

# From molecular precursors to gels: What happens in between?

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## Research Article

**Keywords:** Oxo clusters, Silsesquioxanes, Polyoxometallates, Condensation reactions, Modular structure

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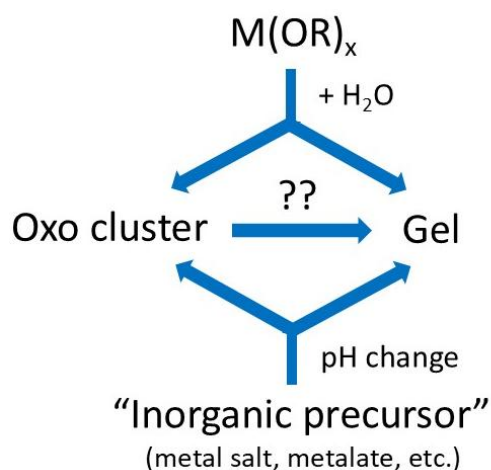
# From molecular precursors to gels: What happens in between?

Ulrich Schubert<sup>1</sup>

## Abstract

Hydrolysis of metal alkoxides or metal salts often results in the formation of charge- or ligand-stabilized molecular oxo clusters instead of gels or microcrystalline precipitates. In most cases, reliable protocols are at hand to synthesize either clusters or gels deliberately. Nevertheless, a prediction of the type of compound formed from a particular precursor under a certain set of reaction conditions is not possible. Many other issues are also unresolved. For example: Are clusters “dead ends” or is their formation reversible? How are large clusters formed? Are clusters building blocks of gels? Why are many large clusters odd-shaped (unlike nanoparticles)? Are oxo clusters “molecular oxides”? The contribution summarizes, for both alkoxysilanes and transition metal precursors, what is known and what is not known, and will address research deficits.

## Graphical Abstract



**Keywords** Oxo clusters • Silsesquioxanes • Polyoxometallates • Condensation reactions • Modular structure

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## Highlights

- Oxo cluster formation is governed by the same parameters as gel formation.
- Structural evidence suggests that small clusters are initially formed, which then assemble to bigger clusters by cluster-monomer or cluster-cluster condensation.
- Cluster structures without an apparent modular composition are also observed.
- Sparse evidence indicates that oxo clusters can dissociate into smaller entities or equilibrate with other species in solution.
- It is most likely that clusters can be structural elements of gels.

## 1. Introduction

The most common precursors in sol-gel syntheses are metal alkoxides,  $M(OR)_n$ , or aqueous solutions of so-called „inorganic precursors”, such as metal salts ( $MX_n$ ) or metalate ions ( $MO_n^{x-}$ ). In order to obtain gels, the former are reacted with water, while gelation is initiated by pH changes for the latter. In both cases, however, metal oxo clusters may be obtained instead of gels, depending on the reaction conditions. According to IUPAC definitions [1], a gel is a “*non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid*”, and a cluster “*a number of metal centres grouped close together which can have direct metal bonding interactions or interactions through a bridging ligand, but are not necessarily held together by these interactions*“. Thus, clusters are molecules, while gels have extended structures. Oxo clusters are characterized by bridging ( $\mu^2$ -,  $\mu^3$ - or rarely  $\mu^4$ -) oxo groups.

In this article, which is the transcript of a plenary lecture given at the 23<sup>rd</sup> International Sol-Gel Conference in Lisbon on September 4, 2026, clues for the interrelationship between gels and metal oxo clusters are summarized. It is not intended to provide a comprehensive review, but instead to identify open questions and eventually suggest experiments remaining to be done.

Similar to nanoparticles, oxo clusters are stabilized by a positive or negative charge, or by groups (ligands) bonded to surface atoms. Examples of charged oxo clusters (isopolyanions and isopolycations) are given in Fig. 1.  $[Si_8O_{20}]^{8-}$  [2] and  $[Ti_6O_8(OH_2)_{20}]^{8+}$  [3] were prepared by hydrolysis of  $Si(OR)_4$  ( $R = Me, Et$ ) or  $TiX_4$  ( $X = Cl, Br$ ),  $[W_{11}O_{34}(OH)_4]^{6-}$  [4] and  $[V_{10}O_{28}]^{6-}$  [5] by pH decrease of aqueous  $[WO_4]^{2-}$  or  $[VO_4]^{3-}$  solutions, and  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$  [6] by pH increase of  $AlCl_3$  solutions.

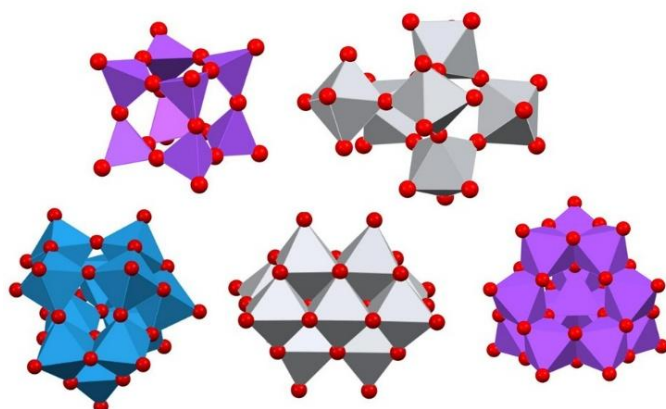


Fig. 1 Examples of isopolyanions and isopolycations. From top left to bottom right:  $[Si_8O_{20}]^{8-}$ ,  $[Ti_6O_8(H_2O)_{20}]^{8+}$ ,  $[W_{11}O_{34}(OH)_4]^{6-}$ ,  $[V_{10}O_{28}]^{6-}$  and  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$  (red: O).

Fig. 2 shows some examples of ligand-stabilized clusters. Ligands can be terminal or can bridge two or more metal atoms. In the case of metal oxo clusters, ligands coordinated to the metal(s) through oxygen atoms are preferred. The most straightforward cases are partially hydrolysed precursors, *i.e.*, oxo clusters which still contain part of the precursor's counter-ions, such as OR groups or halogen atoms. The degree of hydrolysis ( $d_c$  = oxo group:metal ratio) can vary considerably. For titanium oxo/alkoxo clusters  $d_c$  ranges from 0,3 in  $Ti_3O(OR)_{10}$  to 1,5 in  $Ti_{18}O_{27}(OH)(O^iBu)_{17}$  [7] and the cluster sizes from  $Ti_3O(OR)_{10}$  to  $Ti_{42}O_{54}(OH)_{18}(O^iPr)_{42}$  [8] (Fig. 2). As for mononuclear metal complexes, ligands with two or more coordinating atoms (bi- or multidentate ligands), such as carboxylates, phosphonates or di- and triketonates (Fig. 2), are more strongly bonded than monodentate ligands. Carboxylate ligands ( $R'COO$ ) are most frequently encountered. This is because reaction of metal alkoxides with carboxylic acids is accompanied by ester formation (Eq. 1) which slowly produces water *in situ*. The anionic ligands balance the charges of the metal atoms; additional neutral ligands may be needed to balance the preferred coordination numbers of the metal too, such as water molecules, or pyridine in the  $Fe_{34}$  cluster.

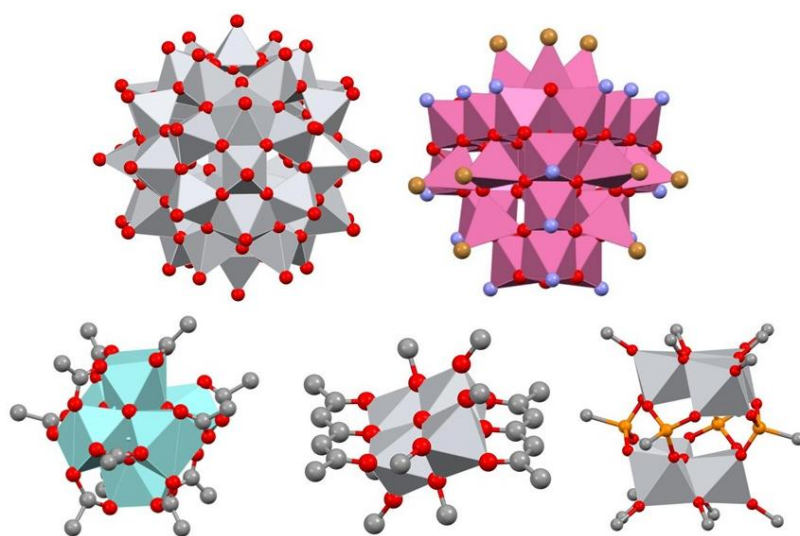
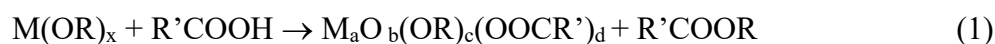


Fig. 2 Examples of ligand-stabilized clusters. From top left to bottom right:  $Ti_{42}O_{54}(OH)_{18}(O^iPr)_{42}$ ,  $[Fe_{34}O_{38}(OH)_{12}Br_{12}(pyridine)_{18}]^{2+}$  [9],  $Zr_6O_4(OH)_4(O_2CR')_{12}$  [10],  $Ti_4O_2(OR)_8[PhC(O)CHC(O)CHC(O)Ph]_2$  [11],  $Ti_6O_2(OR)_{12}(O_3PPh)_4$  [12] (organic substituents are not drawn for clarity. Blue: N; grey: C; brown: Br).

In the following, the role of metal oxo clusters in sol-gel systems will be brought into question, with regard to four aspects:

- Are the clusters structural models of metal oxides? (This is included, because in many articles it is claimed that oxo clusters are “molecular models” of metal oxides)(Q1)
- How are big clusters formed? (Q2)

- Are clusters „dead ends“ or is their formation reversible (equilibria between different species in solution)? (Q3)
- Are clusters (or segments thereof) structural elements of gels? (Q4)

As a kind of benchmark, the four questions (Q1–Q4) are first briefly discussed for alkoxysilanes  $R'Si(OR)_3$ .

## 2. A glimpse of silsesquioxanes

In the early days of sol-gel science, the early steps of  $Si(OR)_4$  or  $R'Si(OR)_3$  hydrolysis and condensation were intensively investigated, as outlined in Brinker's and Scherer's "sol-gel bible" [13]. The end product of  $R'Si(OR)_3$  are silsesquioxanes,  $R'SiO_{3/2}$ , in three different manifestations (Fig. 3): (i) random networks, (ii) ladder structures or segments thereof, or (iii) POSS (polyhedral oligomeric silsesquioxanes,  $R'_nSi_nO_{3n/2}$ ) as molecular compounds. Incomplete condensation results in defect structures, with  $\equiv Si-OH$  groups instead of  $\equiv Si-O-Si \equiv$ , such as "open" cages or ladder structures with missing rungs. In passing: the "ladders" are quite buckled, as shown in Fig. 4 for an OH-terminated  $Si_8$  ladder segment [14] (I would not step on such a ladder).

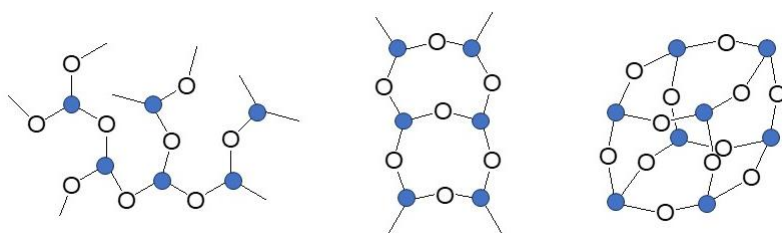


Fig. 3 Silsesquioxane structures (blue:  $RSi$ ; white:  $O$ ). Left: random network; centre: ladder; right:  $R_8Si_8O_{12}$  ("T<sub>8</sub>") as an example of a cage structure (POSS).

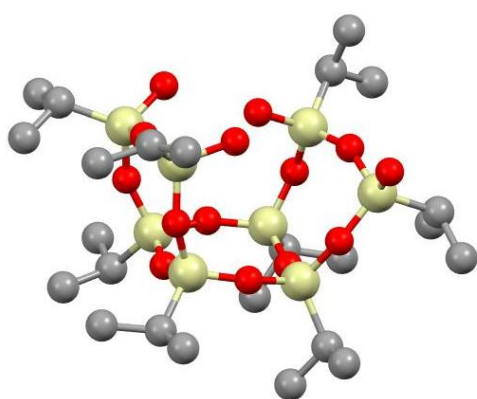


Fig. 4 The structure of  ${}^1Pr_8Si_8O_{10}(OH)_4$ .

As early as 1965, Brown suggested a pathway of  $PhSi(OH)_3$  polycondensation (Fig. 5) [15] with T<sub>4</sub> and T<sub>8</sub> units as key intermediates (a T unit is  $RSiO_{3/2}$ ; incompletely condensed structures are labelled T<sub>x</sub>(OH)<sub>y</sub>). Note that T<sub>8</sub>(OH)<sub>4</sub> corresponds to a ladder segment, as in Fig. 4. The

results of several studies on the hydrolysis of various  $R'Si(OR)_3$  in the 1960–90s were in line with this mechanism. An example from own work is the hydrolysis of  $(MeO)_3Si(CH_2)_3NEt_2$  with 1,5 equivalents of water (no catalyst, no solvent, Fig. 6) [16]. Within the accuracy of molecular mass determinations from GPC, the bands evolving after 30 min can be assigned to  $T_2$ ,  $T_3$  and  $T_4$  structures, while  $T_8$  dominates the chromatogram after 75 min. After 6 d, just before the gel point, a broad band can be tentatively assigned to  $T_{16}$  structures. When 3 equivalents of water were employed, only the  $T_8$  band was observed after 30 min. The GPC bands most likely also include incompletely closed cages with similar molecular mass, as suggested by mass spectrometry of  $NMe_2(CH_2Ph)$ -catalysed hydrolysis of glycidoxypropytrimethoxysilane (GLYMO, Fig. 7) [17].

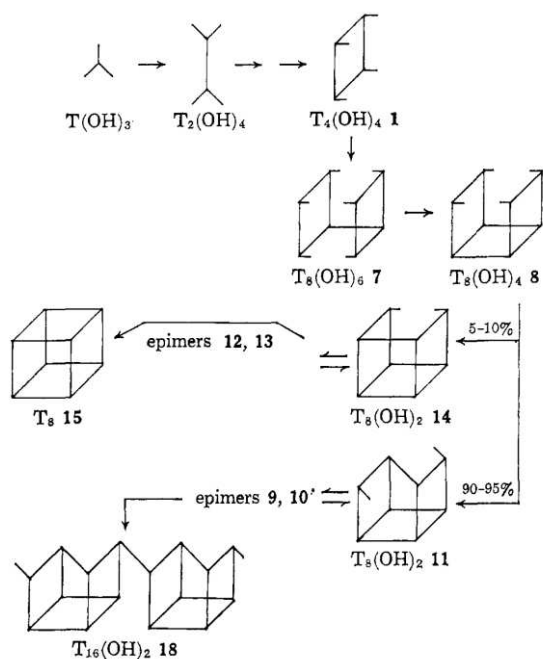


Fig. 5 Pathway for  $PhSi(OH)_3$  polycondensation as suggested by Brown. Each line connecting two corners is a Si–O–Si unit.

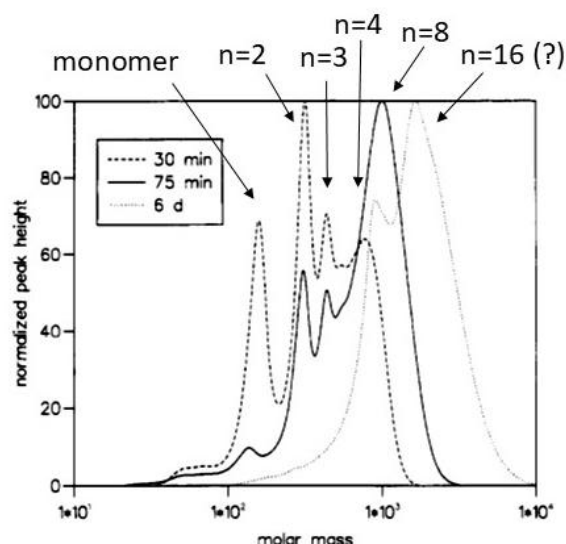


Fig. 6 Gel permeation chromatogram of  $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NEt}_2$  hydrolysis ( $r_w = 1,5$ ).

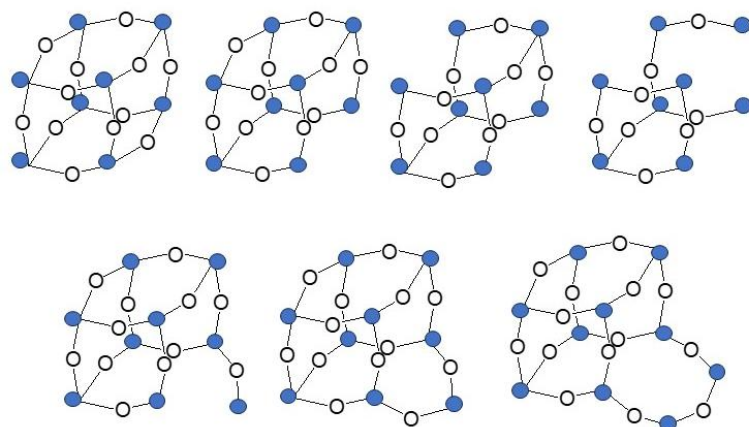


Fig. 7 Possible schematic structures assigned to some of the most intense peaks in the mass spectrum of hydrolysed GLYMO in the  $T_8$  region (blue:  $\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{C}_2\text{H}_3\text{O}$  ; white: O). Open edges or dangling silicon atoms are terminated by OH or OMe groups.

Quite a number of closed and open POSS cages, ranging from  $T_6$  to  $T_{14}$ , were structurally characterized. Some examples are shown in Fig. 8. Although all  $[\text{SiO}_3\text{C}]$  tetrahedra share corners, their arrangement is quite different from the  $\text{SiO}_2$  polymorphs. The  $[\text{SiO}_4]$  tetrahedra in tridymite and cristobalite form exclusively six-membered rings, and in quartz the projection of the spiral of tetrahedra is also a six-membered ring. In contrast, the  $[\text{SiO}_3\text{C}]$  tetrahedra in POSS cages form 3-, 4- or 5-membered rings as well. Although 6-membered rings can be identified in the  $T_{10}$  and  $T_{12}$  structures shown in Fig. 8, they are combined with 4-membered rings (the  $T_{12}$  structure is a hexagonal prism). Thus, POSS cannot be considered as “molecular  $\text{SiO}_2$ ” from a structural point of view (Q1).

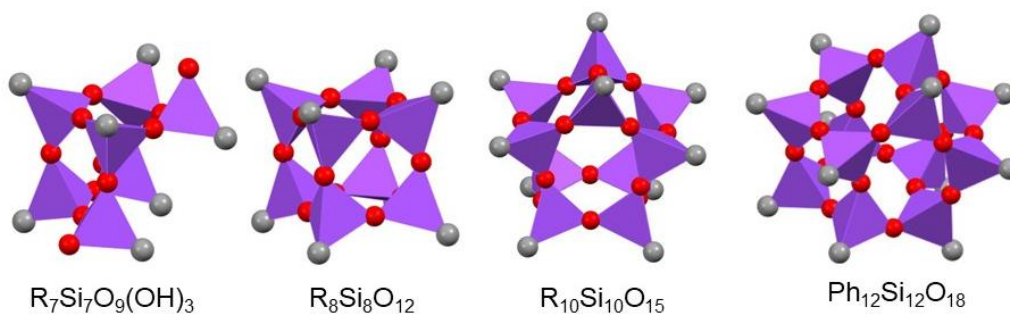
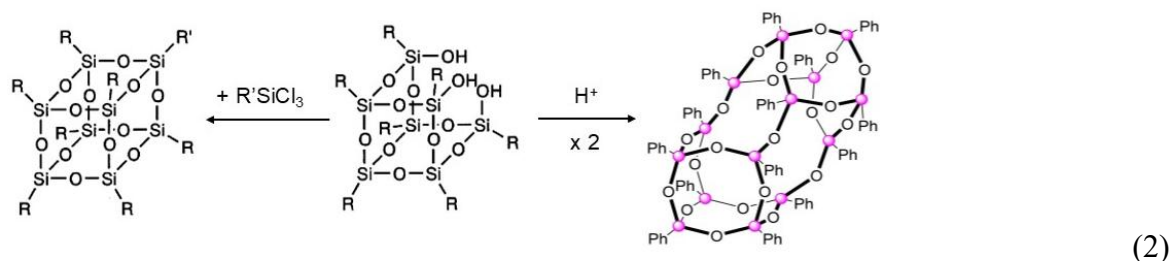


Fig. 8 Examples of POSS structures.

Cluster-monomer and cluster-cluster aggregation are accepted models for the growth of silica gels [13]. They also rationalize the different gel structures (polymeric or colloidal) when sol-gel processing is performed under acidic or basic conditions. One can find analogous reactions on a molecular scale for the expansion of POSS structures, as exemplified for the open  $T_7$  cage  $R_7Si_8O_9(OH)_3$  (Fig. 8, left). Reaction with  $R'SiCl_3$  is an established method for the preparation of closed  $T_8$  cages with two different organic groups,  $R_7R'Si_8O_{12}$ , and corresponds to a cluster-monomer condensation (Eq. 2, left). The group of Scheschkewitz has recently shown that the open  $T_7$  cage can be dimerized to give a  $T_{14}$  POSS [18] (Eq. 2, right) – an example for the condensation of two clusters (cages). Another example is the condensation of  $Me_4Si_4O_4(OEt)_4$  (corresponding to  $T_4(OH)_4$  in Fig. 5) to extended ladder structures [19]. Examples such as those are strong evidence that reactions of clusters with either the same or other clusters or with monomers might be a more general way to expand the size of (molecular) siloxane structures (Q2).



This brings us to the question whether POSS formation is reversible (Q3). Any Si–O–Si can of course be split at high pH, but this is not the issue here. It is well documented in the early literature on sol-gel reactions [13] that both hydrolysis of alkoxy silanes and condensation of silanols with concomitant water or alcohol elimination are in principle reversible, regardless of the fact that the equilibria are strongly shifted towards Si–O–Si formation. A very recent example was published by the Kroke group [20]. They prepared a gel from  $Me(EtO)_2Si-O-SiMe_2-O-Si(OEt)_2Me$  and then treated the gel with ethanol at 38°C. After two days, they identified, *inter alia*, small amounts of  $Me_2Si(OEt)_2$ ,  $Me_2Si(OEt)(OH)$ ,  $Me_2Si(OH)_2$  and  $MeSi(OEt)_3$ . Complete degradation of POSS by analogous treatment with alcohols is not too likely, but breaking of single Si–O–Si bonds, such as opening of closed cages, or generally the edge of a cage, appears possible. Species as in Fig. 7 might even be in equilibrium, as long as none of the compounds precipitates from solution.

With this in mind, it is most likely that gels obtained from  $R'Si(OR)_3$  are not just random networks (Fig. 3), as often implied, but also contain ladder- or cluster-like building blocks (Q4). As a matter of fact, this is difficult to verify, because the different structures do not have too significant fingerprints and are therefore difficult to identify. The group of Kickelbick analysed gels obtained from  $PhSi(OMe)_3$  with a combination of various spectroscopic and analytical techniques and indeed identified local ladder-type segments with defect-rich structures in the gels [21]. A computational simulation of complete hydrolysis and condensation of GLYMO (Fig. 9) visualized a randomly connected 3D network in combination with rings, ladder fragments and open cages [22].

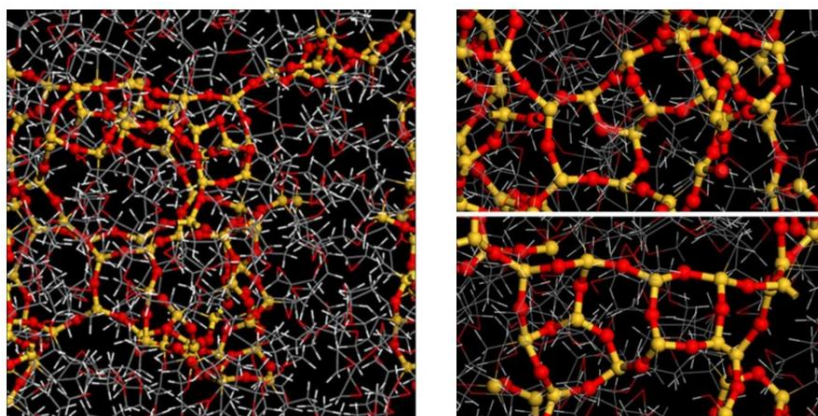


Fig. 9 Section of the network model obtained by computational simulation of fully hydrolysed GLYMO.

### 3. Metal oxo clusters

Metal oxo clusters are coordination compounds. Therefore, some relevant basics of coordination chemistry are briefly recollected before examining the role of metal oxo clusters in sol-gel chemistry.

- Most metals have higher coordination numbers than silicon, and their coordination number is generally greater than their charge. Therefore, the coordination polyhedra in polynuclear compounds must also share edges and (less often) faces to balance charges and coordination numbers, in contrast to siloxane chemistry which is based on corner-sharing tetrahedra. Edge-sharing of polyhedra decreases the structural degrees of freedom. Random networks (amorphous structures) are therefore less easily formed. In other words, (most) metal oxides have a much higher crystallization tendency than  $SiO_2$ .
- Substituents/ligands influence the bond strengths and thus reactivity of neighbouring ligands, depending on their mutual position, if the coordination number of the metal is  $>4$  (this issue is therefore not relevant for tetrahedral silicon compounds). For example, the reactivity of OR groups *cis* or *trans* to a bridging oxygen in an octahedrally coordinated compound is different. An excellent example for the *trans* influence in sol-gel materials is the pH dependence on the vanadia structure prepared from V(V) solutions [23].
- The protecting ligands L are subject to coordination-decoordination equilibria. They can be exchanged against more strongly bonded groups ( $L'$ ). In contrast, organic substituents in silicon chemistry are covalently bonded and cannot be exchanged or do not migrate.

The precursor chemistry of metal compounds is much more multifarious than that of silicon compounds. First, “inorganic precursors” play a more important role. Most solutions of metal or metalate ions, however, are complex pH- and dilution-dependent equilibria of different species – different aqua/hydroxo/oxo as well as monomeric/dimeric/oligomeric species [24]. A clear correlation between the exact composition of the precursor solutions and the outcome of sol-gel processes was only very rarely investigated (one of the exceptions is again Livage’s work on vanadia [23]). Second, organically modified metal alkoxides are rarely employed as such (in contrast to  $\text{R}'\text{Si}(\text{OR})_3$ ). Instead, the metal alkoxide and ligand (or ligand precursor) are co-processed. The most frequent procedure is that  $\text{M}(\text{OR})_n$  is reacted with a protic organic compound (HL), resulting in ROH elimination and *in situ* formation of a modified metal alkoxide  $\text{L}_x\text{M}(\text{OR})_{n-x}$ . Because of the coordination equilibria mentioned before, the modifying ligand may move from one metal atom to another during the formation of gels or clusters, yielding nonuniformly substituted metal atoms.

Coming back to the questions raised above, the more complex chemistry of metal compounds obfuscates the view on what happens on the way from the molecular precursors to any final product, be it a gel, microcrystalline precipitate or oxo cluster. A relatively clear answer can only be given to Q1. Since more than 500 homometallic Ti(IV) oxo clusters have been investigated by single crystal X-ray structure analyses [25-26], this subset of oxo clusters is especially suited to look for similarities to the  $\text{TiO}_2$  polymorphs. The latter are characterized by  $[\text{TiO}_6]$  octahedra, which are connected with each other in a way that each oxygen atom is bonded to three Ti atoms. Each  $\text{TiO}_2$  structure can be constructed from such  $\text{Ti}_3\text{O}$  units (*i.e.*, three  $[\text{TiO}_6]$  octahedra linked by a  $\mu_3\text{-O}$ ) as a sole building block. One way to distinguish the polymorphs is the different arrangement of the  $[\text{TiO}_6]$  octahedra in the  $\text{Ti}_3\text{O}$  units. In rutile, they share one edge (“T-shaped  $\text{Ti}_3\text{O}$ ”, Fig. 10, left) and in anatase two edges (“L-shaped  $\text{Ti}_3\text{O}$ ”, Fig. 10, right). Brookite consists of both T- and L-shaped  $\text{Ti}_3\text{O}$  units.

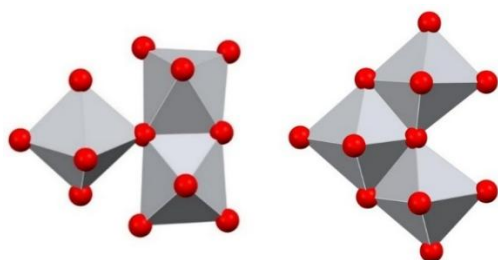


Fig. 10 T- and L-shaped  $\text{Ti}_3\text{O}$  subunits in the  $\text{TiO}_2$  polymorphs.

The  $\text{Ti}_3\text{O}$  building blocks are found in titanium oxo clusters again and again, especially in smaller clusters. This led to the conclusion that  $\text{Ti}_3\text{O}$  compounds, such as  $\text{Ti}_3\text{O}(\text{OR})_{10}$  or  $\text{Ti}_3\text{O}(\text{OR})_8(\text{O}_2\text{CR}')_2$ , might be initial reaction products when molecular titanium precursors are hydrolysed. Nevertheless, only few clusters, mainly several  $\text{Ti}_6\text{O}_x$  cluster types, can be constructed exclusively from  $\text{Ti}_3\text{O}$  units. Fig. 11 shows that two  $\text{Ti}_3\text{O}$  units can be differently condensed to  $\text{Ti}_6\text{O}_x$  structures (remarkably no  $\text{Ti}_6\text{O}_x$  cluster is known, where a T- and a L-shaped  $\text{Ti}_3\text{O}$  unit are condensed). The  $\text{Ti}_6$  clusters are, however, not small segments of the  $\text{TiO}_2$  structures, because of the different mutual arrangement of the  $\text{Ti}_3\text{O}$  units.

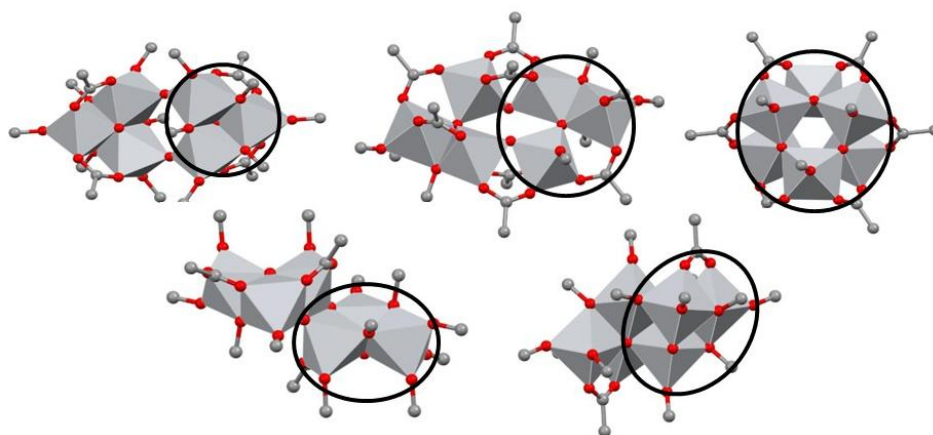


Fig. 11 The structures of carboxylate-substituted  $\text{Ti}_6\text{O}_x$  clusters composed of two  $\text{Ti}_3\text{O}$  building blocks (highlighted by a circle), From top left to bottom right:  $\text{Ti}_6\text{O}_4(\text{OR})_{12}(\text{O}_2\text{CR}')_4$  (type 1),  $\text{Ti}_6\text{O}_4(\text{OR})_8(\text{O}_2\text{CR}')_8$ ,  $\text{Ti}_6\text{O}_6(\text{OR})_6(\text{O}_2\text{CR}')_6$ ,  $\text{Ti}_6\text{O}_4(\text{OR})_{12}(\text{O}_2\text{CR}')_4$  (type 2) and  $\text{Ti}_6\text{O}_4(\text{OR})_{14}(\text{O}_2\text{R}')_2$ .

A similar analysis of other metal oxo clusters leads in the same conclusion that they are not “molecular oxides” (Q1), at least from a structural point of view (the surface chemistry, however, is analogous [27], also to nanoparticles – coordination chemistry!). Fig. 2 contains two examples of the very, very rare exceptions: The cluster core of  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCR}')_{12}$  corresponds to the smallest three-dimensional section of tetragonal  $\text{ZrO}_2$  and the core structure of  $[\text{Fe}_{34}\text{O}_{38}(\text{OH})_{12}\text{Br}_{12}(\text{pyridine})_{18}]^{2+}$ , obtained by hydrolysis of  $\text{FeBr}_3$  in aqueous pyridine, is very similar to  $\gamma\text{-Fe}_2\text{O}_3$ .

Structures as in Fig. 11 correspond to cluster-cluster condensations.  $2 \text{Ti}_3 \rightarrow \text{Ti}_6$  appears to be an analogue to  $2 \text{T}_4 \rightarrow \text{T}_8$  (Fig. 5) or  $2 \text{T}_7 \rightarrow \text{T}_{14}$  (Eq. 2) in silicon chemistry. In the same manner, structures can be identified which correspond to cluster-monomer condensations, as shown in Fig. 12 for  $\text{Ti}_4\text{O}_x$  clusters. Another example is  $\text{Zr}_{10}\text{O}_8(\text{OR})_{16}(\text{OOCR}')_8$ , where four  $\text{Zr}(\text{OR})_4$  are condensed with the OH groups of  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOCR}')_{12}$  (with elimination of four  $\text{R}'\text{COOH}$ ) [28].

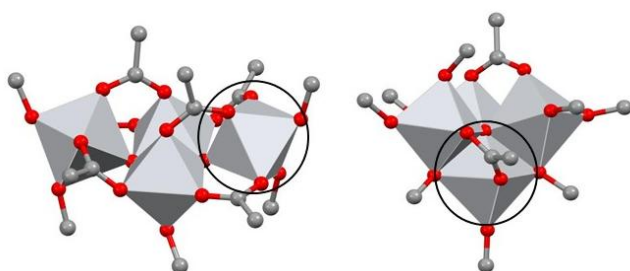


Fig. 12 The structures of two carboxylate-substituted  $\text{Ti}_4\text{O}_x$  clusters which can be dissected in a  $\text{Ti}_3\text{O}$  building block (left: T-shaped; right: L-shaped) and a monomeric  $[\text{TiO}_6]$  unit (highlighted by a circle), Left:  $\text{Ti}_4\text{O}_2(\text{OR})_6(\text{O}_2\text{CR}')_6$ ; right:  $\text{Ti}_4\text{O}_2(\text{OR})_{10}(\text{O}_2\text{CR}')_2$ .

A modular composition, as outlined for  $\text{Ti}_4\text{O}_x$  and  $\text{Ti}_6\text{O}_x$  clusters, can also be found in many (but not all) big(ger) metal oxo cluster. Fig. 13 shows two examples where cluster units of the

same kind (encircled) are condensed. The  $\text{Ti}_{32}\text{O}_{16}$  cluster consists of eight equal  $\text{Ti}_4\text{O}_2$  subunits ( $= [\text{Ti}_4\text{O}_2(\text{OR})_{10}(\text{O}_2\text{CR}')_2]_8$ ) [29], and  $\text{Ti}_{44}\text{O}_{62}$  is a dimer of  $\text{Ti}_{22}$  clusters [30]. In the same manner, clusters can be assembled from *different* subunits. Many examples are known for polyoxometallates [31], the illustrative case of  $[\text{W}_{36}\text{O}_{108}(\text{OH})_{12}]^{12-}$  is shown in Fig. 14 [32]. In a first step, the  $\text{W}_{36}$  cycle can be dissected into three  $\text{W}_{11}$  units which are interlinked by three monomeric  $[\text{WO}_6]$  units. The structure of the  $\text{W}_{11}$  units corresponds to that of the cluster  $[\text{W}_{11}\text{O}_{34}(\text{OH})_4]^{6-}$  [33] which for its part is composed from one  $\text{W}_4$ , one  $\text{W}_3$  and two  $\text{W}_2$  units. The structure of the  $\text{W}_4$  unit mirrors that of  $[\text{W}_4\text{O}_{16}]^{8-}$  [34].

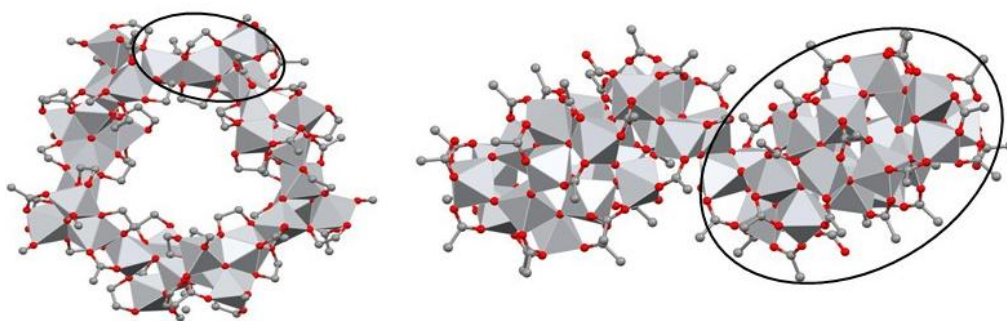


Fig. 13 The structures of  $\text{Ti}_{32}\text{O}_{16}(\text{OR})_{80}(\text{O}_2\text{CR}')_{16}$  (left) and  $\text{Ti}_{44}\text{O}_{62}(\text{OH})_4(\text{O}_2\text{CR}')_{48}$  (right).

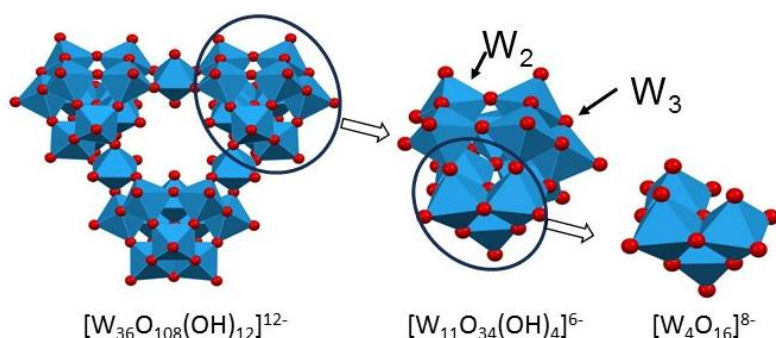


Fig. 14 Modular composition of  $[\text{W}_{36}\text{O}_{108}(\text{OH})_{12}]^{12-}$ .

At this point it is important to note that the above deliberations may provide a too simplified picture.

- The hypotheses on cluster formation by cluster-cluster and cluster-monomer condensations are solely based on analysing structures. It is unknown whether the respective clusters are formed in such a way in reality (for  $\text{Ti}_{14}$  this was proven experimentally – see above).
- Many high-nuclearity cluster structures have no obvious modular composition. Even if clusters can undergo cluster-cluster and cluster-monomer condensations, other possibilities for cluster formation or growth must also be in operation.
- Seemingly minor changes of the reaction conditions often result in different cluster structures. An example from own work are reactions of  $\text{Ti}(\text{OR})_4$  with methacrylic acid ( $\text{McOH}$ ) in a 1:3 ratio. Hexanuclear  $\text{Ti}_6\text{O}_4(\text{OR})_8(\text{OMc})_8$  (Fig. 11, upper row in the centre) was obtained for  $\text{OR} = \text{O}^n\text{Pr}$ , but tetranuclear  $\text{Ti}_4\text{O}_2(\text{OR})_6(\text{OMc})_6$  (Fig. 12, left) for the

bulkier O<sup>i</sup>Pr groups [35]. Corresponding to the above reasoning, two T-shaped Ti<sub>3</sub>O units are condensed to yield the Ti<sub>6</sub> cluster, while the Ti<sub>4</sub> cluster corresponds to condensation of a T-shaped Ti<sub>3</sub>O unit with a monomer. One can only speculate on the reason for this difference. A clue is the different degree of hydrolysis ( $d_c = 0,67$  for the Ti<sub>6</sub> and 0,5 for the Ti<sub>4</sub> cluster), which could be due to a faster ester + water formation for R = <sup>n</sup>Pr, thus possibly favoring the formation of Ti<sub>3</sub>O units. The example shows, however, that we are far away from understanding what is going on in the early stages of such reactions. Even if most oxo cluster can be reproducibly prepared (provided that the specific reaction conditions are precisely observed), it is not possible to predict which cluster will be formed. (In passing: predictions about which cluster types *cannot* be formed are possible [36]).

The question about reversibility of cluster-forming reactions (Q3) is difficult to answer, due to the lack of good experimental evidence. Oxo clusters can be partially or fully degraded upon reaction with strongly bonded ligands, such as β-diketonates. This is not too surprising, however, from the viewpoint of coordination chemistry and not too relevant to the reversibility issue. An observation for reflection, however, is that the oxo clusters typically crystallize from the reaction solution, but many cannot be re-crystallized. A possible explanation is that such clusters equilibrate with other species upon dissolution. Conversely, several species may be in equilibrium during synthesis and the one crystallizing best is eventually isolated (most publications do not comment on dissolved by-products). The following experiment is in line with this theory. When Ti<sub>7</sub>O<sub>4</sub>(OEt)<sub>20</sub> [37] was reacted with benzoic acid in a 1:1,5 ratio, the cluster Ti<sub>6</sub>O<sub>4</sub>(OEt)<sub>14</sub>(OOCPh)<sub>2</sub> was obtained (Fig. 15) [38], *i.e.*, one [TiO<sub>6</sub>] unit was expelled. The only common feature of both structures are two L-shaped Ti<sub>3</sub>O units (encircled), which are, however, differently condensed (and different to the examples in Fig. 11). In the Ti<sub>7</sub> cluster, they additionally clasp a [TiO<sub>6</sub>] unit (which is hidden by the two Ti<sub>3</sub>O units in Fig. 15). Difficult to imagine that the Ti<sub>7</sub> to Ti<sub>6</sub> transformation is based on an intramolecular rearrangement. It appears more likely that the Ti<sub>7</sub> cluster dissociates into smaller units (Ti<sub>3</sub>O units?) which reassemble in a different manner after substitution of two OEt groups. This notion was supported by the <sup>13</sup>C NMR spectrum of the reaction solution which indicated the presence of a single unknown compound (compound X). The Ti<sub>6</sub> crystallized from this solution, but had a somewhat different solution NMR spectrum than compound X. When the Ti<sub>6</sub> cluster was re-dissolved in the mother liquid, only the spectrum of compound X was observed, but not the spectrum of the Ti<sub>6</sub> cluster. This indicates an equilibrium between initially formed compound(s) and the Ti<sub>6</sub> cluster.

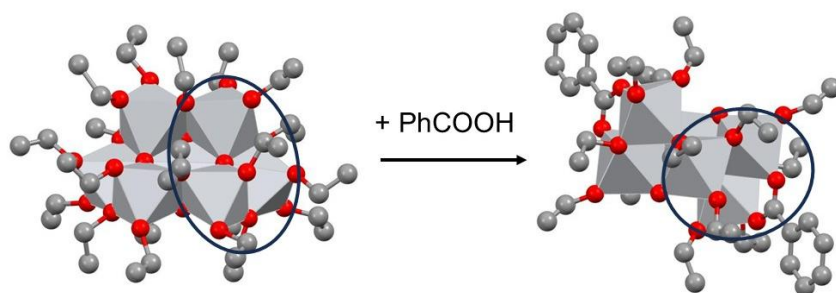


Fig. 15. Reaction of Ti<sub>7</sub>O<sub>4</sub>(OEt)<sub>20</sub> with benzoic acid.

Most metal oxo clusters have reactive surface groups, such as OR, OH, O<sup>-</sup> or Cl. Furthermore, ancillary ligands can be de-coordinated. This is the chemical basis for the presumed cluster-cluster or cluster-monomer condensations discussed above. If one accepts the notion that bigger clusters can be formed by such reactions or that clusters can be “re-activated” by equilibration reactions, then it is quite likely that clusters can be integrated in gel structures (Q4). All kinds of building blocks with reactive groups, such as monomers, small oligomers or smaller and bigger clusters could react with each other (with some reactivity differences) and result in gel structures composed from different building blocks. This would be similar to Fig. 9, but with differently connected polyhedra. As a matter of fact, the primary particle diameters determined from the radii of gyration in SAXS studies are often in the range of typical cluster sizes. An example from own work is shown in Fig. 16, where reaction of the Ti/Si mixed-metal precursor with water was investigated [39]. Immediately after the start of the reaction small primary particles were formed, the size of which ( $d = 1,0 \pm 0,2$  nm, assuming spherical particles) remained constant after 15 min and through the gelation and aging process. Anomalous SAXS measurements near the Ti K absorption edge indicated that this were Ti/O structures. Condensation then proceeds by a slower aggregation of the primary particles, probably by subsequent hydrolysis and condensation of (less reactive) Si(OMe)<sub>3</sub>. Similar particle sizes were measured upon hydrolysis of the parent compound [Ti(O<sup>i</sup>Pr)<sub>3</sub>(acetylacetonate)<sub>2</sub>] [40], a mixed-metal precursor where Ti and Zn were linked through a *p*-carboxybenzaldehyde oximate group [41] or TiOCl<sub>2</sub> in N,N-dimethylformamide [42]. Primary particle diameters of ~1 nm correspond to the size (Ti···Ti space diagonal) of Ti<sub>12</sub> – Ti<sub>18</sub> oxo clusters.

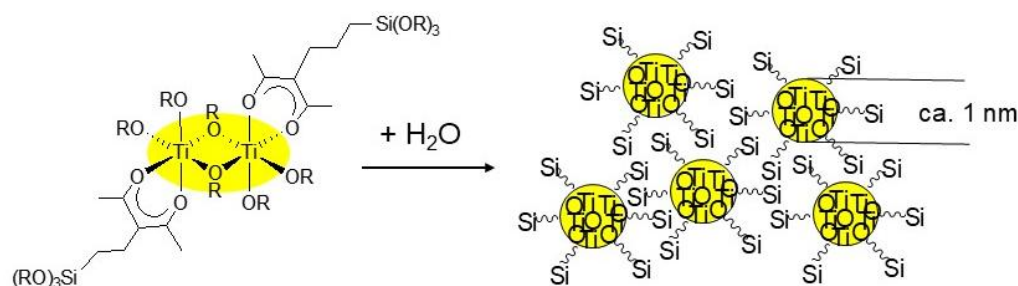


Fig. 16 Hydrolysis of 3-oxoethyl-6-trimethoxysilyl-hexan-2-onate-modified Ti(O<sup>i</sup>Pr)<sub>4</sub>.

#### 4. Conclusions and Outlook

When summarizing the experimental evidence concerning the initially raised questions, one arrives at the following conclusions. Very interestingly, they are very similar for silica- and metal oxide-based systems, despite their different coordination chemistry.

- Q1. The vast majority of metal oxide clusters are no structural models of metal oxides; there is no structural relationship.
- Q2. Oxo cluster formation is governed by the same parameters as gel formation. Variations of the parameter space result in different cluster structures. There is strong structural (!) evidence that small clusters are initially formed, which then assemble to bigger clusters by cluster-monomer or cluster-cluster condensation. However, there are also (mainly large) cluster structures without an apparent modular composition.

- Q3. Sparse evidence indicates that oxo clusters can dissociate into smaller entities or equilibrate with other species in solution. There are currently no indications that cluster formation is completely reversible, leaving aside the fact that clusters can be deliberately degraded.
- Q4. It is most likely that clusters can be structural elements of gels, because most clusters have reactive surface groups and can thus undergo the same reactions as monomers or small oligomers.

This leads to a number of open questions, such as

- What are the chemical principles by which building blocks (clusters, small oligomers, monomers) are assembled to larger clusters? Can cluster-forming reactions be controlled in a way that a predetermined composition/structure is obtained?
- Why are many (large) oxo clusters very odd-shaped (unlike nanoparticles)?
- Is cluster formation controlled by equilibria in solution? May isolation of a specific cluster just be due to a high(er) tendency for crystallization?
- Can M–O–M bonds be cleaved by alcohols?

Apart from investigations with up-to-date physical and theoretical methods, controlled reactions of isolated (!) clusters could answer such questions, such as cautious and stepwise hydrolysis of OR groups in oxo-alkoxo clusters, reactions with monomers (of the same metal), *e.g.*, reactions of oxo-alkoxo clusters with metal alkoxides or polyoxometallates with monomeric or oligomeric compounds (cluster expansion?), or deliberate condensation reactions between clusters of the same kind or between different clusters.

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### Compliance with ethical standards

The author declares no competing interests.

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