo by a carboxylato ligand. As previously noticed for the clusters $Ti_6O_4(OR)_{16-x}(O_2CR')_x$ with $x = 2$, 4, 6 and 8 (Section 2.3), such substitutions may lead to a reorganization of the cluster core.

Although individual structural relationships between two cluster types can be rationalized by such deliberations, it is quite obvious that especially the structure build-up of larger clusters must be a complicated interplay of many steps, including unknown rearrangement reactions, some of them probably being reversible. An interesting aspect, however, is that the same basic processes are postulated for the growth of sol-gel materials.

Conflict of Interest

The author declares no conflict of interest.

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