

Structural Chemistry of Titanium (IV) Oxo Clusters, Part 2: Clusters Without Carboxylate or Phosphonate Ligands

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Homometallic titanium oxo clusters (TOC) are one of the most important groups of metal oxo clusters. In a previous article, TOC structures with carboxylato and phosphonato ligands were reviewed and categorized. This work is now extended to clusters with other ligands. Comparison of the different cluster

types shows how the interplay between condensation of the titanium polyhedra by means of bridging oxygen atoms and the coordination characteristics of the ligands influences the cluster structures and allows working out basic construction principles of the cluster core.

1. Introduction

Metal oxo clusters are molecular compounds with more than two metal atoms, where each metal atom is connected to at least two others by means of μ_2 -, μ_3 - or μ_4 -O. Titanium exhibits an especially rich structural chemistry of oxo compounds. Its preferred coordination number is six; however, 5- (and very rarely 4- or 7-) coordinated atoms are sometimes also observed. More than 500 polynuclear homometallic Ti(IV) compounds have been investigated by single crystal X-ray structure analyses. They are characterized by the O/Ti ratio (where only O/OH groups are counted, but not oxygen atoms of coordinated ligands); in the currently known examples this value is between 0.33 and ~1.5 (the maximum is 2 in TiO₂). The residual charge of the Ti_xO_y core ($y < 2x$) must be offset by anionic groups ("ligands") which thus stabilize the cluster and also complete the coordination sphere of the titanium atoms in an interplay with the varying coordination of the oxo groups (μ_2 , μ_3 or μ_4). According to the above definition, polynuclear compounds in which isolated titanium polyhedra and/or dimeric units with Ti–O–Ti or Ti₂O₂ linkages are only bridged by ligands but not by μ -O, are not considered titanium oxo clusters (TOC).

In a previous review article (part 1),^[1] we have analyzed the structures of homometallic carboxylato- and phosphonato/phosphinato-substituted TOC, published until early 2021 (excluding clusters with hydroxycarboxylato ligands which are covered in the current article). The large number of examples (> 300) allowed elucidation of common construction principles

as well as assumptions on how bigger clusters might be formed from smaller ones.

TOC with a great variety of other ligands were structurally characterized. Systematization of their structures is more difficult because the ligands differ strongly in their coordination characteristics and their influence on the cluster formation. In the current article, we nevertheless undergo the challenge of comparing the structures of Ti(IV) clusters with other ligands than RCO₂ and RPO₃/R₂PO₂. Clusters with combinations of carboxylato/phosphonato and other ligands were already treated in the previous review article,^[1] because their structures are mainly (but not exclusively) determined by the RCO₂ or RPO₃ ligands.

A special case is titanyl compounds, *i.e.*, compounds with a O/Ti ratio of 1 and only corner-sharing titanium polyhedra (*i.e.*, only μ_2 -O). Their structures have been analyzed in another review article and will not be repeated here.^[2] Also excluded are heterometallic clusters, *i.e.*, clusters in which two or more different metals are part of the metal oxide core. The presence of different metals results in a much greater variety of possible structures^[3] which are therefore difficult to categorize. We also restrict ourselves to structures determined by single crystal structure analyses. Since many ligands can easily change their position at the surface of the clusters in solution, or their coordination mode (*e.g.*, terminal/bridging),^[4] comparison of structures determined by spectroscopic methods with solid state structures is difficult. Even equilibria between different cluster species in solution cannot be excluded.

This article is organized according to increasing nuclearity of the clusters. If a particular compound consists of two or more Ti/O subunits which are only interconnected by bi- or multi-dentate ligands or groups but not by additional μ -O, then this compound is treated in the Section dealing with the clusters of lower nuclearity. For example, two parallel Ti₃O units are linked only via two triazolyl groups in dimeric [Ti₃O-(OⁱPr)₇(pyrazolyl)₂(triazolyl)]₂.^[5] This cluster is therefore discussed in Section 2.1, dealing with Ti₃O clusters. Metal-organic framework structures (MOF) with TOC as connectors are not covered in this article, because they are no molecular compounds.

Hydrogen atoms often cannot be directly located in metal oxo clusters by X-ray diffraction and therefore their allocation

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to a certain oxygen atom is not always obvious. On the other hand, charge neutrality sometimes requires that some group must be protonated (e.g., OH instead of O, or ROH instead of OR). In such cases, the formulas reported in the cited articles were used or adjusted according to chemically reasonable criteria. It must be emphasized, however, that without clear crystallographic or spectroscopic evidence alternative positions of the protons are conceivable. For example, two OR groups in the cluster “Ti₈O₁₀(OR)₁₄” (OR = O*i*Pr and OC₆H₂Br₃) must be protonated (protonation of oxygen atoms is less likely). The composition is thus Ti₈O₁₀(OR)₁₂(ROH)₂ (see Section 6), but it is not proven whether O*i*Pr or OC₆H₂Br₃ groups are protonated.^[6]

2. Ti₃O_x Clusters

2.1. Ti₃O Clusters

In clusters with a Ti₃O core, three octahedra are connected via a common μ₃-O. The three arrangements shown in Figure 1 differ by the number of shared edges, *viz.* three, two or one shared edges from left to right, where the second corner of a shared edge is a single-atom bridge, such as OR, Cl or similar. Compounds in which the three Ti polyhedra are only connected through a common corner (the μ₃-O) are unknown.

In the most symmetrical structure (C_{3v} symmetry, Figure 1 left), the polyhedra share three edges. The Ti atoms form an equilateral triangle and the Ti₃O unit is pyramidal. Crystalline TiO₂ modifications do not contain C_{3v}-type Ti₃O units, because such building blocks do not allow for the formation of 3-dimensional networks. The other two Ti₃O types have a lower symmetry with an approximately planar Ti₃O unit. They can be broken down in a pair of edge-sharing polyhedra to which a third polyhedron is differently connected. In the “roof form” (Figure 1, center), the three polyhedra share two edges, while in the “T-form” (Figure 1, right) the third polyhedron shares a corner with the other two (edge-sharing) octahedra.

Three structure types of clusters with a Ti₃O core have been observed: a C_{3v}-symmetric with an additional μ₃-X group (type 1), a C_{3v}-symmetric without an additional μ₃-X group (type 2) and clusters with a planar Ti₃O unit (type 3).

Type 1. In uncharged clusters of this type, one ligand (X) is μ₃ (in addition to the μ₃-O) and three ligands bridge the three

Ti...Ti edges. The lead structure is that of Ti₃OX(OR)₉ derivatives [X = Cl, R = *i*Pr,^[7] CH₂CMe₃ (Figure 2, left);^[8] X = F, R = *i*Pr,^[9] X = OH, R = *i*Pr^[10]], where an equilateral Ti₃ triangle is capped by both a pyramidal μ₃-O and μ₃-X, and each Ti...Ti edge is bridged by a μ₂-OR. Two terminal OR groups per Ti atom complete the octahedral coordination. Several derivatives of the general formula Ti₃O(OR)₁₀ with one μ₃-OR group (in place of Cl or F in the previous examples) are known, such as Ti₃O(OR)₉(OMe) (R = *i*Pr,^[11] CH₂CMe₃^[12]) with OMe in the μ₃ position, or Ti₃O(O*i*Pr)₁₀.^[11] In the cluster Ti₃O(O*i*Pr)₇[Me₂C(O)CH=C(O)CH₂C(O)Me₂]₃,^[13] the 2,6-oxygen atoms of the [2,6-dimethylhept-3-en-2,4,6-trionato]³⁻ ligand are in place of two terminal OR ligands, and the oxygen atom in the 4-position in place of the μ₃-OR. μ₃-Capped Ti₃O units are also part of Ti₁₂O₄(O*i*Pr)₂₈(C-propylpyrogallol[4]arene).^[14] One oxygen atom of each (deprotonated) trihydroxyaryl group of the pyrogallolarene ring caps a Ti₃O(O*i*Pr)₇ subunit and the other two oxygen atoms are in place of terminal OR groups (compared with Ti₃O(OR)₁₀). The four Ti₃O units are not connected with each other by additional μ-O.

Type 2. In a second cluster type with a C_{3v}-symmetric core, a second μ₃-group is not necessary due to a different set of ligands. In Ti₃O(C₆H₄O₂)₄[C₆H₄O(OH)]₂ (Figure 2, center)^[15] three catecholato ligands are chelating and three chelating-bridging, thus complementing the octahedral coordination of the titanium atoms (two catecholate ligands must be protonated for charge balancing). A related structure is that of [Ti₃O(O*i*Pr)₃(OC₇H₆Me₃NCH₂CH₂O)₃]⁺,^[16] where the N and one O atoms of the tridentate terpenoid C₁₂H₁₉NO₂³⁻ ligands chelate the titanium atoms, while each CH₂O oxygen bridges two Ti atoms. The octahedral coordination of each Ti is completed by a terminal O*i*Pr ligand. In [Ti₃OCP₃(OMe)₆]⁺ (Cp = η⁵-C₅H₅) each Ti atom is coordinated by a Cp and a terminal OMe ligand, while the other three OMe groups bridge the Ti...Ti edges. The Cp ligands are positioned at the same side of the Ti₃ triangle as the pyramidal μ₃-O.^[17] A purely inorganic example is [Ti₃O(S₂)₃Cl₆]²⁻^[18] where the three S₂²⁻ groups bridge the edges of the Ti₃ triangle and are perpendicular to the Ti₃ plane. The central part of [Ti₄O(O₃SiR)₃Cl₇(THF)]²⁻ [R = N(SiMe₃)C₆H₃Pr₂]^[19] is a Ti₃(μ₃-O)Cl₆ unit, with three terminal and three bridging Cl atoms. Each edge of the Ti₃ triangle is additionally bridged by an RSiO₃³⁻ group, the third oxygen of which is coordinated to a



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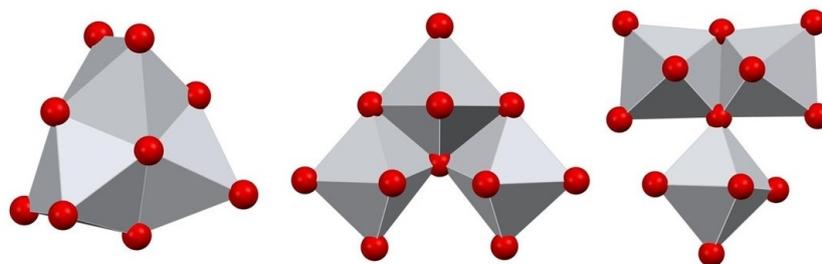


Figure 1. Three arrangements of octahedra in Ti_3O units, drawn for $[\text{TiO}_6]$ octahedra (red: O). See text for explanation.

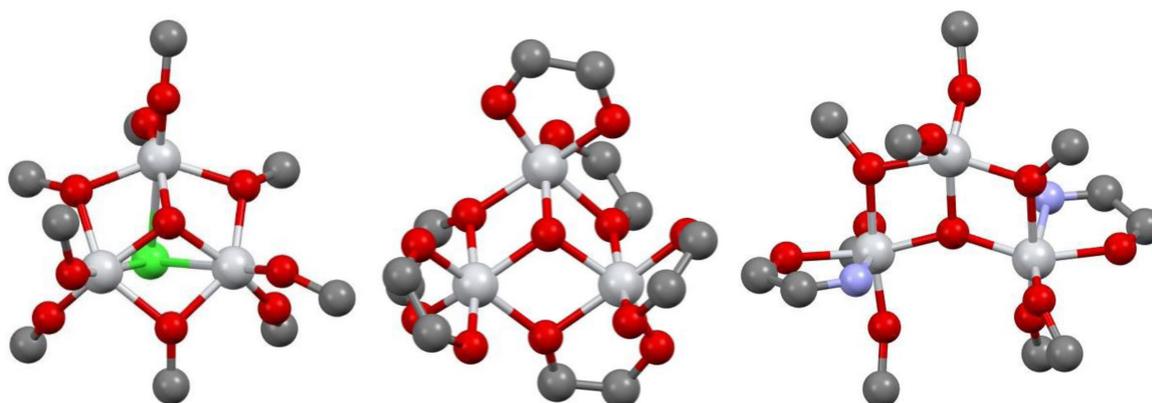


Figure 2. Structural examples for the three cluster types with a Ti_3O core: $\text{Ti}_3\text{OCl}(\text{OCMe}_3)_9$ (type 1; green: Cl), $\text{Ti}_3\text{O}(\text{C}_6\text{H}_4\text{O}_2)_4[\text{C}_6\text{H}_4\text{O}(\text{OH})]_2$ (type 2) and $\text{Ti}_3\text{O}(\text{OiPr})_8[\text{C}_5\text{NH}_4\text{-C}(\text{O})=\text{NR}]_2$ (type 3; blue: N). All organic groups were reduced to a minimum for clarity.

$\text{TiCl}(\text{THF})$ moiety. The latter thus ties the three RSiO_3^{3-} groups and is not directly connected to the Ti_3O unit.

Type 3. Roof-type Ti_3O clusters (Figure 1, center) are characterized by a triangle of three titanium atoms, with one longer and two shorter $\text{Ti}\cdots\text{Ti}$ edges. The previously described Ti_3O clusters with combinations of alkoxo and carboxylato ligands belong to this type.^[1] The two shorter edges in the cluster $\text{Ti}_3\text{O}(\text{OiPr})_8[\text{C}_5\text{NH}_4\text{-C}(\text{O})=\text{NR}]_2$ ($\text{R}=\text{C}_6\text{H}_4\text{NO}_2$)^[20] (Figure 2, right) are bridged by OR groups and the Ti atoms at the longer edge are chelated by the picolinamide ligands. Coordination of the titanium atoms in $\text{Ti}_3\text{O}(\text{OiPr})_8[3,3'\text{-bis}(\text{methoxymethyl})\text{binol}]_2$ (binol = dianion of 1,1'-bi-2-naphthol) is very similar, with the O^- and OMe group of the methoxymethylnaphtholato units chelating the titanium atoms.^[21] $\text{Ti}_3\text{O}(\text{NMe}_2)_8[\text{C}_2\text{B}_9\text{H}_9(\text{CH}_2\text{NMe}_2)_2]_2$ has basically the same structure as the picolinamide derivative, with the NMe_2 groups in place of the OiPr and the amino-methyl-substituted carborane in place of the picolinamide ligands.^[22] In $\text{Ti}_3\text{OCl}_8[\text{PhC}(\text{O})\text{C}(\text{O})\text{OMe}]_2$, the anions of mandelic acid methyl ester are coordinated in a way that the ester $\text{C}=\text{O}$ groups are bonded to the inner Ti atom and the O^- group bridges the shorter $\text{Ti}\cdots\text{Ti}$ edges of the Ti_3 triangle.^[23] All chlorine atoms are terminal.

Although T-shaped Ti_3O building blocks can be identified in higher-nuclearity clusters, T-shaped Ti_3O clusters are not known. However, two parallel T-shaped Ti_3O units are linked via two triazolyl groups in dimeric $[\text{Ti}_3\text{O}(\text{OiPr})_7(\text{pyrazolyl})_2(\text{triazolyl})]_2$.^[5] Each nitrogen atom of both triazolyl groups is coordinated to

one Ti atom. The two long edges of each Ti_3O unit are bridged by the pyrazolyl ligands.

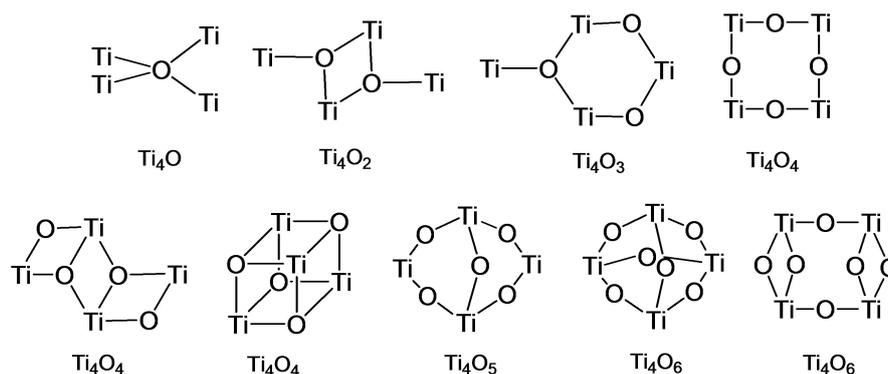
2.2. Ti_3 Oxo Compounds Without $\mu_3\text{-O}$ Linkages

In Ti_3O_2 strings and trimeric cyclic titanyl compounds (Ti_3O_3) all Ti coordination polyhedra are only connected by means of $\mu_2\text{-O}$ (only $\text{Ti}-\text{O}-\text{Ti}$ linkages, but no $\mu_3\text{-O}$ or $\mu_4\text{-O}$). Such compounds are not treated here, because they were subject to another recent review article.^[2] However, Ti_3O_3 subunits play a role as building blocks in bigger cluster structures, as will be outlined later.

Two clusters were structurally characterized which also contain only $\mu_2\text{-O}$ linkages, but where the O/Ti ratio is higher than 1. In the compound $\text{Ti}_3\text{O}_4\text{Cp}^*(\text{NCTolPh})$ ($\text{Cp}^*=\eta^5\text{-C}_5\text{Me}_5$, Tol = o-tolyl),^[24] one edge of the Ti_3 triangle is bridged by two $\mu_2\text{-O}$ (i.e., two Ti polyhedra share an edge) and the other two by only one. Finally, in $\text{Ti}_3\text{O}_3(\text{OH})_3(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)$ each edge is bridged by two $\mu_2\text{-O}/\text{OH}$.^[25]

3. Ti_4O_x Clusters

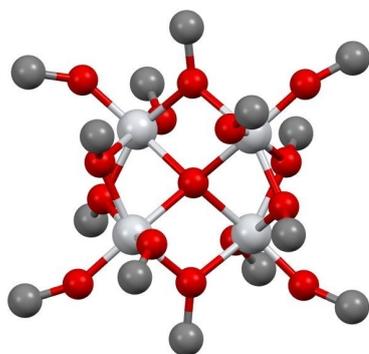
Several types of tetranuclear TOC are known, with O/Ti ratios ranging from 0.25 to 1.5 (Scheme 1). It is interesting to note that in the previously reviewed carboxylato- and phosphonato-substituted clusters^[1] this ratio is never > 1 .

Scheme 1. Schematic core structures of Ti_4O_x clusters.

3.1. Ti_4O Clusters

In Ti_4O clusters, the four titanium atoms typically form a flattened tetrahedron around a central μ_4 -O. A pivotal structure is that of $Ti_4O(OCH_2R)_{14}$ (R = furyl,^[26] thienyl^[27]) (Figure 3). Opposing edges of the Ti_4 tetrahedron are pairwise non-bridged, bridged by one or bridged by two OR groups, and the Ti atoms are correspondingly substituted by either two or three terminal OR ligands. Other bridging ligands can take the place of the four OR groups at the two doubly bridged edges (left and right side in Figure 3), such as N_3^- in $Ti_4O(OiPr)_{10}(N_3)_{4,4}$,^[28] catecholato ligands in $Ti_4O(OiPr)_6(di-t-butylcatecholate)_4$ ^[29] or salicylaloximato ligands in $Ti_4O(OMe)_6(OC_6H_4-CH=NO)_4$.^[30] Since the catecholato and salicylato ligands are di-anionic, each of them additionally replaces a terminal OR (*i.e.*, the ligands are chelating-bridging).

A different positioning of the OR ligands is observed when the co-ligands occupy more than two coordination sites. Each tridentate silanolato ligand in $Ti_4O(OEt)_9(O_3SiR)[O_2Si(OEt)R]$ (R = 9-trimethylsilyl-9-fluorenyl) caps one Ti_3 triangle (the Si–OEt oxygen is also coordinated).^[31] This requires five bridging and four terminal OEt to fill the remaining 14 coordination sites of the octahedrally coordinated Ti atoms. The hexadentate [*t*-butylcalix[6]arene]⁶⁻ anion in $Ti_4O(OMe)_8(calixarene)(MeOH)$ is coordinated to two titanium atoms, with three calixarene oxygen atoms bonded to each Ti atom, while the other five

Figure 3. The structures of $Ti_4O(OCH_2R)_{14}$ (without the groups R).

edges of the (distorted) Ti_4 tetrahedron are bridged by OMe groups.^[32]

The cluster $Ti_6O(OiPr)_{10}(catecholate)_6$ belongs to the same structure type, since the core is a distorted Ti_4O moiety. Two $Ti(OiPr)_3$ groups are connected to this Ti_4O unit only through two chelating-bridging catecholate ligands each, without additional μ -O.^[33]

Special cases are $Ti_4O(S_2)_4Cl_6$ ^[18b] and $Ti_4OCp_4(Se_2)_2Se_3$.^[34] All edges of the Ti_4 tetrahedron in the S derivative are bridged, *viz.* four by the S_2^{2-} groups and two opposite edges by Cl^- . In contrast, each Se_2^{2-} in the Se derivative caps a Ti_3 triangle, and the three Se^{2-} bridge two edges.

3.2. Ti_4O_2 Clusters

Clusters with a rhombic or rhomboidal $Ti_4(\mu_3-O)_2$ core are relatively common. The conformation of the Ti_4O_2 unit can be “double cube-type”, with pyramidal μ_3 -O, or “ladder-type”, where the μ_3 -O are approximately coplanar with the four Ti atoms. Examples of both are shown in Figure 4. Ti_4O_2 units appear to be resilient, since they are even retained if part or all titanium atoms are only 5-coordinate. Furthermore, they can accommodate a variety of bridging ligands with varying distances between the coordinated atoms, including the previously discussed carboxylates.^[1]

“Double cube-type” Ti_4O_2 clusters are not very abundant, but play a role as subunits in higher-nuclearity clusters. The parent structure is that of $Ti_4(OMe)_{16}$ (= tetrameric $Ti(OMe)_4$)^[35] with two μ_3 -OMe. If the two μ_3 -OMe⁻ groups are replaced by two μ_3 -O²⁻, two other OR⁻ ligands must be removed for charge balancing. The double-cube structure, with octahedral $[TiO_6]$ building blocks, can only be retained with ligands not only balancing the charges but also filling the emptied coordination sites. This is the case for $Ti_4O_2(OiPr)_8[PhC(O)CHC(O)CHC(O)Ph]_2$ (Figure 4, left).^[36] The outer oxygen atoms of each triketonato ligand take the place of two terminal OR, and the inner oxygen bridges two titanium atoms. $Ti_4O_2(OEt)_2(OR')_2[Me_2C(O)CH-C(O)CH_2C(O)Me_2]_2L_2$ ($L = Me_2C(O)CH_2-C(O)CH=C(OH)Me_2$; $R'OH$ = triclosane [5-chloro-2-(2,4-dichlorophenoxy) phenolate]) has the same structure, with the

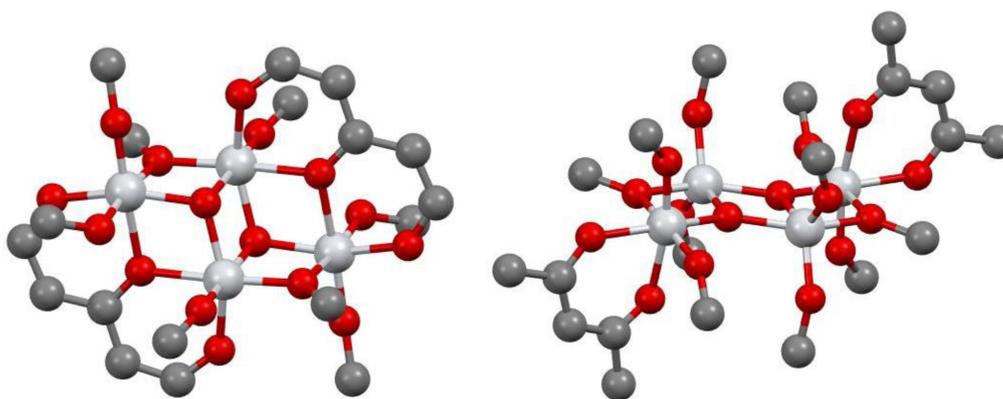


Figure 4. The structures of double cube-type $\text{Ti}_4\text{O}_2(\text{OiPr})_8(1,3\text{-dibenzoylacetate})_2$ (left) and ladder-type $\text{Ti}_4\text{O}_2(\text{OiPr})_{10}(\text{acac})_2$ (right) (the methyl groups of the OiPr ligands and the phenyl groups are not drawn).

oxygen atoms of the chelating ligands L and terminal OR' groups in place of six OiPr groups.^[37] Other examples for double cube-type Ti_4O_2 clusters are $\text{Ti}_4\text{O}_2(\text{OiPr})_6(\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O})_2[\text{O}_2\text{P}(\text{OiPr})_2]_2$ ^[38] and $\text{Ti}_4\text{O}_2[2,6\text{-bis}(\text{hydroxymethyl})\text{-p-cresolate}]_6$ ^[39] (the protonation state and coordination of the hydroxymethylcresolato ligands is rather complex).

Many more examples are known for ladder-type Ti_4O_2 structures, presumably because the ligands can bridge Ti–Ti distances of different lengths which allows a wider variation of the (bridging) ligands. In the subsequent discussion, the two Ti atoms connected to both $\mu_3\text{-O}$ are denoted as “inner” and the other two as “outer” Ti atoms. Although oxo-alkoxo derivatives $\text{Ti}_4\text{O}_2(\text{OR})_{12}$ are unknown (or have not been structurally characterized), compounds with oxygen donor atoms of bi- or multidentate ligands instead of OR^- groups have been investigated. A first example is $\text{Ti}_4\text{O}_2(\text{OiPr})_8(\text{octahydro-binol})_2$ ^[40] with only five-coordinate Ti atoms. The binol ligands bridge the long and two OiPr ligands the short edges of the Ti_4 rhomboid. $\text{Ti}_4\text{O}_2\text{Cl}_8(\text{O}-\text{SiMeR}-\text{SiMeR}-\text{O})_2$ [$\text{R}=\text{Si}(\text{SiMe}_3)_3$] has the same structure, with Cl in place of OiPr and the bis-silanolato in place of the binol ligands.^[41] In $\text{Ti}_4\text{O}_2(\text{OR})_4(\text{binol})_4$ ($\text{R}=\text{iPr}$,^[42] CHiPr_2 ^[43]), the two additional binol ligands are chelating-bridging and are thus in place of two pairs of bridging and terminal OR ligands of the octahydro-binol derivative.

In other examples, only the “inner” Ti atoms are five-coordinate, and the “outer” six-coordinate, due to different coordination characteristics of the ligands. A representative example is $\text{Ti}_4\text{O}_2(\text{OiPr})_{10}(\text{acac})_2$ (acac = acetylacetonate) (Figure 4, right), where the chelating acac ligand provides an additional donor atom to the outer Ti atoms.^[44] A related case is $\text{Ti}_4\text{O}_2(\text{OiPr})_6\text{Cl}_2[(\text{OC}_6\text{H}_4)_2\text{PPh}]_2$.^[45] The short edges of the Ti_4 unit are bridged by the bis(o-phenolato)phenylphosphine oxygen atoms, and the octahedral coordination of the outer Ti atoms is completed by the P atoms.

Six-coordination of all Ti atoms is possible with additional uncharged donor atoms, as the pyrazol ligands in $\text{Ti}_4\text{O}_2(\text{OiPr})_4(\text{catecholate})_4(\text{pyrazol})_4$,^[5] where two catecholato ligands are chelating-bridging the short edges and the other two chelate the inner Ti atoms. Two pyrazol ligands comple-

ment the octahedral coordination of the outer Ti atoms. The structure of $\text{Ti}_4\text{O}_2(\text{OiPr})_2[(\text{OCH}_2\text{CH}_2)_3\text{N}]_2[(\text{OCH}_2\text{CH}_2)_2\text{NMe}]_2$ ^[46] is very similar, with coordinated nitrogen atoms (instead of the pyrazol ligands in the previous example). The aminotriolato ligands are in place of (OR + catechol) at the outer Ti atoms, and the aminodiolato ligands replace the catecholato ligands at the inner Ti atoms. Another example is $\text{Ti}_4\text{O}_2[(\text{O}-\text{CHPh}-\text{CH}_2)_3\text{N}]_4$ with two aminotriolato ligands coordinated to the outer Ti atoms by means of both the oxygen and nitrogen atoms, and the other two chelating-bridging the short edges of the Ti_4 unit.^[47]

Clusters of the composition $\text{Ti}_6\text{O}_2(\text{OiPr})_4\text{X}_4(\text{O}_3\text{SiR})_4$ ($\text{X}=\text{OiPr}$, acac; $\text{R}=\text{9-trimethylsilyl-9-fluorenyl}$) belong to the same structure type, since the basic unit is a ladder-type $\text{Ti}_4\text{O}_2(\text{OiPr})_4\text{X}_2$ moiety to which four RSiO_3^{3-} groups are attached via one or two oxygen atoms. The RSiO_3^{3-} oxygen atoms not being coordinated to the Ti_4 unit are stapled together by two TiX groups.^[48]

An exceptional compound, from a structural point of view, is $\text{Ti}_4\text{O}_2[\text{O}_2(\text{OH})\text{SiR}]_6(\text{THF})_2$ ($\text{R}=\text{N}(\text{SiMe}_3)_2\text{C}_6\text{H}_3\text{Pr}_2$).^[19] The Ti_4O_2 core is approximately planar, as in the previous examples, but the edges are of equal length. Four silanetriolato bridge the edges of the Ti_4 rhombus (the Si–OH groups are not coordinated), and two cap each Ti_3 subunit. The THF molecules are bonded to the outer Ti atoms. This renders the inner Ti atoms six-coordinate and the outer five-coordinate.

Quite a few calixarene-substituted Ti_4O_2 derivatives were structurally characterized and therefore merit separate treatment. The cavity size of (deprotonated) calix[8]arene is big enough to bind in the names of the calixarenes a Ti_4O_2 unit by means of all of its oxygen atoms, but not big enough to retain the flat geometry of a ladder-type Ti_4O_2 unit. Contrary to the previous examples, the Ti_4O_2 core in $\text{Ti}_4\text{O}_2\text{X}_4(\text{t-butylcalix[8]arene})\text{L}_2$ ($\text{X}=\text{OiPr}$, $\text{L}=\text{ROH}$, MeCN, DMF and others,^[32,49] $\text{X}=\text{Cl}$, Br, I, $\text{L}=\text{NCMe}$ ^[50]) is therefore slightly dome-shaped. The groups X are bonded to the five-coordinate inner Ti atoms at the upper side of the dome. The neutral ligands L are coordinated to the outer Ti atoms which thus become six-coordinate.

When deprotonated calix[4]arenes are used as ligands, the cluster composition is $Ti_4O_2X_4(calix[4]arene)_2$, optionally also with two neutral ligands L. Two different coordination modes of the calixarene ligands were observed, viz. coordination to the two outer and one inner Ti atom vs. coordination to the two inner and one outer Ti atom of the Ti_4O_2 unit (Figure 5).

The first was observed in $Ti_4O_2Cl_4(t\text{-butylcalix[4]arene})_2$,^[51] resulting in a ladder-type structure with two five- and two six-coordinate Ti atoms and the Cl atoms bonded to the *outer* Ti atoms (Figure 5, left). $[Ti_4O_2(calix[4]arene)(O\text{i}Pr)_3(PO_4)_4]_4$ contains only one calixarene ligand coordinated in this manner.^[52] The Ti_4O_2 units in this TOC are interlinked by the PO_4^{3-} anions and thus form a ring of four Ti_4O_2 units, with two oxygen atoms of each PO_4^{3-} bridging an edge of a Ti_4O_2 unit. Both the long and short edge opposite the calixarene ligand is thus bridged by a PO_4^{3-} anion. Two *OiPr* groups are bonded to each outer Ti atom, and one to each inner Ti atom (which is thus bonded to two phosphate oxygens, two $\mu_3\text{-O}$ and an *OiPr* group).

The second possibility is a symmetric double cube-type structure and all Ti atoms octahedrally coordinated (Figure 5, right), as found in the clusters $Ti_4O_2X_4(calix[4]arene)_2L_2$ ($Ti_4O_2Cl_2[O(CH_2)_4Cl]_2(t\text{-butylcalix[4]arene})_2(NCMe)_2$)^[50,53] and $Ti_4O_2(O\text{i}Pr)_4(calix[4]arene)_2(OCH\text{-}NR_2)_2$ [$R = Et$,^[32] Me ^[52]]. The groups X are coordinated to the *inner* Ti atoms, and the ligands L are *trans* to the $\mu_3\text{-O}$ at the outer Ti atoms.

While four mono-anionic groups X are necessary to balance the charge of the Ti_4O_2 core in the calix[8]arene or calix[4]arene derivatives, two fully deprotonated calix[6]arene ligands are sufficient. Each calixarene ligand in $Ti_4O_2(t\text{-butylcalix[6]arene})_2$ ^[54] bridges a long + short edge of the planar Ti_4O_2 unit. Three oxygen atoms are coordinated to one outer Ti atom and two only to the inner Ti atom; the 6th oxygen atom is chelating-bridging the short edge (as in Figure 5, left, with two additional calixarene oxygen atoms in place of the two groups X). The deprotonated dioxacalix [6] arene ligand in $Ti_4O_2(t\text{-butyl-tetrahomodioxacalix[6]arene})_2(H_2O)$ is similarly bonded, the two

calixarene oxo groups render the outer Ti atoms octahedrally coordinated.^[55]

3.3. Ti_4O_3 Cluster

The only Ti_4O_3 cluster is $[Ti_4O_3(OEt)_6(OCH_2CH_2NH_2)_4]_2$,^[56] where the two Ti_4O_3 units (see Scheme 1) are dimerized by means of two $\mu_2\text{-OEt}$. Their structure can be described as a Ti_3O_3 ring to which an additional Ti atom is condensed (Scheme 1). Each Ti atom is chelated by an aminoethanolato ligand. However, Ti_4O_3 subunits are frequent building blocks in high-nuclearity clusters (see Section 6).

3.4. Ti_4O_4 Clusters

The core of Ti_4O_4 clusters can have different structures (Scheme 1), depending on the proportion of $\mu_2\text{-O}$ and $\mu_3\text{-O}$ (which in turn depends on the stabilizing ligands). Cyclic Ti_4O_4 compounds with only $\mu_2\text{-O}$ (titanyl compounds) were already subject to another recent review article.^[2]

If two oxygen atoms are μ_2 and two μ_3 , the cluster core structure is related to that of the double cube-type Ti_4O_2 clusters, with two $Ti\cdots Ti$ edges additionally bridged by $\mu_2\text{-O}$ (Scheme 1). Octahedral coordination of all titanium atoms is attained, if the ligands stabilizing the $Ti_4O_4^{8+}$ unit occupy the 14 remaining coordination sites. In $Ti_4O_4(O\text{i}Pr)_4(OCHPh\text{-}CHMe\text{-}NHMe)_4$ this is achieved by two aminoethanolato ligands chelating the outer Ti atoms and two chelating-bridging the two edges of the Ti_4 unit not bridged by $\mu_2\text{-O}$.^[56] $Ti_4O_4(OCH_2CH_2NMe_2)_8$ ^[57] is isostructural, with four η^1 -coordinated aminoethanolato ligands taking the place of the *OiPr* ligands in the first example.

The cluster core of a greater number of Ti_4O_4 structures can be described as a Ti_4 tetrahedron with $\mu_3\text{-O}$ capped faces (= cube of alternating O and Ti atoms) or as four edge-sharing

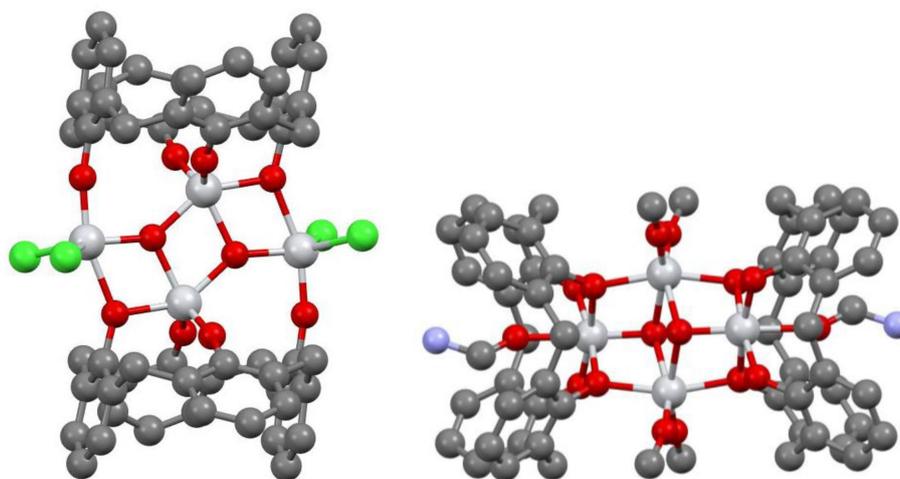


Figure 5. Structures of $Ti_4O_2Cl_4(t\text{-butylcalix[4]arene})_2$ (left; green: Cl) and $Ti_4O_2(O\text{i}Pr)_4(calix[4]arene)_2(DMF)_2$ (right, blue: N) (the *tBu* and *Me* groups were not drawn for clarity).

[Ti₆O₆] octahedra. If six bidentate ligands occupy the 12 remaining coordination sites by bridging the edges of the Ti₄ tetrahedron, the resulting structure has the highest symmetry among the Ti₄ clusters, as found for several binol derivatives Ti₄(OH)₄(binol)₆^[58] (Figure 6) and Ti₄(OH)₄[(C₆H₁₁)₆Si₆O₁₀]₃ with chiral T symmetry (the μ₃ groups must be OH instead of O for charge balancing). In the latter cluster, each [R₆Si₆O₁₀]²⁻ ligand is tetradentate and thus replaces two binol ligands.^[59] The previously discussed clusters Ti₄O₄(OR)₄(O₂CR')₄ and Ti₄O₄(OR)₄(O₂PR')₄ also belong to this structure type.^[1] Since the carboxylato or phosphonato ligands bridge only four edges of the Ti₄ tetrahedron; the symmetry of the cluster is thus lowered. Each titanium atom is surrounded by three μ₃-O, one terminal OR and two oxygen atoms of the bridging O₂CR' or O₂PR'₂ ligands. Ti₄O₄(O*i*Pr)₄(F₈-binol)₄ is isostructural.^[58b]

3.5. Ti₄O₅ Clusters

Only few Ti₄O₅ clusters are known which all have the composition Ti₄O₅Cp*₃X₂ (X = F,^[60] Cl,^[60,61] OH,^[62] Me^[63]). Their structures are related to that of the cyclic Ti₄O₄ derivatives, with an additional μ₂-O bridge across the ring, as schematically shown in Scheme 1. This buckles the Ti₄ ring into a butterfly shape. Two diagonal Ti atoms are thus bonded to three μ₂-O and a Cp* ligand, and the other two Ti atoms to two μ₂-O and an X ligand.

3.6. Ti₄O₆ Clusters

The most obvious structure of Ti₄O₆ cores is that each edge of a Ti₄ tetrahedron is bridged by a μ₂-O, *i.e.*, an adamantane-like structure. This is in series with the cyclic Ti₄O₄ structures and Ti₄O₅ derivatives, where the number of μ₂-O bridged edges is gradually increased from four to six, hand in hand with an increased folding of the Ti₄ unit (Ti₄O₄ flat, Ti₄O₅ butterfly, Ti₄O₆ tetrahedral). Such Ti₄O₆ structures were found for the cyclopentadienyl derivatives Ti₄O₆(η⁵-C₅R₅)₆ (C₅R₅ = C₅H₅(SiMe₃)₂,^[64] Cp*^[61,65] C₅Me₄Ph,^[66] C₅Me₄SiMe₂NHNMe₂^[67]) as well as [Ti₄O₆(OSMe₂)₁₂]⁴⁺^[68] and [Ti₄O₆(triazacyclononane)₄]⁴⁺.^[69]

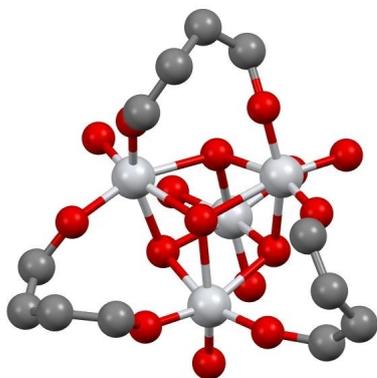


Figure 6. Schematic structure of Ti₄(OH)₄(binol)₆ clusters. Only three binol ligands in front of the structure are hinted for clarity.

However, another distribution of the μ₂-O was also observed (Scheme 1). This structure type can be derived from the cyclic Ti₄O₄ derivatives by doubly bridging two opposite edges of the Ti₄ unit. In this case the Ti₄ unit remains planar. Not surprisingly, this structure type is found for derivatives substituted by two polyoxometallate (POM) “ligands”, namely [Ti₄O₂(OH)₄(EW₁₀O₃₄)₂]⁸⁻ (E = Si,^[70] Ge^[71]). The clusters consist of two [Ti₂(OH)₂(EW₁₀O₃₄)₂]²⁻ units which are interconnected by two μ₂-O. Each POM ligand is bonded to a Ti₂(OH)₂ unit via six oxygen atoms. This does not allow formation of an adamantane-like structure of the Ti₄O₆ core. The methylated derivative [Ti₄O₂(OH)₂(OMe)₂(SiW₁₀O₃₄)₂]⁸⁻ has the same structure.^[70]

4. Ti₅O_x Clusters

Only very few Ti₅O_x clusters have been isolated, and therefore no overarching structural motifs can be extracted. Two Ti₅O₂ clusters are based on two Ti₃(μ₃-O) units sharing one Ti atom which is thus bonded to two μ₃-O. In Ti₅O₂(OR)₆(binol)₄ (R = O*i*Pr, OBU),^[72] the binaphtholate ligands are chelating-bridging and connect the two Ti₃ units symmetrically. Ti₅O₂(OH)(OMe)₃(salicylaldoximate)₆ contains an additionally μ₂-OH bridge between the two Ti₃ units.^[30] The OMe and chelating-bridging aldoximate ligands are unsymmetrically distributed. Despite the overall composition Ti₇O₂(OEt)₁₈(salicylhydroxamate)₂, this cluster has the same Ti₅O₂ core. Two additional Ti atoms are attached to the Ti₅O₂ unit by means of two μ₂-OEt and one chelating-bridging hydroxamate ligand each.^[30]

The two Ti₅O₃ units of [Ti₅O₃(OBU)₆(pyrocatecholate)₄(BuOH)]₂ are only interconnected through chelating-bridging catecholato ligands.^[73] Each Ti₅O₃ unit is formed from a trigonal pyramidal Ti₄O group with a fifth Ti atom connected to its base by means of two μ₂-O.

The structure of Ti₅O₂(OEt)₁₃(OR)[PhC(O)CHC(O)CHC(O)Ph] [OR = 5-chloro-2-(2,4-dichlorophenoxy) phenolate]^[37b] can formally be attained by attachment of a Ti(OEt)₄ unit to one μ₃-O of a double cube-type Ti₄O₂ structure (see Figure 4, left) which is thus converted into a μ₄-O. The triketonato ligand bridges one edge of the opposite Ti₃O subunit.

Ti₅O₆Cp*₂[PhC(O)CHC(O)Ph]₆ is based on a Ti₅ trigonal-bipyramid. μ₂-O bridge the six edges connecting the apical and equatorial Ti atoms.^[74] The Cp* ligands are coordinated to the apical, and two chelating diketonate ligands to the equatorial Ti atoms.

The very unsymmetric structure of Ti₅O₃(O*i*Pr)₈(binol)₃ can be described as an assembly of two roof-shaped, edge-sharing Ti₃O units to which an additional [TiO₅] polyhedron is attached via an μ₂-O and two chelating-bridging binaphtholate ligands.^[42]

5. Ti₆O_x Clusters

Hexanuclear Ti₆O_x clusters, especially those with x = 4, dominate the structural chemistry of carboxylato- or phosphonato-

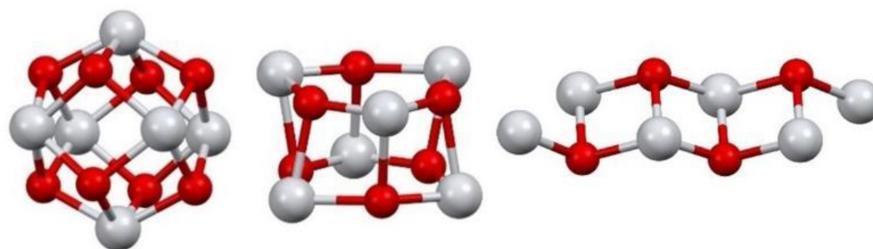


Figure 7. The Ti_6O_8 , Ti_6O_6 and Ti_6O_6 cluster cores (only the Ti and μ -O atoms are drawn).

substituted titanium oxo clusters. In contrast, Ti_6O_x clusters with other ligands are much less abundant.

5.1. Ti_6 Clusters with only μ_3 -O

If the arrangement of the six titanium atoms is octahedral, eight oxygen atoms can cap the triangular faces (Figure 7, left). This is the most important type of zirconium oxo clusters,^[75] but there is only one example in titanium chemistry, *viz.* the cationic clusters $[\text{Ti}_6\text{O}_8(\text{C}_5\text{H}_4\text{R})_6]^{2+}$ ($\text{R} = \text{Me}$,^[76] $\text{CH}_2\text{CH}_2\text{OMe}$ ^[77]). Each titanium atom is connected to a $\text{C}_5\text{H}_4\text{R}$ ligand and three μ_3 -O.

The symmetry of the Ti_6 unit is lowered to that of a trigonal antiprism (D_{3d} , Figure 7, center) if only six faces are capped by a μ_3 -O, as found in several carboxylate derivatives $\text{Ti}_6\text{O}_6(\text{OR})_6(\text{OOCR})_6$ ^[1] and two oximate derivatives $\text{Ti}_6\text{O}_6(\text{OR})_6(\text{ON}=\text{CR}'_2)_6$ ($\text{R} = i\text{Pr}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Bu}$; $\text{R}'_2 = \text{C}_5\text{H}_8$).^[78] The Ti_6O_6 core has the shape of a hexagonal prism of alternating Ti and O atoms; the six oximate (or carboxylate) ligands bridge the Ti atoms of the Ti_2O_2 squares in the prism.

A third structural possibility for Ti_6 clusters with only μ_3 -O was found for $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_4(\text{binol})_6(i\text{PrOH})_2$.^[73] This is an extension of the double cube-type Ti_4O_4 cluster core (Scheme 1) by adding an additional Ti polyhedron to each μ_2 -O which is thus converted to μ_3 -O (Figure 7, right). Two binol ligands are bridging, and the other four chelating-bridging.

5.2. Ti_6 Clusters with Both μ_2 - and μ_3 -O

In clusters with the composition $\text{Ti}_6\text{O}_4(\text{OR})_{12}(\text{OOCR})_4$ or $\text{Ti}_6\text{O}_4(\text{OR})_8(\text{OOCR})_8$,^[1] two Ti_3O units are interconnected by two μ_2 -O. This is also the case for $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_4(\text{naphthalene-2,3-diolate})_6(i\text{PrOH})_4$ (Figure 8),^[79] $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{10}(\text{O}_3\text{SiR})_2(\text{NH}_2\text{Ph})_2$ ($\text{R} = 9\text{-methylfluorenyl}$)^[31] and $\text{Ti}_6\text{O}_2(\text{OH})_2(\text{O}i\text{Pr})_{10}(\text{SO}_4)_4$.^[80] The Ti_3O units in the naphthalene diolate derivative are pyramidal and the edges of each Ti_3 triangle bridged by either an *O*/*Pr* or a chelating-bridging diolate ligand. The two halves of the cluster are only linked by the two μ_2 -O. In the other two derivatives, the two roof-shaped Ti_3O units are additionally bridged by two silicate or sulfate ligands, resulting in an approximately cubic Ti_6E_2 ($\text{E} = \text{Si}$, S) arrangement. The other two SO_4^{2-} groups in the sulfate derivative cap the Ti_3O units.

In the cluster $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{12}(\text{salicylhydroxamate})_4$, a puckered Ti_6O_4 unit is decorated with two additional Ti polyhedra which

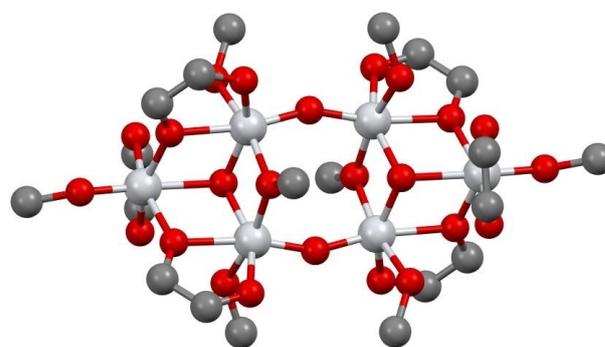


Figure 8. The structure of $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_4(\text{naphthalene-2,3-diolate})_6(i\text{PrOH})_4$ (only the O–C–C–O units of the diolate ligands and the *ipso* carbon atoms of the *O*/*Pr* groups are drawn).

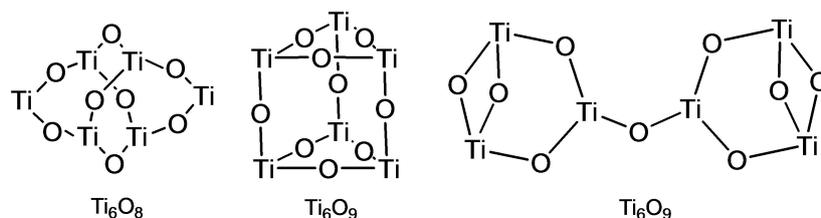
are connected to the Ti_6O_4 unit only by means of salicylhydroxamate and bridging OR ligands.^[81]

In the foregoing examples, the two $\text{Ti}_3(\mu_3\text{-O})$ units are connected by two μ_2 -O, *i.e.*, only two Ti atoms per Ti_3 unit are bonded to both the μ_3 -O and an μ_2 -O. Introduction of a third μ_2 -O between the two Ti_3O units results in a structure with a trigonal-prismatic arrangement of the six Ti atoms, with two (eclipsed) Ti_3O faces and three (parallel) Ti–O–Ti edges. This arrangement is found in $[\text{Ti}_6\text{O}_5(\text{OMe})_6\text{L}_2(\text{HL})_4]^{6-}$ ($\text{H}_3\text{L} = \text{piperidine-2,6-dione dioxime}$),^[82] where the chelating-bridging L/HL ligands are approximately coplanar with the Ti_3O unit and the OMe ligands *trans* to the μ_2 -O.

5.3. Ti_6 Clusters with only μ_2 -O

The few examples of cyclic Ti_6O_6 titanil compounds (with only μ_2 -O bridges and $\text{O}/\text{Ti} = 1$) have been treated elsewhere.^[2] Hexanuclear clusters with more than six μ_2 -O bridges have Ti_6O_8 and Ti_6O_9 cores, as schematically shown in Scheme 2.

The Ti_6O_8 units can be described as strongly puckered Ti_6O_6 rings, of which the four inner Ti atoms are bridged by two additional μ_2 -O across the ring (Scheme 2), similar to the Ti_4O_6 unit. The inner Ti atoms are thus bonded to three μ_2 -O, and the two outer Ti atoms to only two μ_2 -O. This cluster type is represented by $[\text{Ti}_6\text{O}_8(\text{H}_2\text{O})_{20}]^{8+}$, where the $\text{Ti}_6\text{O}_8^{8+}$ unit is stabilized exclusively by coordinated water molecules.^[83] Compared with the octahedral $\text{Ti}_6(\mu_3\text{-O})_8$ clusters described in Section 5.1, more ligand atoms are necessary to reach an octahedral coordination of the Ti atoms because eight μ_2 -O



Scheme 2. Schematic core structures of Ti_6O_8 and Ti_6O_9 clusters with only μ_2 -O.

occupy less coordination sites than eight μ_3 -O. A metal-organic derivative of the same structure type as $[Ti_6O_8(H_2O)_{20}]^{8+}$ is $Ti_6O_8L_2(phen)_6(H_2O)_4$ ($L = 5$ -sulfosalicylate, phen = phenanthroline).^[84] Each Ti atom is coordinated by a phenanthroline ligand, the inner Ti atoms additionally by an aqua and the outer Ti atoms by a chelating ligand L. Each Ti atom is thus 6-coordinate.

Two structure types of Ti_6O_9 clusters are known (Scheme 2): In the most symmetrical one (D_{3h}), the six titanium atoms form a trigonal prism, with all nine edges bridged by an oxygen atom. A representative example is $Ti_6O_9L_6$ [$L = 2$ -(benzoxazol-2-yl)-4,6-bis(*t*-butyl) phenolate].^[85] Each Ti atom is coordinated to a chelating ligand L. A few clusters in which both Ti_3O_3 subunits are capped by POM "ligands"^[86] as well as the cyclopentadienyl derivative $Ti_6O_9(C_5H_4SiMe_3)_6$ ^[87] have the same core structure. Note the difference to the aforementioned Ti_6O_5 clusters, where the six Ti atoms also form a trigonal prism. However, the triangular faces there are Ti_3O rather than Ti_3O_3 units. The structure of another cyclopentadienyl derivative, *viz.* $Ti_6O_9Cp^*_6$ ^[88] consists of two Ti_3O_4 rings which are connected via a μ_2 -O. Each Ti atom is bonded to three μ_2 -O and a Cp^* ligand.

6. TOC with Nuclearities ≥ 7

Clusters with nuclearities of seven and above can (somewhat arbitrarily) be classified in clusters in which identical smaller units are condensed with each other, cage-like clusters, and clusters with highly condensed cores.

6.1. Clusters Built from Smaller Subunits

The term "smaller subunits" refers to cluster types discussed in the previous Sections, mainly tri- and tetranuclear clusters. Such clusters are connected with each other by dimerization or are linked by additional μ -O. The latter formally corresponds to a condensation process. This is just an intellectual perception and does not necessarily reflect the formation process of the clusters. Figure 9 shows two examples; several others were discussed in the previous review article on carboxylato- and phosphonato-substituted clusters.^[1] In some compounds, the subunits are connected *via* O–Ti–O groups.

- In $Ti_7O_{10}Cl_2Cp^*_6$, two Ti_3O_3 rings are connected through a tetrahedral $Ti(\mu_2-O)_4$ unit. Two Ti atoms of each ring are bonded to the central $[TiO_4]$, and the third to a Cl atom.^[89]

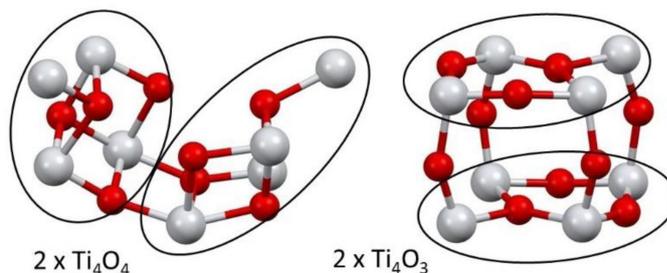


Figure 9. The cluster cores of $Ti_6O_8(OH)_2(OPr)_2(calix[8]arene)_2(acetone)_2$ and $Ti_8O_{10}(O^iPr)_4(OC_6H_2Br_3)_8(iPrOH)_2$ (see text).

- Two polyoxotungstate-substituted Ti_9O_{12} clusters can be dissected in three Ti_3O_3 rings^[2] which are connected via three μ_2 -O (*i. e.*, a ring of rings).^[90] The Ti_9O_{12} unit thus contains only μ_2 -O. In a similar manner, four POM-substituted Ti_3O_3 rings are interlinked by μ_2 -O in several derivatives resulting in a tetrahedral $(Ti_3O_3)_4$ arrangement.^[91] In a further extension of this structure, the four Ti_3O_3 rings are linked by O–Ti–O groups (instead of μ_2 -O).^[92]
- In $Ti_{12}O_{18}(OEt)_{20}(salicylhydroxamate)_4$,^[30] two Ti_3O_3 rings are linked by a μ_2 -O. Two additional Ti atoms are condensed to two oxygen atom of each ring (resulting in Ti_5O_3 subunits), and two other Ti atoms are only connected through the hydroxamate ligands. Condensation of two such Ti_5O_3 subunits with a Ti_4O_4 ring gives the Ti/O backbone of $Ti_{14}O_{12}(O^iPr)_{18}L_6(HL)_2$ ($H_2L = 4$ -chlorosalicylic acid).^[93] Both structures contain additional μ_2 -O.
- In $Ti_8O_5(OPr)_6(3,5$ -di-*t*-butylcatecholate)₈(PrOH)₂, two distorted tetrahedral Ti_4O units (see Section 3.1) face each other and are connected by three parallel μ_2 -O (resulting in a doubly capped trigonal prismatic Ti_8 arrangement with two μ_4 -O and three μ_2 -O).^[94] A seemingly minor modification of the ligand sphere, *i. e.* an additional catecholate ligand in place of two OR, and *O*^{*i*}Pr instead of *O*^{*n*}Pr, results in a complete restructuring of the Ti_8O_5 core. The Ti polyhedra in $Ti_8O_5(O^iPr)_4(catechol)_9(iPrOH)_2$ are connected through two μ_4 -O, two μ_3 -O and one μ_2 -O, and no straightforward subunits can be identified.^[95]
- The central structural motif in $Ti_9O_6(O^iPr)_8[(OCH_2CH_2)_3N]_2[(OCH_2CH_2)_2NH]_5$ ^[96] and $Ti_{11}O_9(O^iPr)_{11}L_7(HL)$ ($H_2L = 4$ -chlorosalicylic acid)^[93] are two ladder-type Ti_4O_2 units (see Section 3.2). In the triethanolamine derivative both subunits are connected to a central (7-coordinate) Ti atom by means of μ_2 -O. In the salicylate derivative, the Ti_4O_2 subunits are approximately parallel, and

three Ti atoms of each Ti_4O_2 unit are pairwise linked to the other subunit by a μ_2 -O and a salicylate ligand. Additionally, a linear Ti_3O_2 string is connected parallel to a long side of this Ti_8O_7 arrangement.

- Two (double cube-type) Ti_4O_4 units (see Section 3.4 and Figure 9, left) are dimerized to give $Ti_8O_8(OH)_2(OPr)_2(t\text{-butylcalix[8]arene})_2(\text{acetone})_2$.^[97] One μ_2 -O of each Ti_4O_4 subunit is coordinated to a Ti atom of the neighboring unit and is thus converted into a μ_3 -O. Each calixarene ligand caps a Ti_4O_4 unit. The OH groups are terminal.
- In $Ti_{16}O_8(OH)_8L_{20}$ (H_2L = catechol or 3-methylcatechol), two trigonal-prismatic Ti_6O_5 units (see Section 5.2) and two Ti_2O_3 strings are condensed, with chelating and chelating-bridging catecholato ligands.^[95]

6.2. Cage-Like Clusters

The structures of TOC with (nearly) spherical, ellipsoidal, or regular polyhedral nets, in which the Ti atoms are connected by μ_2 -O and/or μ_3 -O, can also be broken up in smaller subunits, predominantly Ti_3O units. The cavity of such structures can be empty or occupied by an additional Ti polyhedron or another atom (if this is another metal atom, the structures are disregarded, because heterometallic clusters are not covered by this article).

A cluster with an *octahedral* Ti_6O_6 core was already introduced in Section 5.1. A *cubic* arrangement of the Ti atoms (eight corner-sharing $[TiO_6]$ octahedra) is found in $[Ti_8O_{12}(OH_2)_{24}]^{8+}$,^[83a,98] i.e., each Ti...Ti edge of a Ti_8 cube is bridged by a μ_2 -O. Three water molecules are coordinated to each Ti atom. $Ti_8O_{12}Cp_8$ is a neutral cluster of this type, with the Cp ligands in place of the water molecules.^[99] The Ti atoms in $Ti_8O_{10}(O\text{Pr})_4(OC_6H_2Br_3)_8(i\text{PrOH})_2$ (Figure 9, right) also form a cube. However, only two oxygen atoms are μ_2 and the other μ_3 . This is equivalent to two interconnected parallel Ti_4O_3 units (see Section 3.3) rotated through 180° (in this cluster two groups must be protonated, possibly two terminal OPr groups).^[6] The same structure of the Ti_8O_9 core was found in $Ti_8O_{10}(\text{citrate})_4(H_2O)_{12}$,^[100] with the tridentate $C_6H_5O_7^{3-}$ anions coordinated to the Ti_3O groups and coplanar with the Ti_4O_3 unit.

The basic structural element of $Ti_{13}O_{14}(t\text{-butylcalix[4]arene})_6$ is a Ti_{12} cuboctahedron in which the eight triangular faces are capped by a μ_3 -O and the six square faces by a (planar) μ_4 -O.^[101] The square faces are additionally capped by the deprotonated calix[4]arene ligands. A 13th Ti atom is squeezed in between one square face and a calix[4]arene ligand and interacts with the four Ti–O–calixarene groups and the corresponding μ_4 -O (which is thus converted into a rare μ_5 -O).

The 5- or 6-coordinated Ti atoms of the cationic cluster $[Ti_{12}O_{14}(O\text{Pr})_{18}]^{2+}$ (Figure 10, left) have a slightly distorted icosahedral arrangement.^[102] Only 14 (out of 20) triangular faces of the icosahedron are capped by a μ_3 -O. The cluster can also be described as a closed network of Ti_3O subunits. In the mono-cationic derivative $[Ti_{12}O_{15}(O\text{Pr})_{17}]^{+}$ ^[102f,103] and uncharged $Ti_{12}O_{16}(OR)_{16}$ ($R = i\text{Pr}$,^[104] $Et/i\text{Pr}$,^[104a] $Et/t\text{Bu}$,^[102g] CH_2tBu ^[105]) the

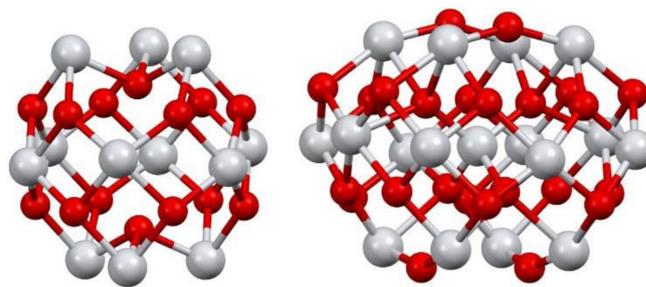


Figure 10. The $Ti_{12}O_{14}$ and $Ti_{17}O_{24}$ cores (only the Ti and μ -O atoms are drawn).

additional oxygen atom(s) are μ_2 and bridge Ti atoms of the Ti_3 layers. This basic structural motif appears to be rather resilient, since it is also retained in the clusters $Ti_{11}O_{13}(OR)_{18}$ ($R = i\text{Pr}$,^[13b,118d] $Et/i\text{Pr}$,^[104a]), where one Ti atom of the central Ti_6 ring is missing (with concomitant adjustment of the O/OR ligand sphere).

When comparing the *ellipsoidal* cluster of $Ti_{17}O_{24}(O\text{Pr})_{20}$ ^[106] with that of the $Ti_{12}O_{14}$ structure (Figure 10), a certain structural relationship can be noticed. The three layers are laterally expanded. The middle layer of the Ti_{17} cluster consists of a ring of eight $[TiO_6]$ octahedra; an additional $[TiO_4]$ tetrahedron in the center of the Ti_8 ring is connected to the surrounding Ti atoms by four μ_4 -O. Sixteen μ_3 -O connect the Ti atoms of the upper and lower Ti_4 layer with the middle layer. The core structure is retained in the pyridine derivative $Ti_{17}O_{24}(O\text{Pr})_{20}(\text{py})$ ^[102g] and upon substitution of some OPr groups by bidentate ligands (rendering all or part of the 5-coordinate Ti atoms 6-coordinate), such as $Ti_{17}O_{24}(O\text{Pr})_{16}(\text{MeC}(\text{O})\text{-CR-C}(\text{O})\text{Me})_4$ ($R = \text{H}$ [acac], $C_6H_4NH_2$, $C_6H_4NO_2$),^[106b,107] $Ti_{17}O_{24}(O\text{Pr})_{18}X_2$ ($X = \text{anion of coumarine 343}$),^[106b] $[Ti_{17}O_{24}(O\text{Pr})_{17}(\text{SO}_4)_3]^{3-}$ ^[108] or several catecholato derivatives $Ti_{17}O_{24}(O\text{Pr})_{20-x}(\text{catecholato})_x$ ($x = 1, 2, 4$).^[109] A carboxylato-substituted cluster of this type is also known, viz. $Ti_{17}O_{24}(O\text{Pr})_{16}(\text{O}_2\text{C-C}_5\text{H}_4\text{N})_4$.^[110] The four additional catecholato ligands in $Ti_{17}O_{24}(O\text{Pr})_{12}(3,5\text{-di-}t\text{-butylcatecholato})_8$ are in place of terminal OPr groups.^[109b] In $Ti_{34}O_{50}(O\text{Pr})_{36}$, two $Ti_{18}O_{27}$ units are condensed with each other in a way that two neighboring polyhedra of the central layer have a common edge with the second $Ti_{18}O_{27}$ unit.^[102g] $Ti_{18}O_{27}(\text{OH})(\text{OtBu})_{17}$ is an extension of the $Ti_{17}O_{24}$ type, with an additional 5-coordinate Ti atom capping one Ti_4 layer (with concomitant rearrangement of the involved oxygen atoms).^[111]

$[Ti_{21}O_{29}(O\text{Pr})_{12}(\text{SO}_4)_8(\text{DMF})_6]^{2-}$ has a Zeppelin-shaped (hollow) core, with sulfate-capped Ti_3O_3 units at the tips. The other sulfate ions connect the 6- and 7-coordinate Ti atoms at the sidewalls.^[112]

The Ti/O skeleton of $Ti_{42}(\mu_3\text{-O})_{54}(\mu_3\text{-OH})_6(\text{OH})_{12}(O\text{Pr})_{42}$ has the shape of a *hollow sphere* (Figure 11, left).^[113] Unlike fullerenes, consisting of 5- and 6-membered rings, the shell structure can be broken down in Ti_4O_3 units (see Scheme 1), with 5-coordinate Ti atoms, which are connected by twelve $[TiO_5]$ pentagonal pyramids. Note that the above mentioned Ti_8O_{10} cluster (Figure 9, right) is the smallest possible cage formed from Ti_4O_3 units. An alternative description of the Ti_{42} cluster is

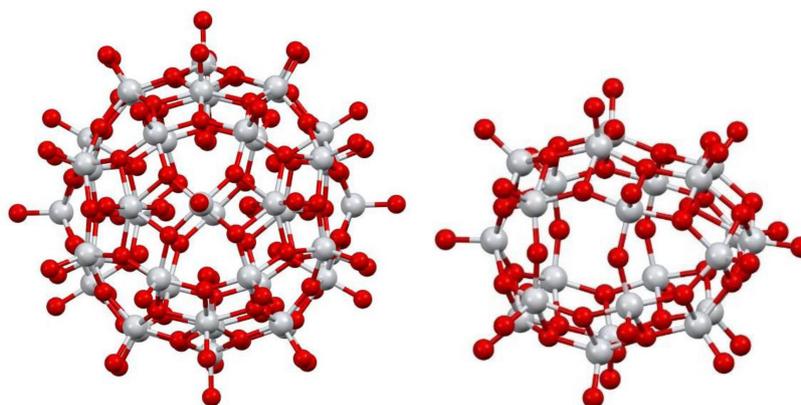


Figure 11. The structures of $\text{Ti}_{42}(\mu_3\text{-O}/\text{OH})_{60}(\text{OH})_{12}(\text{O}i\text{Pr})_{42}$ and $[\text{Ti}_{22}\text{O}_{32}(\text{O}i\text{Pr})_{22}(\text{iPrOH})]^{2+}$ (the *iPr* groups are omitted for clarity).

a net of Ti_2O_2 and Ti_3O_3 rings with only $\mu_3\text{-O}/\text{OH}$ in the shell. Each Ti atom is coordinated by a *OiPr* ligand covering the surface of the sphere. A terminal OH group, pointing into the interior of the hollow sphere, is bonded to each 7-coordinate Ti atom. The clusters $[\text{Ti}_{22}\text{O}_{32}(\text{O}i\text{Pr})_{22}(\text{iPrOH})]^{2+}$ and $[\text{Ti}_{22}\text{O}_{30}(\text{OH})_2(\text{O}i\text{Pr})_{20}(\text{di-}t\text{-butylcatechol})_2]^{2+}$ are less symmetrical, but have a very similar network structure, based on Ti_4O_3 units with 5-coordinate Ti atoms (Figure 11, right).^[102a] Instead of the 7-coordinate Ti atoms with terminal OH groups, the clusters contain a $\text{Ti}_3(\mu_3\text{-O})$ unit with octahedrally coordinated Ti atoms. The cavity is occupied by an I^- ion. Furthermore, four Ti_4O_4 rings can be identified in the cage network, in addition to the Ti_2O_2 and Ti_3O_3 rings. The Ti_{18} shell of $\text{Ti}_{19}\text{O}_{29}(\text{O}i\text{Pr})_{18}(\text{phen})_2$ is very similarly structured.^[108] A tetrahedral $[\text{TiO}_4]$ unit in the cavity is bonded to four octahedrally coordinated Ti atoms of the shell by means of $\mu_3\text{-O}$. The cage of $\text{Ti}_{11}\text{O}_{11}(\text{O}i\text{Pr})_{14}[(\text{OCH}_2\text{CH}_2)_2\text{NH}]_4$ ^[96] is even smaller and more distorted, but the shell network is built from the same subunits. In $\text{Ti}_{16}\text{O}_{14}(\text{OH})_2(\text{O}i\text{Pr})_{22}(\text{2,5-dihydroxybenzoate})_4$, two similarly structured $\text{Ti}_8\text{O}_7(\text{OH})$ hemispheres are interconnected by the four dihydroxybenzoate ligands.^[114]

6.3. Clusters with Highly Condensed Cores

Clusters in which (distorted) edge- and corner-sharing $[\text{TiO}_6]$ octahedra are only connected by $\mu_3\text{-O}$ in three dimensions as in rutile, anatase or brookite are unknown (apart from Ti_3O_6 clusters, the smallest subsection TiO_2). It is sometimes claimed that TOCs are molecular models of TiO_2 . This cannot be supported from a structural point of view. In high-nuclearity clusters, the Ti polyhedra are differently connected with each other, and $\mu_4\text{-O}$ are frequent.

- The structure of $\text{Ti}_8\text{O}_6(\text{OCH}_2\text{Ph})_{20}$ is best described as a Ti_4O_6 tetrahedron (see Section 3.6) with additional Ti atoms condensed to four $\mu_2\text{-O}$. These four oxygen atoms are thus converted to $\mu_3\text{-O}$, with the two remaining $\mu_2\text{-O}$ being opposite (Figure 12, left).^[118b]
- The core of $\text{Ti}_{10}\text{O}_{12}(\text{catecholate})_8\text{L}_8$ (L = picoline and several pyridine derivatives)^[115] and $\text{Ti}_{10}\text{O}_{12}(\text{O}i\text{Pr})_8\text{L}_8(\text{HL})_4$ (HL =

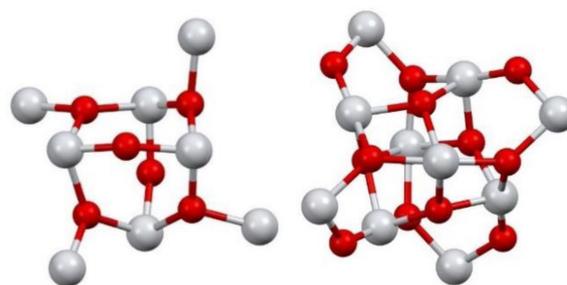


Figure 12. Structure of the Ti_8O_6 and $\text{Ti}_{10}\text{O}_{12}$ cores (only the Ti and $\mu\text{-O}$ atoms are drawn).

pyrazol)^[5] has S_4 symmetry (Figure 12, right), with eight $\mu_3\text{-O}$ and four $\mu_2\text{-O}$. All pyrazolyl anions are bridging, and the neutral pyrazol ligands terminal. Octahedral coordination of all Ti atoms in the catecholato cluster is reached in a way that four ligands are chelating-bridging.

- The central part of the $\text{Ti}_{18}\text{O}_{20}(\text{OEt})_{30}(\text{ONMe}_2)_2$ structure is a Ti_4O_6 tetrahedron to which two Ti_7O_7 units are condensed.^[30]
 - In the cluster $\text{Ti}_{18}\text{O}_{22}(\text{O}i\text{Pr})_{26}(\text{acac})_2$, two Ti_4O_6 units are condensed onto a Z-shaped, acac-substituted Ti_{10} unit of edge-sharing Ti polyhedra by means of $\mu_2\text{-O}$ and $\mu_3\text{-O}$.^[116]
- The condensed Ti polyhedra (or part of the polyhedra) in some higher-nuclearity clusters are arranged in layers.
- The Ti/O part of $[\text{Ti}_7\text{O}_6(\text{AsW}_9\text{O}_{33})_4]^{20-}$ is a single layer consisting of an octahedral $[\text{TiO}_6]$ unit surrounded by a ring of six square-pyramidal Ti atoms. Each heteropolymetallate anion is bonded to three Ti atoms of the ring.^[117]
 - A layer of edge-sharing $[\text{TiO}_6]$ polyhedra is the central unit of $[\text{Ti}_{19}\text{O}_{18}((\text{OCH}_2\text{CH}_2)_2\text{NH})_{18}]^{14+}$.^[96] The layer is formed by a ring of six $[\text{TiO}_6]$ octahedra centered by a 7th octahedron. Six Ti_2 units, each substituted by three aminoethanolato ligands, are condensed to two Ti atoms of the Ti_6 ring each, alternatingly above and below the ring plane.
 - In $\text{Ti}_{10}\text{O}_8(\text{OEt})_{24}$ ^[118b] (Figure 13, left), two layers of five edge-sharing $[\text{TiO}_6]$ octahedra are condensed in an offset manner, resulting in four $\mu_4\text{-O}$, two $\mu_3\text{-O}$ and two $\mu_2\text{-O}$. Ten OEt ligands are bridging to reach an octahedral coordination of all Ti atoms.

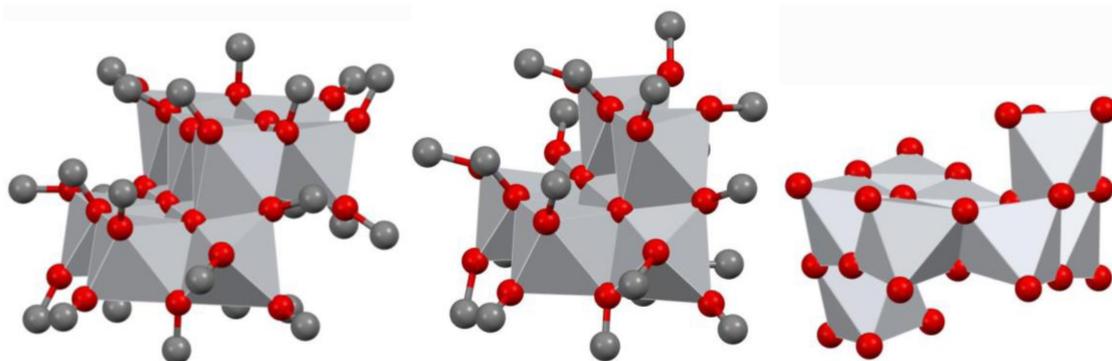


Figure 13. Structure of $\text{Ti}_{10}\text{O}_8(\text{OEt})_{24}$ (left) and $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ (the methyl groups are not drawn for clarity), and the Ti/O skeleton of a Ti_8 subunit in $\text{Ti}_{16}\text{O}_{16}(\text{OR})_{32}$ (right).

- The structure of $\text{Ti}_7\text{O}_4(\text{OR})_{20}$ is related, as it consists of the same layer of five edge-sharing $[\text{TiO}_6]$ octahedra to which, however, only two additional edge-sharing $[\text{TiO}_6]$ octahedra are condensed (Figure 13, center), with two μ_4 -O and two μ_3 -O and eight μ_2 -OR (see discussion in Section 7). The parent compound is $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$.^[118] In the derivatives $\text{Ti}_7\text{O}_4(\text{OEt})_{18}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})$ ^[119] and $\text{Ti}_7\text{O}_4(\text{OMe})_{12}(t\text{-butylcalix}[8]\text{arene})$,^[49b] part of the OR groups is substituted, viz. the two μ_2 -OR groups in the propanediolato derivative, and terminal OR groups in the calixarene derivative.

The core of $[\text{Ti}_{28}\text{O}_{48}(\text{OPh})_{14}(\text{phen})_{14}]^{2+}$ also contains two such Ti_5 layers which, however, are separated by two single $[\text{TiO}_6]$ octahedra.^[120] This Ti_{12} arrangement is decorated by 14 phenolato- and phenanthroline-substituted Ti polyhedra, resulting in four μ_4 -O, 20 μ_3 -O and 24 μ_2 -O atoms.

- The cluster cores of $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32-x}(\text{OR})_x$ ($\text{R} = \text{Et}$,^[118c,d,121] Pr [$x = 4, 8$],^[122] CH_2CCl_3 [$x = 6$]^[123]) are composed of two Ti_8 units rotated 90° relative to each other. Each Ti_8 unit (Figure 13, right) consists of a layer of six edge-sharing $[\text{TiO}_6]$ octahedra (an additional $[\text{TiO}_6]$ condensed to the Ti_5 layers in the previous examples), with two additional $[\text{TiO}_6]$ octahedra above and below this plane. $\text{Ti}_{15}\text{O}_{14}(\text{OEt})_{32}$ has the same structure as the $\text{Ti}_{16}\text{O}_{16}$ clusters, with one TiO_2 unit missing.^[102g] In $\text{Ti}_{28}\text{O}_{34}(\text{OEt})_{44}$ (Figure 14, right) two such Ti_8 units are connected by a group of twelve $[\text{TiO}_6]$ octahedra.^[124]

The latter are arranged in three interconnected layers of $5 + 2 + 5$ octahedra.

- $\text{Ti}_{18}\text{O}_{27}(\text{EO}_4)_9(\text{H}_2\text{O})_{24}$ ($\text{E} = \text{S}, \text{Se}$), $[\text{Ti}_{18}\text{O}_{27}(\text{SO}_4)_8(\text{H}_2\text{O})_{28}]^{2+}$ and $[\text{Ti}_{18}\text{O}_{27}(\text{SO}_4)_6(\text{H}_2\text{O})_{31}]^{6+}$ have a pentagonal-prismatic structure consisting of three layers. In the center of each layer is a pentagonal-bipyramidal $[\text{TiO}_7]$ unit sharing the equatorial edges with five surrounding $[\text{TiO}_6]$ octahedra. The layers are stacked above each other and mutually connected by μ_2 -O between two neighboring Ti polyhedra (Figure 14, left).^[125]

7. Discussion

This article is based on the cluster core structures rather than the kind of stabilizing ligands. This approach allows a better focus on common structural features.

The O/Ti ratio in all structurally characterized TOC is below ~ 1.5 . This means that anionic ligands other than O or OH are necessary to balance the charges. However, the ligands have a twofold role since they must also complete the coordination sphere of the Ti atoms. Since the preferred coordination number of titanium atoms (six, or, less often, five) is higher than their $+4$ charge, one solution is the coordination of uncharged co-ligands (such as alcohols or N-donor ligands) or groups (such as the nitrogen atom of di- or triethanolato ligands). A more

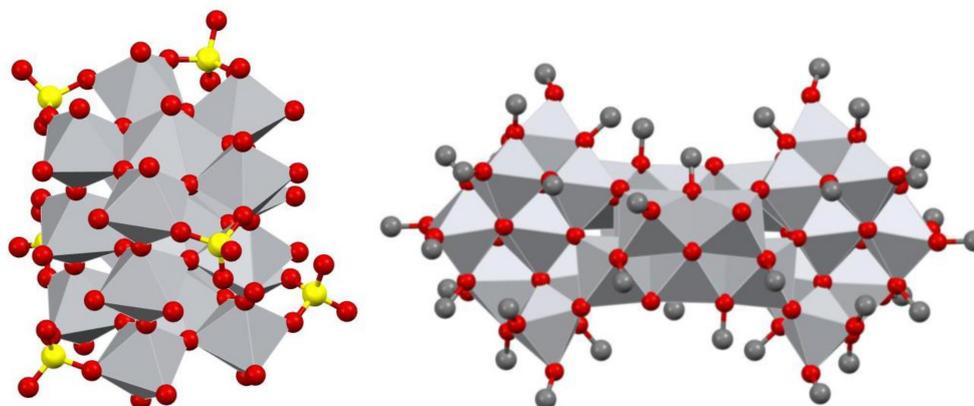


Figure 14. Polyhedral representation of $[\text{Ti}_{18}\text{O}_{27}(\text{SO}_4)_6(\text{H}_2\text{O})_{31}]^{6+}$ (yellow: S) and $\text{Ti}_{28}\text{O}_{34}(\text{OEt})_{44}$ (the methyl groups are omitted for clarity).

frequent possibility is that some ligands compensate more coordination sites than charges. An example may underline this point: The core of $\text{Ti}_7\text{O}_4(\text{OR})_{20}$ (Figure 9) consists of seven $[\text{TiO}_6]$ octahedra which are interconnected by two $\mu_4\text{-O}$ and two $\mu_3\text{-O}$. The twenty OR^- must thus fill the remaining 28 coordination sites, *i.e.* eight OR^- must be bridging (μ_2). Even if part of the Ti atoms were only 5-coordinate, some OR bridges would be required.

Most ligands in TOCs fulfil the requirement that the number of occupied coordination sites is greater than their charge. However, there are differences regarding the ligand geometries and rigidity. TOCs often contain alkoxo groups, because they are frequently prepared from $\text{Ti}(\text{OR})_4$, and OR/OR' exchange is straightforward. $\mu_2\text{-OR}$ groups result in TOCs with edge-sharing Ti polyhedra with Ti...Ti distances of $\sim 310\text{--}320$ pm, similar to that of the titania modifications rutile, anatase and brookite (295–305 pm). Many anionic bi- and multidentate ligands in TOCs are equivalents of simple OR groups in a way that the oxygen atoms of the multidentate ligand are in place of some terminal and/or bridging OR groups. Contrary to OR groups, however, the coordinated oxygen atoms are bound together. This may result in geometrical restrictions. Some ligands of this kind are relatively flexible, such as diols or calixarenes (replacing 2–8 OR groups), others are very rigid, such as catecholate, triketonate or POM derivatives.

A good example for geometrical restrictions imposed by the ligands is carboxylate-substituted TOC. The $\text{Ti}_2(\text{OOCR})$ five-membered rings formed with bridging RCOO^- ligands are approximately planar (*i.e.*, the Ti polyhedra cannot be strongly twisted relative to each other) and the Ti–O–C angles cannot be strongly widened. The range of Ti...Ti distances that can be spanned by carboxylate ligands is therefore restricted (typically 300–360 pm). In contrast, the Ti–O–P–O–Ti units of coordinated RPO_3^{2-} ligands can be strongly twisted and can thus connect Ti atoms up to ~ 650 pm.

Cyclopentadienyl (Cp) ligands block three adjacent coordination sites at the same metal atom and thus limit the possibilities how the Ti polyhedra can be connected with each other. This explains the somewhat special structural chemistry of CpTi compounds.

However, reducing the influence of the ligands just to geometric (steric) effects would be an over-simplification. Electronic and/or kinetic effects also play an important role, mainly due to the initial formation of modified precursors during the cluster syntheses. The composition of the precursors also depends on the ligand proportion in the mixture of starting compounds.^[126] The modified precursors have different reactivities or may form different intermediates. The mechanism how a particular cluster type is formed is largely unknown. However, a frequent observation is that seemingly minor variations of the precursors result in different cluster structures, such as the organic group in OR ligands or the Ti:ligand ratio in the precursor mixture. The catecholato-substituted Ti_8O_5 clusters (Section 6.1) are a good example.

Different to the arrangement of the Ti polyhedra in the TiO_2 modifications, the geometry of the Ti/O core in TOCs can be varied (in addition to distortion of the polyhedra) to compro-

mise between the preferred arrangement of the Ti polyhedra and the coordination requirements of the ligands, as observed for the clusters being subject of this article:

- Edge-sharing Ti polyhedra can be tilted relative to each other. Corner-sharing polyhedra have more degrees of freedom, as they can also be twisted. Both tilting and twisting are a mismatch to a regular arrangement of the polyhedra as in the TiO_2 modifications.
- Especially (but not exclusively) in high-nuclearity clusters, part of the Ti atoms is only 5-coordinate (almost always square-pyramidal). This reduces the total number of coordination sites to be occupied by the ligands. Furthermore, coordination sites bound to the center of the cluster core are sometimes inaccessible for ligands (see Figure 11 for illustrative examples).
- Connecting the Ti polyhedra with $\mu_4\text{-O}$ instead of $\mu_3\text{-O}$ (as in the TiO_2 modifications) is an alternative to achieve highly condensed structures especially for high-nuclearity clusters and also reduces the number of coordination sites to be occupied by the ligands.

Despite the many parameters influencing the TOC structures, some common structural features can be identified. Roof- or T-shaped, Ti_3O units are very frequent building blocks in carboxylato-substituted clusters with medium to high nuclearities. Ti_3O clusters or Ti_3O building blocks are found with other stabilizing ligands as well, but they do not prevail to the same extent as in carboxylato-substituted clusters. In contrast, other building blocks are much more pronounced, such as $\text{Ti}_4(\mu_4\text{-O})$ tetrahedra, Ti_3O_3 rings or Ti_4O_3 units. While carboxylate-substituted Ti_4O clusters are unknown, clusters of this type have been structurally characterized with several other ligands (including RPO_3 ligands^[11]) as outlined in Section 3.1. Only few ligand-stabilized Ti_3O_3 rings^[2] or Ti_3O_4 clusters are known, but such structures can be identified as building blocks in several TOC with higher nuclearities, as outlined before.

The influence of ligands on the cluster structure can also be assessed from the prevalence of certain cluster types. Hexanuclear compounds are the most abundant carboxylato-substituted TOC and have the greatest structural diversity. All are formed from two $\text{Ti}_3(\mu_3\text{-O})$ subunits which are interconnected in various ways by bridging oxygen atoms.^[11] Only a few of these structures are also found with other ligands, such as the prismatic Ti_6O_6 or $\mu_2\text{-O}$ bridged Ti_6O_4 clusters (Figures 7 and 8). On the other hand, several Ti_6O_x structure types without carboxylate counterparts are observed (albeit based on only few representatives). A possible reason for the abundance of carboxylato-substituted Ti_6O_x clusters may be that carboxylato-substituted Ti_3O are formed easily which then undergo dimerization or cluster-cluster condensation reactions (see Figure 9 for other cluster units). This appears to be less straightforward with other ligands or ligand combinations.

The situation is reversed for tetranuclear TOCs. Only some of the structure types shown in Scheme 1 have carboxylato-substituted equivalents (such as Ti_4O_2 or cubic Ti_4O_4 units), especially because $\mu_2\text{-O}$ and $\mu_4\text{-O}$ play a less important role there. Furthermore, the proportion of Ti_4 clusters is much higher. This might be an indication that different modified

precursors or intermediates are formed which influence the cluster growth, for example by blocking or deblocking coordination sites or having a *trans*-influence on condensation processes.

In summary, although the diversity of ligands, regarding geometrical as well as electronic properties (not to mention different reaction conditions in the cluster syntheses), is too big to allow correlations between the coordination characteristics of a particular ligand and the structure of the cluster core, some influence of the ligands on the TOC structures is evident. On the other hand, some structural motifs of the cluster core appear to be rather resistant to influences of the stabilizing ligands.

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Conflict of Interests

The authors declare no conflict of interest

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Structural chemistry · Titanium oxo compounds · Cluster geometries · Cage compounds · Multidentate ligands

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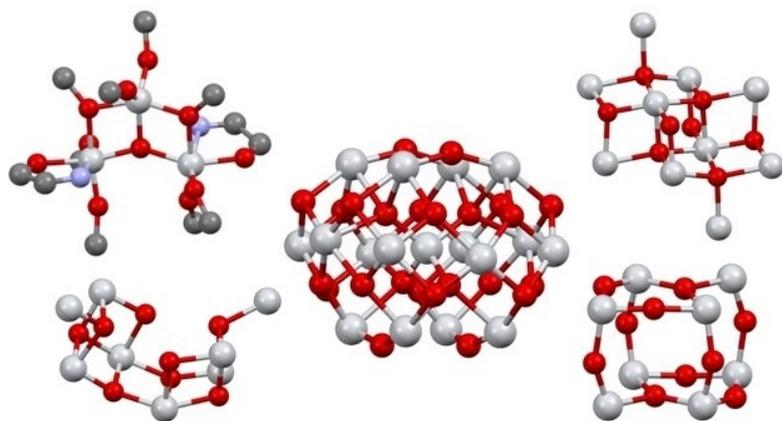
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REVIEW



This review completes a series of three articles which provide a comprehensive coverage of the structural chemistry of polynuclear titanium oxo compounds. The interplay of

structure-influencing coordination characteristics of the ligands and preferred arrangement of the Ti/O polyhedra in the cluster cores is worked out.

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Structural Chemistry of Titanium (IV) Oxo Clusters, Part 2: Clusters Without Carboxylate or Phosphonate Ligands