



En route from metal alkoxides to metal oxides: metal oxo/alkoxo clusters

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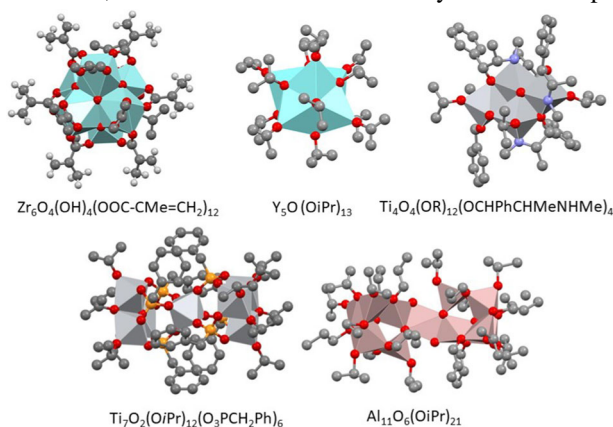
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Abstract

Molecular metal oxo or oxo/alkoxo clusters, $M_wO_x(OH/OR)_y(L/X)_z$ (L or X = organic ligands), can often be isolated upon (partial) hydrolysis of metal alkoxides. Investigation of such clusters leads to a better understanding of the basic processes of sol–gel chemistry. The ligands not only stabilize the cluster core but also influence to some extent the cluster structures. They can easily change their position on the cluster surface, thus adapting to changing cluster geometries, and can be exchanged under certain conditions. A close inspection of titanium oxo/alkoxo cluster structures, taken as an informative example, shows that Ti_3O units (with or without organic ligands) are the basic building blocks. Clusters with higher nuclearities appear to be predominantly formed by cluster–cluster or by cluster–monomer condensations. Ligand substitution or condensation reactions within a cluster unit are also possible.

Graphical Abstract

Instead of extended metal oxide networks, metal oxo/alkoxo clusters may be formed upon hydrolysis of metal alkoxides.



Keywords Ligand dynamics · Ligand exchange · Cluster structures · Cluster–cluster growth · Cluster–monomer growth

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Highlights

- Comparison of metal oxo cluster structures allows conclusions on the mechanisms by which the clusters might be formed or modified.
- Organic ligands protecting the cluster core are dynamic and can be exchanged.
- Organic ligands influence the cluster structure.
- Ti_3O units are the basic building blocks in titanium oxo clusters.

1 Introduction

Metal alkoxides, $M(OR)_n$, are common precursors in sol–gel chemistry, often modified by neutral (L) or anionic (X) organic ligands. They are converted into the corresponding oxides by means of hydrolysis and condensation reactions. Under certain conditions, however, molecular metal oxo or oxo/alkoxo clusters, $M_wO_x(OH/OR)_y(L/X)_z$, can be isolated instead.

This article is the written version of a talk in the eSeminar series of the International Sol–Gel–Society on November 3, 2021, and will mainly deal with the question what insight can be gained for sol–gel chemistry of metals in general when investigating such oxo/alkoxo clusters. This will be outlined for selected cases (mainly taken from own research), with no intention to cover the existing literature comprehensively.

The clusters are typically synthesized by adding a substoichiometric amount of water to an organically modified or unmodified metal alkoxide (or other hydrolysable metal compounds) and/or by very slow supply of water. There are basically two synthesis protocols: (i) Slow (intended or accidental) water addition to the precursor solution (such as exposure to ambient moisture, hydrated metal salts as precursors, etc.) and (ii) in situ generation of water by a water-producing organic reaction, mostly ester formation, but also aldol condensations and the like.

One of the central questions is whether the clusters are intermediates or side products in the hydrolysis and condensation reactions of metal alkoxides. Connected to that: how are the clusters assembled, how do they grow, and can different cluster types convert into each other? A second group of questions relates to the ligands. “Naked” oxo clusters are not stable, their surface must be protected by ligands. In the clusters discussed in this article, the most obvious type of ligands are residual OR groups. Most clusters also contain other surface groups, mostly anionic ligands, due to their preparation. The denotation “ligands” is justified, because the organic groups capping the cluster cores comply with the principles of coordination chemistry. Two important questions are: are the ligands firmly attached to one particular site at the cluster surface, and to what extent do the ligands influence the cluster structures?

Before coming back to these questions, a brief look at Si/O cage compounds, obtained by hydrolysis of silicon

alkoxides or chlorides, SiX_4 and $R'SiX_3$ ($X = OR$ or Cl), will mark some important differences between silicon and (transition or main group) metal chemistry.

2 Si/O cage compounds

The equivalent to metal oxo clusters are spherosilicates, $[Si_nO_{m+x}]^{x-}$ or $(R''_3SiO)_xSi_nO_m$, or polyhedral oligomeric silsesquioxanes (POSS, $R'_xSi_nO_m$) (Fig. 1). Already in the 1960s it was proposed that such cage compounds are formed during hydrolysis of $R'SiCl_3$, which then become part of the three-dimensional siloxane networks [1]. Various types of spherosilicates and POSS, with closed or open cages and a variety of functional or non-functional groups R' , have been synthesized since then and are used as valuable building blocks for materials syntheses.

There are two important differences between the silicon-based cage compounds and metal oxo clusters: (i) Silicon is always tetrahedrally coordinated, and interconnected Si tetrahedra only share corners ($\equiv Si-O-Si \equiv$) (Fig. 1, right) rather than edges or faces, and (ii) the groups R' or OR' at silicon cannot be exchanged and do not move from one Si to another because they are linked to the core of the Si/O cage through strong covalent bonds. This makes the chemistry of the silicon compounds less diverse than that of metal oxo clusters, although their genesis (partial hydrolysis of SiX_4 or $R'SiX_3$) is the same.

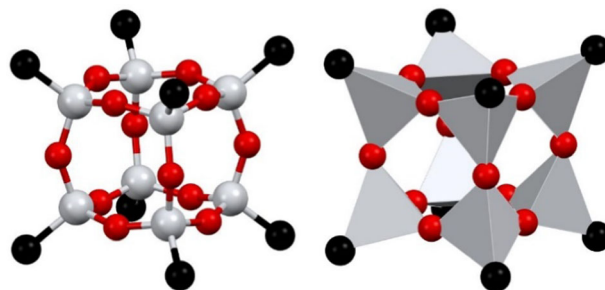


Fig. 1 $Si_8O_{12}(OH)_8$ as an example of spherosilicates ($\bullet = O^-$ or $OSiR''_3$) or POSS ($\bullet = R'$). Left: ball-and-stick representation; right: polyhedral representation. Red: bridging oxygen atoms

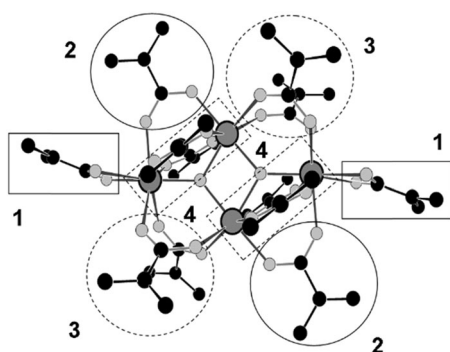
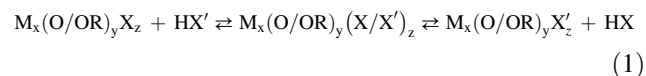


Fig. 2 The cluster $Zr_4O_2(\text{methacrylate})_{12}$ with four chemically inequivalent methacrylate ligands (marked with the numbers 1–4) (with permission from ref. [4])

3 The ligands

A variety of anionic organic ligands has been used for the modification or functionalization of metal alkoxides or the derived sol–gel materials, such as carboxylates, phosphonates, β -diketonates, oximates, aminoalcoholates, etc. [2]. Consequently, these groups are also found as capping ligands in metal oxo clusters. Anionic ligands (X^{n-}) are preferred over neutral ligands (L) because they are more tightly bonded. Neutral ligands, however, may complement the coordination environment of metal atoms on the cluster surface (adduct formation). Anionic organic ligands are mostly bi- or tridentate and can be chelating or bridging. They occupy more than one coordination site, i.e., more than one ligand atom is bonded to the metal(s), and are therefore more strongly bonded than monodentate ligands. In passing, OR groups can also bridge two metals, and thus occupy two coordination sites, as it is well known from many metal alkoxide oligomers. However, since only one atom (the oxygen atom of the OR group) links two metal atoms, the mutual orientation of their coordination polyhedra is different to a situation where the bridging unit consists of more than one atom. We will delve into this subject later on.

A central issue of coordination chemistry is that bonding of coordinatively bonded ligands is, in principle, reversible. This means that the ligands can be de-coordinated again, even if the coordination equilibrium may be far on the product side. One of the consequences of this reversibility is that cluster ligands can be exchanged quite easily (as generally in coordination compounds) (Eq. 1).



A second important aspect is that ligands of metal oxo clusters are dynamic [3]. They can change their position on the cluster surface as well as their coordination mode and

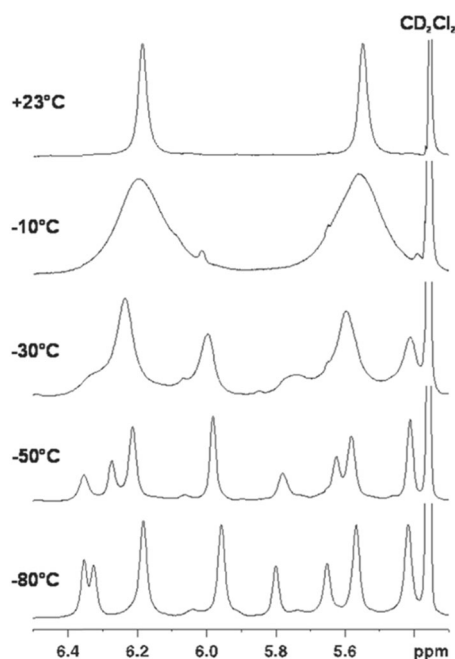


Fig. 3 Temperature-dependent ^1H NMR spectra of $Zr_4O_2(\text{methacrylate})_{12}$ in the CH_2 group region (with permission from ref. [4])

can therefore easily adjust themselves to a varied cluster core geometry. We will see later that this is important for understanding cluster structures. Finally, the ligands influence the kind of formed cluster due to their electronic and steric properties.

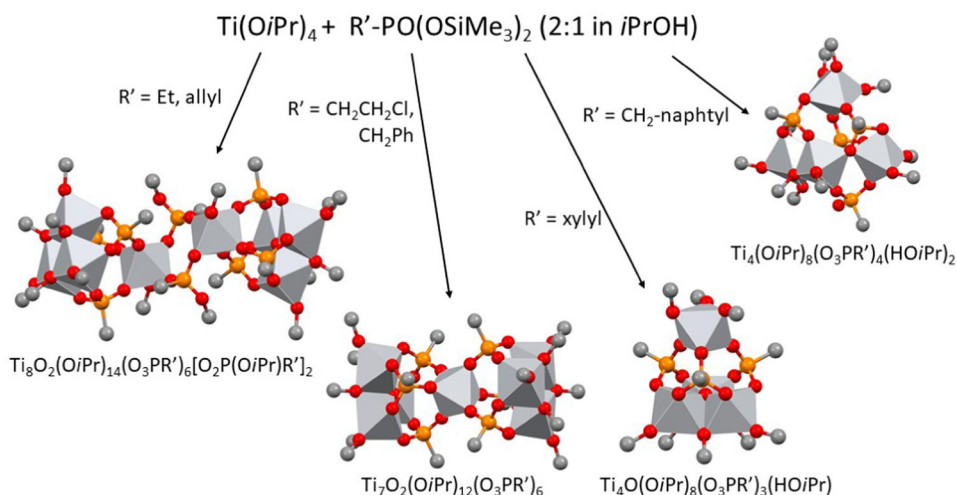
These three issues (reversibility of bonding, ligand dynamics and influence on the cluster structure) will be exemplarily highlighted in the following.

3.1 Ligand dynamics

An often observed phenomenon is that the ligands show only one set of signals in room-temperature n.m.r. spectra, even if they are chemically non-equivalent. This is due to fast intramolecular site exchange processes. An illustrative example is $Zr_4O_2(\text{methacrylate})_{12}$ (Fig. 2), obtained from the reaction of $Zr(\text{OPr})_4$ with methacrylic acid. At room temperature only one set of signals was observed for the methacrylate ligands (Fig. 3). The signals broadened by stepwise cooling of the solution. At -10°C the signals showed a broad coalescence and then split into multiple sets upon further cooling. At -80°C eight sharp signals of olefinic protons were observed, according to four different sets of ligands (bottom spectrum); the ratio of the four non-equivalent ligands was $\sim 1:1:2:2$, indicating the C_{2h} symmetry of the cluster in solution at this temperature, which is in line with the structure in the crystalline state [4].

Further analysis of the temperature-dependent n.m.r. spectra showed that exchange of the chelating methacrylate

Fig. 4 Formation of different cluster types upon variation of the organic group R' in the phosphonic acid. In this and the following figures, R and R' groups were omitted for clarity



(marked 1 in Fig. 2) with the bridging ligands 3 and/or 4 starts at -70°C and thus has the lowest activation energy. At -60°C additional exchange with the ligands marked 2 sets in, and at $T > -50^\circ\text{C}$ exchange of all groups.

There are also many cases where such a dynamic behavior of cluster ligands is not observed at room temperature. No obvious relation between the cluster structure, or the coordination of the ligands, and their dynamics is noted. It must be pointed out, however, that n.m.r. investigations at higher temperatures were hardly performed; the onset temperature of the site exchange may just be above ambient temperature.

3.2 Ligand exchange

Post-synthesis ligand exchange is a valuable tool for the modification and functionalization of nanoparticles. This is also possible for metal oxo clusters. However, there are limitations, the most important is that the clusters may rearrange or degrade during ligand exchange (as is also known for nanoparticles).

Capping ligands must compensate the charge of the cluster core and also allow the metal atoms to reach certain coordination numbers. The basic success formula for ligand exchange with retention of the cluster core structure is that the leaving and entering ligand should have the same charge and should occupy the same number of coordination sites. For example, a mono-anionic μ_2 ligand should be exchanged for another mono-anionic μ_2 ligand. Furthermore, the “bite angle” and related ligand characteristics should be similar. Following this recipe, the methacrylate ligands in $\text{Zr}_4\text{O}_2(\text{methacrylate})_{12}$ were completely replaced by pivalate ligands. Both $\text{Zr}_4\text{O}_2(\text{OOCR}')_{12}$ clusters have the same structure, as proven by X-ray structure analyses. When exposing isolated $\text{Zr}_4\text{O}_2(\text{pivalate})_{12}$ to an excess of methacrylic acid, the original $\text{Zr}_4\text{O}_2(\text{methacrylate})_{12}$ was

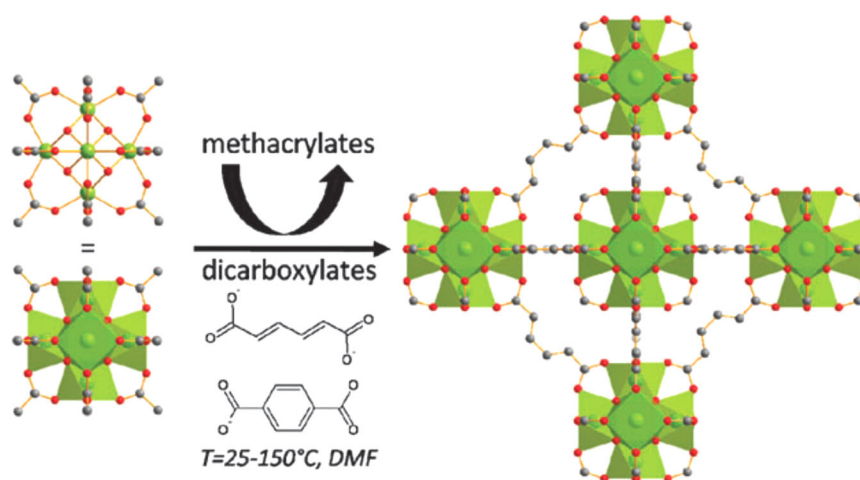
re-formed [5]. Mixed-ligand clusters can be prepared by partial ligand exchange.

However, even if the aforementioned requirements are met (or pretty much met), cluster rearrangement or degradation may occur. Thus, reaction of the same cluster, *viz.* $\text{Zr}_4\text{O}_2(\text{methacrylate})_{12}$, with acetylacetonate (acac-H) led to complete degradation of the cluster and formation of $\text{Zr}(\text{acac})_2(\text{methacrylate})_2$ [6]. The lesson learnt from this is that it has to be carefully checked in each case, whether the cluster core structure is retained if one kind of ligand is replaced by another.

3.3 Influence on the cluster structure

Several studies have shown that cluster formation by partial hydrolysis of metal alkoxides is influenced by basically the same reaction parameters as sol–gel syntheses in general. 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. Apart from the steric bulk of the OR groups, the $\text{M}(\text{OR})_n/\text{carboxylic acid}$ ratio, the reaction temperature and the solvent (if any), the kind of acid plays an important role. It is not clear until present whether steric or electronic effects (or a combination of both) influence the outcome of the reactions. This influence has been demonstrated in several studies. The example in Fig. 4 is taken from our own work [7] and shows how different cluster types are formed when all reaction parameters are kept constant except the organic group R' of the acid (in this example the corresponding phosphonic acid is liberated in situ upon reaction of the silyl ester with the employed alcohol). A closer inspection of the cluster structures in Fig. 4 shows, however, that they are constructed from the same building

Fig. 5 Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ -based MOFs via reaction of $\text{Zr}_6\text{O}_4(\text{OH})_4$ (methacrylate)₁₂ with dicarboxylic acids (from ref. [18])



blocks (Ti_3O units + single $[\text{TiO}_6]$ octahedra). This will be discussed in more detail later on.

4 Uses of metal oxo clusters

Apart from the general interest in metal oxo clusters and their relation to sol-gel chemistry—as outlined in the Introduction—some applications are noteworthy. They will only briefly be addressed here without going into details.

1. Clusters are used for crosslinking organic polymers—similar to POSS. To this end, the clusters must be decorated with polymerizable organic groups. Methacrylate ligands are very efficient in this respect, but several other polymerizable or initiator groups have been used as well. A general synthesis protocol is that a mixture of the clusters and organic monomers is co-polymerized. The resulting cluster-reinforced polymers, being organic-inorganic hybrid materials, have interesting materials properties, which were summarized elsewhere [8].

2. Connector units in metal-organic framework structures (MOF) are often metal oxo clusters [9]. The most popular is $[\text{Zn}_4\text{O}]^{6+}$, but $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ has also gained some importance [10]. Two approaches are pursued for the synthesis of such MOF. The first is hydrolysis of a molecular precursor, such as ZrOCl_2 or $\text{Zr}(\text{OR})_4$ in the case of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ -based MOFs, in the presence of a di-, tri-, or tetracarboxylic acid. The second route is ligand exchange between a pre-formed $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCR}')_{12}$ cluster and a polyfunctional carboxylic acid (Fig. 5 as an example).

3. Titanium oxo clusters have recently gained some attention because of their optical properties [11].

5 Structures

The structures of more than 350 homometallic titanium oxo clusters (TOC) have been determined. This group of

clusters is therefore best suited to discuss exemplarily some structural principles and derive conclusions on the cluster formation [12].

An often repeated claim is that TOC are molecular models for titania. The structures of rutile and anatase may therefore serve as points of reference. Both TiO_2 modifications have in common that all titanium atoms are octahedrally surrounded by six oxygen atoms ($[\text{TiO}_6]$ building blocks) and that all oxygen atoms are bonded to three Ti atoms ($\mu_3\text{-O}$). The basic structural motif is a Ti_3O unit, i.e., three $[\text{TiO}_6]$ octahedra connected via a common $\mu_3\text{-O}$. However, the shapes of the Ti_3O units in rutile and anatase are different (Fig. 6). In rutile, two $[\text{TiO}_6]$ octahedra share an edge, and the third $[\text{TiO}_6]$ is connected via a shared corner. This gives a T-shaped Ti_3O unit in rutile. In anatase, the three $[\text{TiO}_6]$ octahedra share two edges, resulting in an L-shaped Ti_3O unit. Such Ti_3O units are found time and again as basic building blocks in TOCs, as will be highlighted in the following Sections.

5.1 Oxo-alkoxo clusters

More than ten clusters of the composition $\text{Ti}_x\text{O}_y(\text{OR})_{4x-2y}$ are known, with different sizes and structures, ranging from $\text{Ti}_3\text{O}(\text{OR})_{10}$ to $\text{Ti}_{42}\text{O}_{54}(\text{OH})_{18}(\text{O}i\text{Pr})_{42}$. Inspection of the structures shows no resemblance of the cluster cores to the TiO_2 polymorphs. This is different to other molecular clusters. The cluster cores of many thiolate-capped cadmium sulfide clusters, for example, have the same structure as solid CdS (corner-sharing tetrahedra), and the dangling bonds at the cluster surface are saturated by SR groups [13]. A rationale for the different structural build-up of the Ti/O cluster cores will be given later. However, the $\text{Ti}_x\text{O}_y(\text{OR})_{4x-2y}$ clusters have in common with the TiO_2 structures that interconnected Ti_3O units are the predominant building blocks (Fig. 7 as an example).

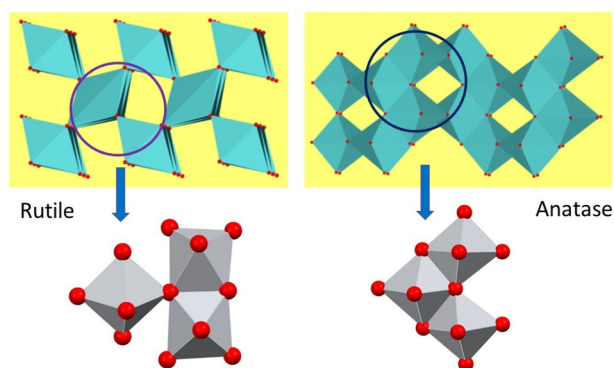


Fig. 6 The structures of rutile and anatase (reproduced from ref. [19]) and the corresponding Ti_3O units

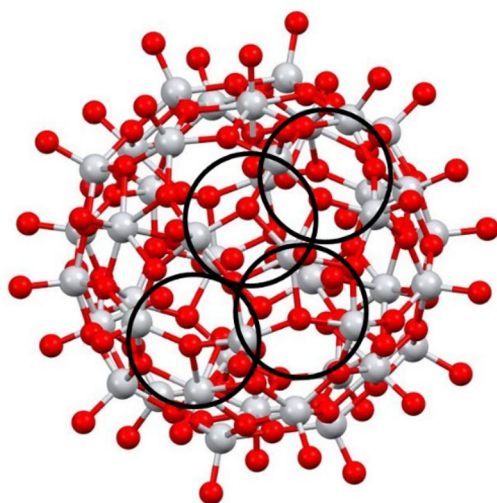


Fig. 7 The structure of $\text{Ti}_{42}\text{O}_{54}(\text{OH})_{18}(\text{OiPr})_{42}$ [20]. The black circles highlight some of the Ti_3O units

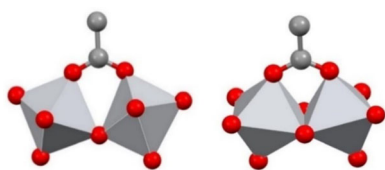


Fig. 8 Carboxylate ligands bridging two corner-sharing (left) and edge-sharing $[\text{TiO}_6]$ octahedra (right). The groups (red dots) connecting the polyhedra can be $\mu_2\text{-O}$, $\mu_2\text{-OR}$, and $\mu_3\text{-O}$ (from ref. [12])

5.2 Carboxylate-substituted oxo clusters

Carboxylate-substituted derivatives are the biggest subset among titanium oxo clusters, with ca. 200 structurally characterized examples. This is due to the straightforward synthesis. The basic protocol just requires mixing of $\text{Ti}(\text{OR})_4$ and a carboxylic acid. Water is produced in situ through ester formation between the acid and the alcohol, which is liberated by substitution of OR against carboxylate groups.

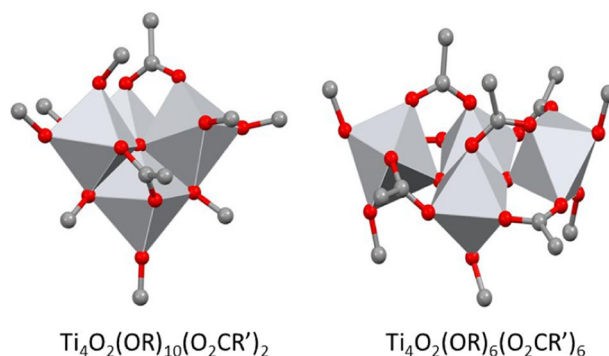


Fig. 9 The structures of $\text{Ti}_4\text{O}_2(\text{OR})_{10}(\text{O}_2\text{CR}')_2$ (d_s 0.5), and $\text{Ti}_4\text{O}_2(\text{OR})_6(\text{O}_2\text{CR}')_6$ (d_s 1.5) clusters (adapted from ref. [12])

Titanium atoms in carboxylate-substituted TOCs are mostly 6-coordinate (distorted $[\text{TiO}_6]$ octahedra), sometimes 5-coordinate, rarely 7- or 4-coordinate. The polyhedra share corners or edges by means of $\mu_2\text{-O}$, $\mu_2\text{-OR}$, and $\mu_3\text{-O}$ (rarely OH). Alkoxo groups can be terminal or bridging, carboxylate ligands are always bridging (Fig. 8). Due to the specific binding characteristics of carboxylate ligands (bite angle, Ti–O bond lengths, O–C–O angle, etc.) the $[\text{TiO}_x]$ polyhedra must be tilted relative to each other. This is an important aspect for understanding TOC structures and also shows how the capping ligands exert an influence on the cluster structure. It also explains that large carboxylate-substituted TOC do not have extended Ti/O cores similar to rutile or anatase: the alignment of the $[\text{TiO}_6]$ octahedra in the TiO_2 modifications is too rigid to allow bridging by carboxylate ligands.

Owing to the dual role of carboxylic acids, as a source of the carboxylate ligands and for the production of water in the system, carboxylate-substituted TOCs can be characterized by the $\text{R}'\text{CO}_2/\text{Ti}$ ratio (“degree of substitution”, d_s) and the O/Ti ratio (“degree of condensation”, d_c). A large excess of acid during the synthesis not necessarily results in a high d_s , because ester (and water) formation is then also facilitated. A particular combination of d_s and d_c is therefore currently not predictable. Notwithstanding this, a higher d_s results in more open structures as shown for the tetranuclear clusters with the same d_c in Fig. 9.

About 70% of the currently known carboxylate-substituted TOCs are tri-, tetra- or hexanuclear (no pentanuclear derivatives are known). When analyzing the structures of tetra- or hexanuclear clusters, one finds that most can be broken down into Ti_3O building blocks, as was the case for the oxo-alkoxo derivatives $\text{Ti}_x\text{O}_y(\text{OR})_{4x-2y}$. Analysis of the Ti_3O_x structures and that of derived compounds thus allows extracting some general principles of cluster formation or modification (It must be emphasized that the following considerations are solely based on the comparison of cluster structures. It is unknown, whether formation of the clusters during

their synthesis goes along the same line). Four “construction principles” can be identified.

5.2.1 Ligand substitution

Although μ_2 -OR and bridging carboxylate ligands have the same charge and occupy the same number of coordination sites, their structural characteristics are fairly different. Structures which just differ by replacement of a μ_2 -OR for a carboxylate ligand (with retention of the structure) are therefore infrequent. The example shown in Fig. 10 is exceptional, because a *terminal* OR group is exchanged for a *bridging* carboxylate ligand. This is only possible, because one of the titanium atoms in $\text{Ti}_3\text{O}(\text{OR})_8(\text{O}_2\text{CR}')_2$ (left in Fig. 10) is only 5-coordinate which is converted into a 6-coordinate upon substitution. Note that this substitution results in some tilting of the two polyhedra with regard to each other.

5.2.2 Internal condensation

Two terminal OR groups at neighboring $[\text{TiO}_x]$ polyhedra can, in principle, undergo an internal condensation reaction. This also requires tilting of the polyhedra relative to each other (while retaining the general cluster core structure) and is therefore also only infrequently found. An example in the

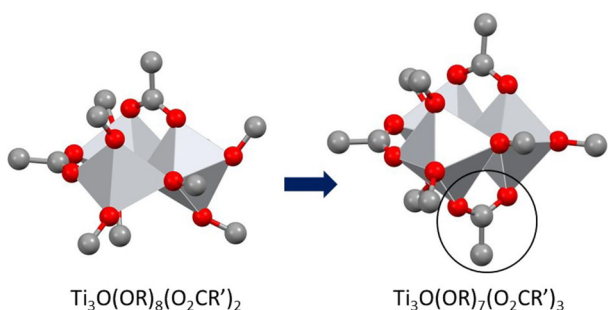


Fig. 10 The structures of $\text{Ti}_3\text{O}(\text{OR})_8(\text{O}_2\text{CR}')_2$ and $\text{Ti}_3\text{O}(\text{OR})_7(\text{O}_2\text{CR}')_3$ clusters (adapted from ref. [12])

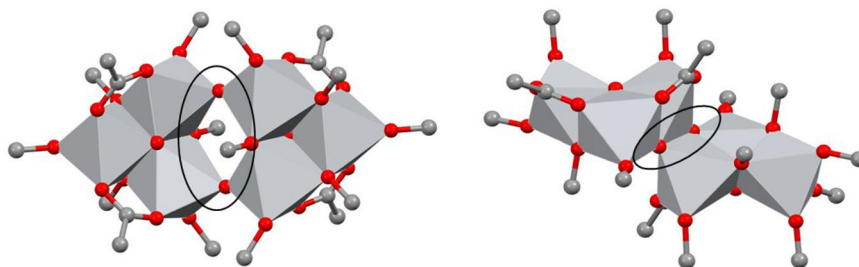
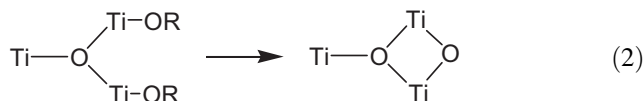


Fig. 11 The two structure types of $\text{Ti}_6\text{O}_4(\text{OR})_{12}(\text{O}_2\text{CR}')_4$. The black ellipsoids mark the sites where the two Ti_3O subunits are condensed (adapted from ref. [12])

Ti_3O_x cluster series is $\text{Ti}_3\text{O}_2(\text{OR})_3(\text{O}_2\text{CR}')_5$. Its structure can be derived from that of $\text{Ti}_3\text{O}(\text{OR})_7(\text{O}_2\text{CR}')_3$ by both an internal condensation and internal substitutions (Eq. 2).



5.2.3 Cluster–monomer condensation

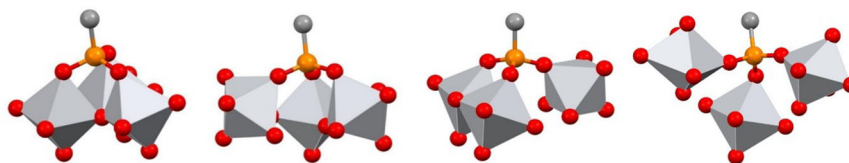
One can hypothesize that the tetranuclear clusters in Fig. 9 are formed by condensation of a $[\text{TiO}_6]$ octahedron and a Ti_3O unit. In $\text{Ti}_4\text{O}_2(\text{OR})_6(\text{O}_2\text{CR}')_6$, the $[\text{TiO}_6]$ octahedron (on the right-hand side in Fig. 9) is condensed to a T-shaped Ti_3O unit via a shared *corner* and in $\text{Ti}_4\text{O}_2(\text{OR})_{10}(\text{O}_2\text{CR}')_2$ (the lower $[\text{TiO}_6]$ octahedron in Fig. 9) to an L-shaped Ti_3O unit via two shared *edges* (Remember: $\text{R}'\text{COO}$ ligands can easily change their position!).

5.2.4 Cluster–cluster condensation

Clusters with the composition $\text{Ti}_6\text{O}_4(\text{OR})_{12}(\text{O}_2\text{CR}')_4$ can have the two structures shown in Fig. 11. The chemical formula and the structures suggest that they might be formed by condensation of two $\text{Ti}_3\text{O}(\text{OR})_8(\text{O}_2\text{CR}')_2$ clusters, either (left in Fig. 11) through condensation via two μ_2 -O (two shared corners) or (right in Fig. 11) via two μ_3 -O (one shared edge).

What has been demonstrated for Ti_3O clusters as aforesaid, especially (formal) cluster–monomer and cluster–cluster condensations, is found repeatedly for other cluster types. For example, in $\text{Ti}_8\text{O}_{10}(\text{O}_2\text{CR}')_{12}$ [14, 15] two $\text{Ti}_4\text{O}_2(\text{OR})_6(\text{O}_2\text{CR}')_6$ units are condensed, and in wheel-shaped $\text{Ti}_{32}\text{O}_{16}(\text{OCH}_2\text{CH}_2\text{O})_{32}(\text{OR})_{16}(\text{O}_2\text{CR}')_{16}$ [16, 17] eight tetranuclear subunits ($=[\text{Ti}_4\text{O}_2(\text{OCH}_2\text{CH}_2\text{O})_4(\text{OR})_2(\text{O}_2\text{CR}')_2]_8$). Cluster–cluster condensations comprise not only the same subunits, but (rarely) also different cluster types. Only few high-nuclearity clusters cannot be broken

Fig. 12 Coordination of phosphonate ligands as found in phosphonate-substituted TOC (from ref. [12])



down into smaller subunits, and even there can Ti_3O units be identified.

5.3 Phosphonate-substituted oxo clusters

The main source of the oxide ions in phosphonate-substituted TOC appears to be moisture introduced into the reaction mixture. Although phosphonic acid esters were identified as a side-product in a few reactions of $\text{Ti}(\text{OR})_4$ and $\text{R}''\text{P}(\text{O})(\text{OH})_2$, their formation (and thus water generation in the reaction mixture) is sluggish. Therefore, a mixture of carboxylic and organophosphonic acids is often employed, where the carboxylic acid reacts with the eliminated ROH and produces water, while $\text{R}''\text{PO}_3$ groups coordinate to Ti. With this protocol, mixed carboxylate-phosphonate-substituted TOCs are often obtained.

Phosphonate ligands have other coordination characteristics than carboxylate ligands. The most important with respect to TOCs are that they (i) can coordinate up to three Ti atoms, (ii) can bridge greater Ti–Ti distances and (iii) have more flexible Ti–O–P angles as well as Ti–O...O–Ti dihedral angles. This results in the coordination possibilities shown in Fig. 12, frequently found in structurally characterized TOC.

The structural diversity of phosphonate-substituted TOC is smaller than that of carboxylate derivatives. However, there are structural alternatives to the formation of higher-nuclearity TOC merely by condensing Ti/O units. As schematically shown in Fig. 12, $\text{R}''\text{PO}_3^{2-}$ ligands can also connect $[\text{TiO}_6]$ polyhedra without additionally sharing corners or edges. Examples of such structures are given in Fig. 4.

6 Conclusions

Coming back to the questions raised in the Introduction, a potential answer to some (but not all) can be suggested. Taking the formation of Ti/O compounds as an example, there is strong *structural* (!) evidence that Ti_3O clusters are the basic building blocks which are initially formed. The cluster cores may grow by cluster–monomer or cluster–cluster condensation. This has also been postulated for sol–gel materials in general and therefore the cluster may give some hints how the structures of sol–gel

materials develop. The clusters can also be modified by substitution or internal condensation reactions. Notwithstanding, several structures of (mainly large) clusters cannot be rationalized by such processes and therefore other growth processes may take place too.

Much more difficult to answer is whether different cluster types can be transformed into each other? Only very few cluster–cluster transformations have been observed experimentally. However, many clusters cannot be re-crystallized. This indicates that equilibria between different species exist in the reaction mixture and isolation of a particular cluster might be controlled by the tendency for crystallization. Experiments for deliberate cluster growth are still lacking, e.g., reaction of an isolated cluster with a cluster of another type or with a metal alkoxide. Although hydrolysis of some metal oxo clusters to give the corresponding metal oxides has been observed, the pathway of such transformations is still unknown. Therefore, the question whether clusters are intermediates in the formation of metal oxides upon hydrolysis of metal alkoxides cannot be answered for sure (although current knowledge suggests that this is the case).

Organic ligands play an important role, not only for controlling the reactivity of metal alkoxides or modifying the properties of sol–gel materials (including metal oxo clusters), but also their structures. There is an interplay between the coordination capabilities of the ligands and the coordination requirements of the metal oxide building blocks. This has been demonstrated for the different structures of carboxylate- and phosphonate-substituted clusters. An analysis of the cluster structures and their n.n.r. spectra also shows that the ligands can change their position at the cluster surface as well as their coordination mode and can therefore easily adapt themselves to changes or extensions of the cluster core.

Deliberate ligand exchange has rarely been investigated in detail. Retention of the cluster core geometry only appears to be feasible without problems, if the bonding characteristics of the incoming and eliminated ligands are similar. Otherwise, one has to reckon with cluster rearrangements.

In summary, investigation of metal oxo clusters obtained by partial hydrolysis of typical sol–gel precursors leads to a better understanding of the basic processes of sol–gel chemistry.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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