



Clusters or paperbags? What can we actually learn from the structure and reactivity of oligonuclear metal-oxo-alkoxide complexes?

Vadim G. Kessler ¹

Received: 20 November 2022 / Accepted: 9 February 2023

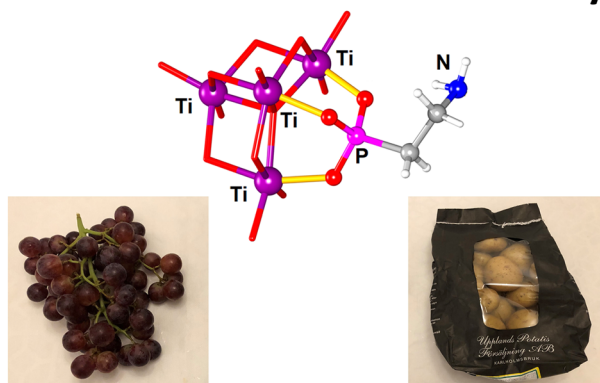
© The Author(s) 2023

Abstract

The term cluster has been proposed in Inorganic Chemistry for species featuring well-defined metal-metal bond based structures and implies inherent stability against metal core transformation. The present article provides additional arguments for the formation of metal oxo-alkoxide species on the action of external self-assembly forces, without invoking such stability. These species are easily restructured on hydrolysis in aqueous medium and their alleged photo and electro catalytic reactivity may actually be due to metal oxide nanoparticles resulting from their transformation. A new term “paperbag compound” is proposed instead of ‘cluster’ to denote oligonuclear non-cluster species. New insights into the reactivity of metal oxide nanoparticles in biological systems can be obtained from analysis of structure and bonding parameters in paperbag compounds as molecular models.

Graphical Abstract

Metal oxo-alkoxides – are they



Clusters? or Paperbags!

Keywords Oxo-alkoxides · Molecular models · Not clusters · Paperbag compounds · Sol-gel chemistry

✉ Vadim G. Kessler
vadim.kessler@slu.se

¹ Department of Molecular Sciences, BioCenter, Swedish University of Agricultural Sciences, SE-75007 Uppsala, Sweden

Highlights

- Self-assembly phenomena have been analyzed for oxo-alkoxide and polyoxometalate (POM) species.
- Trends in preservation and transformation of metal-oxide cores have been illustrated by new and literature-based single crystal data.
- Reactivity of metal oxo-alkoxides in water leading to their transformation into metal oxide nanoparticles has been traced using literature data.
- A new term, “paperbag compound” has been proposed for metal oxo-alkoxides and POMs as an alternative to misleading term cluster.

1 Introduction

The exciting field of cluster chemistry was pioneered and originally shaped by the works of F.A. Cotton at the Massachusetts Institute of Technology in the early 1960s [1]. As brilliantly formulated in the Obituary to Frank Albert Cotton written by M.H. Chisholm for Biography Mems of the Fellows of the Royal Society in 2008, “Cotton defined the term ‘metal cluster compounds’ as those compounds or complex ions consisting of three or more metal atoms held together at least in part by metal–metal bonds. These he considered to be different from polyoxometallates and polynuclear metal alkoxide or carboxylate compounds, in which ligand bridges are involved in bringing the metal atoms together” [2]. The most fascinating feature of these compounds, derived from transition metal cations in low oxidation states, was their well pronounced chemical stability. Already in the very first works in the field, it was noticed, for example, that tri-nuclear rhenium clusters derived from “ ReCl_3 ” such as $\text{Re}_3\text{Cl}_9(\text{H}_2\text{O})_3$ could exchange the water molecules for chloride ions, but did not release the “core” chloride ligands for precipitation with Ag^+ cations [3]. This exceptional stability along with the presence of specific ligand-exchanging active sites on the surface of clusters reserved for them a special role in catalysis, where especially octahedral species of Mo, W, Nb and Ta such as, for example, $[\text{Mo}_6\text{Cl}_8]^{4+}$ units, have received special attention [4]. Clusters have also been considered as promising building blocks in functional nanomaterials [5]. The reasons behind the observed geometry and stability of cluster cores have received their explanation in the Nobel prize winning research of Roald Hoffmann [6].

With the development of nano science in the late 1980s, the term cluster has been picked up by physicists in a very different manner, as chemical thermodynamics started to approach a quantitative description of nucleation phenomena. Thus, the process of material formation was generally assumed to proceed from molecules via clusters to bulk solids. These studies actually were not in any way related to chemistry. A very typical example can be found in the ground-breaking works of the Chemical Physics school at the Paris-Sud University, where, in particular crystallization

of CO_2 , N_2 and SF_6 was followed, revealing intermediate formation of such aggregates as $(\text{CO}_2)_{13}$ [7]. This vision of transformation from molecules to bulk material became surprisingly attractive to members of the sol-gel community, where an erroneous (in relation to metal oxide precursors) hypothesis of “kinetically controlled hydrolysis and condensation” was dominating at that time [8]. The fundamental assumption in this hypothesis was that the M-O-M bond once formed, either by hydrolysis, or in non-hydrolytic approaches, by ester [9, 10] or ether [11–13] elimination reactions, was rigid, and resistant to further breakdown. Thus, the process of transformation of alkoxide precursors into oxide gels was seen as a kind of inorganic polymerization. In agreement with this vision of the sol-gel phenomenon, if some aggregates were formed and isolated, they were seen as “stable oligomers”. Their structure was assumed to be preserved in any further transformations. In the literature at that time, the oxo-alkoxides were compared, quite correctly, to the polyoxometalates in aqueous media. The matter, however, is that polyoxometalates are distinctly not clusters in their behavior – they are products of thermodynamic equilibrium resulting from applied acidity, concentration and temperature conditions and easily re-transform if the conditions are changed. Even phase diagrams can be produced for them, showing the effects of concentration and acidity (Fig. 1).

The breakdown and restructuring of polyoxometalates in water is a relatively rapidly proceeding reaction. The rate constant for the 1st order dissociation of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ in MilliQ water was found to be $6.96 \times 10^{-3} \text{ s}^{-1}$ giving the reaction half-time of 100 s—a seemingly quick reaction [14].

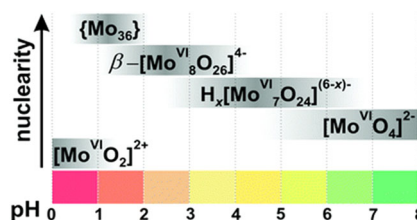


Fig. 1 Phase diagram for isopoly-molybdate compounds' formation in solution with Mo concentration in the range 0.1–0.4 M. Reprinted with permission from [55]

The nature of the metal oxide and specifically titanium and zirconium oxides formation in sol-gel processes has been beyond doubt proven to be thermodynamically controlled nucleation, followed by aggregation without growth, guided by diffusion and heterogeneous kinetics. Homogeneous reaction kinetics is no issue in metal oxide sol-gel chemistry [15–18].

The erroneous ideas about the nature of oligonuclear oxo-alkoxides have led to a number of spectacularly complicated synthetic approaches to some oligonuclear species. For example, for production of $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(\text{}^i\text{PrOH})_2]_2$, to avoid formation of Ba:Zr 2:1 and 1:2 “clusters” formed with iso-propoxide ligands, first, a 1:1 complex with *t*-butoxide ligands was formed by reaction of pre-formed $\text{Ba}(\text{O}^t\text{Bu})_2$ with the industrially available $\text{Zr}(\text{O}^t\text{Bu})_4$. Then, it was hydrolyzed by a stoichiometric amount of water and later subjected to ligand exchange with an excess of ${}^i\text{PrOH}$ [19]. In fact, this compound could instead be produced with very high yields just by dissolving barium metal in a solution of the commercially available zirconium iso-propoxide, with subsequent careful addition of a stoichiometric amount of water in the parent alcohol [20]. The non-cluster nature of complex precursors has even been a pitfall and damaged the image of sol-gel chemistry in the synthesis of High-Temperature HTSC, because formation of an oligonuclear oxo-alkoxide intermediate did not show any effect on further formation of complex oxide phases. The oxide phase did form, but only under conditions where it was thermodynamically stable and kinetically accessible (diffusion of cations was rapid enough) [21].

The idea of “cluster nature” seemed finally to be abandoned and consensus achieved among people working with metal alkoxide chemistry at Materials Discussion VII in 2004 in London dedicated to Donald C. Bradley. It returned, however, recently with the growing modern interest in molecular models of oxides. The idea of using oxo-alkoxides as molecular models for the forming oxide phases is, however, not in any sense new. It has been advocated by the classics of alkoxide chemistry, in particular, by Don Bradley already in 1960s [22]. Then in the late 1980s and beginning of the 1990s, came the works by Malcolm Chisholm et al. on metal alkoxides generally as models of oxides, with a focus on mechanisms of catalytic processes [23–25], and of Walter Klemperer, who tracked the structural analogy between oxo-alkoxides and polyoxometalates [26]. An important contribution was made also by Nataliya Turova et al., with the idea about oxo-alkoxides as true precursors of oxides [27]. The concept of modeling the properties of especially nanosized oxides with oxo-alkoxide species received a new lease of life with the interest in titania as a photocatalyst. A huge effort has been made by the group of Philip Coppens that produced—in a

small fraction, also in collaboration with our group—a plethora of oligonuclear titanium oxo-alkoxides and investigated their electronic spectra, relating ligand properties to the bonding in their structures [28]. This gave, on one hand, indications for the ligand influences the bandgap in surface-modified TiO_2 , and, on the other hand, insights into how the ligands, used in surface grafting of organic functions on titania surface, can and cannot be attached. These insights were very valuable and helped in regulating the photo activity of hybrid nano titania [29, 30] and in building up hybrid adsorbents for recycling of critical metals [31, 32].

In the present contribution, we demonstrate that the reactivity with structural transformation on ligand exchange, where hydrolysis can be considered as a particular case, have general characteristics for metal oxo-alkoxides and are not only specific for titanium or zirconium derivatives. We provide also insights in possible approaches enabling the composition of heterometallic oxo-alkoxides of titanium to be exploited for understanding the biological activity of titanium oxide. A new term, “paperbag” is proposed for non-cluster oligonuclear complexes.

2 Experimental

All chemicals were obtained from Sigma-Aldrich Sweden. Alcohols were purified and distilled before use from barium ethoxide for EtOH and from aluminum normal propoxide—for ${}^i\text{PrOH}$. Toluene was purified via distillation over lithium aluminum hydride.

2.1 Preparation and synthesis

Niobium *n*-propoxide, $\text{Nb}_2(\text{O}^n\text{Pr})_{10}(\text{l})$, Cas. No. 38874-17-8, was received as a colorless transparent viscous liquid. A portion of ca. 3 ml of the product was transferred to a Schlenk flask (further sealed with a stopper well-smearred with silicon grease and Parafilm) under nitrogen atmosphere and left in a refrigerator at 3 °C for a period of several months. Colorless rod-shaped crystals discovered on the bottom of the stored flask were separated by decantation and characterized by single-crystal X-ray study.

A portion of niobium ethoxide, $\text{Nb}_2(\text{OEt})_{10}(\text{l})$, Cas. No. 3236-82-6, was received as a colorless transparent viscous liquid. A portion of ca. 2 ml of the product was transferred to a Schlenk flask and a portion of 10 ml *nPrOH* along with 10 ml toluene was added to it by syringe. The formed transparent solution was evacuated to dryness without heating and the procedure was repeated twice, leaving a viscous transparent liquid that was stored for 1 week at 3 °C, producing a crop of rod-shaped crystals, identical to those obtained on storage of $\text{Nb}_2(\text{O}^n\text{Pr})_{10}(\text{l})$.

2.2 X-ray crystallography

Data collection was carried out at room temperature with Bruker SMART Apex-II CCD diffractometer for a full hemisphere in the 2θ range $2.68\text{--}50.05^\circ$ using graphite-monochromated $\text{MoK}\alpha$ radiation (sealed tube), $\lambda = 0.71073 \text{ \AA}$. Integration of the data was performed with Bruker SAINTPLUS and data reduction with the Bruker SADABS program. $\text{C}_{60}\text{H}_{140}\text{Nb}_8\text{O}_{30}$, $M = 2084.99 \text{ Da}$, Orthorhombic, Space group Pbca , $a = 22.314(4)$, $b = 17.157(3)$, $c = 24.459(4) \text{ \AA}$, $V = 9364(3) \text{ \AA}^3$, $Z = 4$. The structure was solved by direct methods. The positions of the majority of non-hydrogen atoms were obtained from the initial solution and those of the residual ones were found in the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined first in isotropic and then in anisotropic approximation. Hydrogen atoms were introduced by geometrical calculation, and included into the final refinement in isotropic approximation, applying a riding model. The refinement converged at discrepancy factors $R1 = 0.0671$, $wR2 = 0.1779$, for 5225 observed reflections ($I > 2\sigma(I)$). Full details of experiment and structure solution and refinement are available free-of-charge from the Cambridge Crystallographic Data Center at <http://www.cam.ac.uk> citing deposition number **2151366**.

3 Results and discussion

Metal alkoxides are, due to the weak σ and strong π -donor properties of alkoxide ligands, stabilizing the highest oxidation states of metal atoms [33]. This feature is also leading to localization of bonding orbitals in the alkoxide complexes on the oxygen atoms, making the charge interactions, i.e. ionic bonding, the dominating force in their formation [34]. The structures of the heterometallic alkoxide complexes have on a broad selection of examples over the whole Periodic Table been proved to result from self-assembly, or maybe more correctly stated molecular assembly, of metal cations and alkoxide anions [34]. The same is true, of course, even for homometallic species. Broadly demonstrated for Ti [35], Zr and Hf [36, 37], the ionic nature and molecular (self-)assembly principles can be traced for oxo-alkoxides and polyoxometalate species of a broad variety of metal cations. In particular, in this work the insights into molecular assembly of niobium oxo-alkoxide species have been complemented. Slow spontaneous decomposition/microhydrolysis of niobium *n*-propoxide was shown to result in formation of the same type of metal-oxide core for the oxo-substituted species as in case of the ethoxide as starting reagent (see Fig. 2). The ether elimination phenomenon leading to

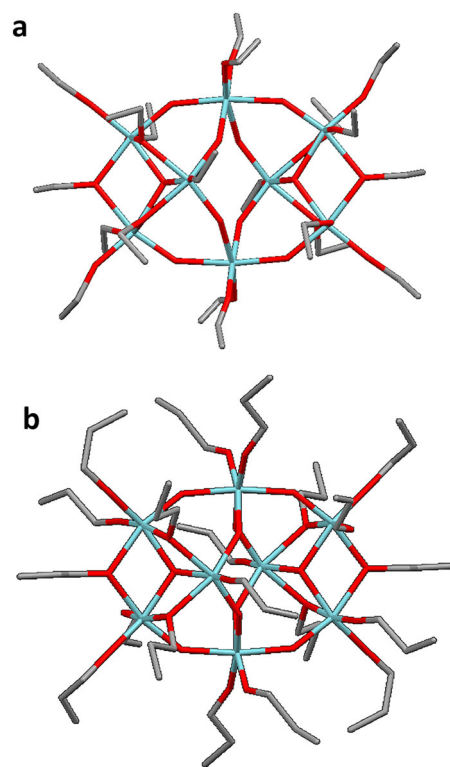


Fig. 2 Molecular structures of $\text{Nb}_8\text{O}_{10}(\text{OEt})_{20}$ (a) [39, 56] and $\text{Nb}_8\text{O}_{10}(\text{O}^i\text{Pr})_{20}$ (b, this work)

spontaneous formation of oxo-substituted species has actually been proved for Nb(V) alkoxides earlier [38, 39].

This fact, however, is not in any way manifesting the existence of a specific stable Nb_8O_{30} “cluster core”. In the same way as was noticed for Zr and Hf alkoxides [20, 36, 37], the addition of a different ligand even in the absence of heating or other high-energy treatment leads for smaller fraction to preservation of the core (just because the smaller primary ligands are still present to permit the same kind of molecular assembly) and for its excess results in a completely different structure with a different number of niobium atoms in the aggregate.

Starting from $\text{Nb}_8\text{O}_{10}(\text{OEt})_{20}$ the addition of 2 equivalents of $\text{HOSi}(\text{SiMe}_3)_3$ [40] gives $\text{Nb}_8\text{O}_{10}(\text{OEt})_{18}(\text{OSi}(\text{SiMe}_3)_3)_2$, making a “flash” of cluster behavior, but the excess of the same ligand without heating(!) produces $\text{Nb}_6\text{O}_{13}(\text{OSi}(\text{SiMe}_3)_3)_6\text{H}_2$, a structure with completely different core Nb_6O_{19} (see Fig. 3a, b), by the way analogous to that of Lindquist type polyoxometalates, well-known for aqueous equilibria [41]. In the same way, the addition of iso-propanol in excess to niobium oxo-ethoxide results in a different but also hexa-nuclear core, Nb_6O_{24} (see Fig. 3c) [42].

It should be noted, of course, that heating, when applied, does often lead to a change in the structure and size of the alkoxide species—either via simple rearrangement as in the case of the aluminum iso-propoxide trimer-tetramer system,

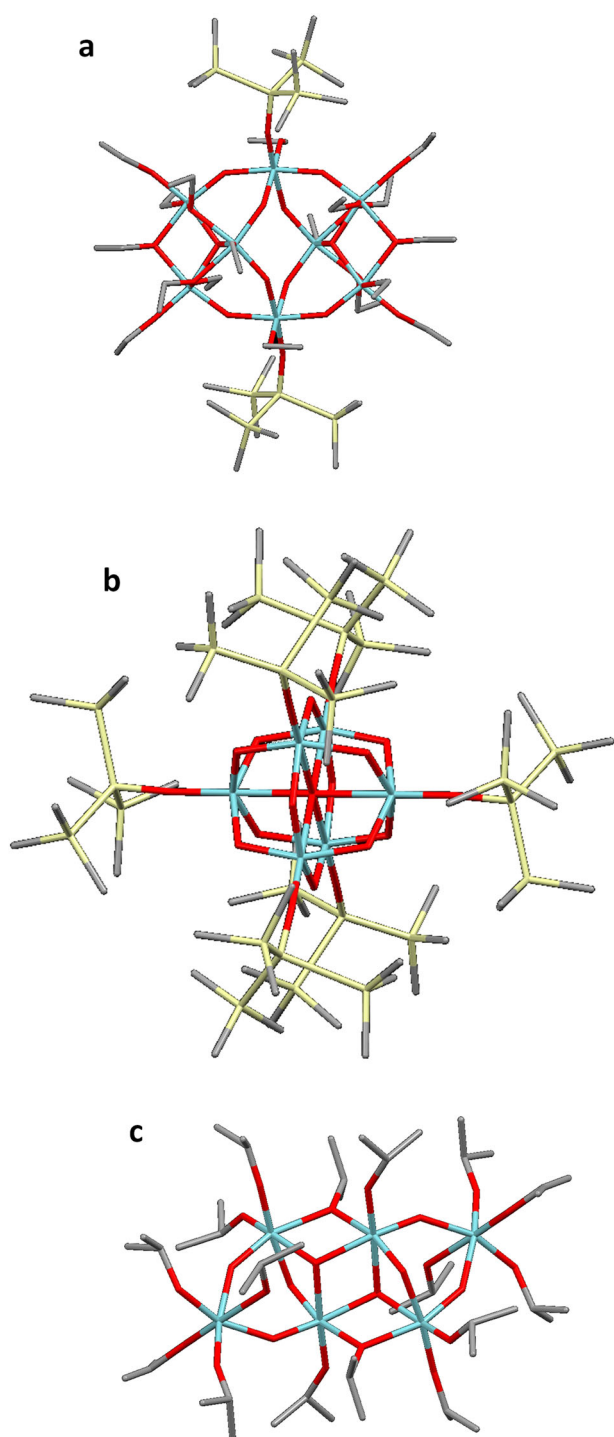


Fig. 3 Molecular structures of $\text{Nb}_8\text{O}_{10}(\text{OEt})_{18}(\text{OSi}(\text{SiMe}_3)_3)_2$ (a) [40], $\text{Nb}_6\text{O}_{13}(\text{OSi}(\text{SiMe}_3)_3)_6\text{H}_2$ (b) [40] and $\text{Nb}_6\text{O}_8(\text{O}^i\text{Pr})_{14}(\text{O}^i\text{PrOH})_2$ (c) [42]

where a kinetically slow $[\text{Al}(\text{OR})_3]_3 \rightleftharpoons [\text{Al}(\text{OR})_3]_4$ equilibrium is shifted [43], or by a change in the ligand composition via ether [11–13] or ester elimination [9, 10]. In structural transformations on heating of titanium and zirconium-titanium paperbags, there may occur the “flashes” of structural resemblance between smaller oxo-

complexes and fragments of the bigger ones [44–46], but just as in the case of Nb(V) they result from mere coincidence.

Unfortunately, the interest in photo and especially photo electro catalysis, in particular, for water splitting has led to an unexpected development based on a belief in the cluster nature of titanium oligonuclear oxo-alkoxide species. In a growing wave of publications, new exciting oxo-alkoxide structures modified by carboxylate, phenoxide, phosphonate ligands, etc. were prepared by solvothermal synthesis, characterized and then put into aqueous medium assuming that they remain intact and that their photocatalytic and photoelectrocatalytic properties observed for derived materials can be attributed to the structurally characterized precursor molecules. This, according to the accumulated knowledge about the actual reactivity of such species, is most probably, never true. Solvothermal synthesis does not provide these very reactive species with any superficial stability. Their structures follow the same motifs as those produced by room temperature hydrolysis. The reactivity of a large number of such complexes in either hot or cold water has been investigated quite thoroughly and showed transformation into ligand-capped TiO_2 . The process was traced for carboxylate [47], phenoxide [48] and alkyl phosphonate [35] bearing oxo-alkoxide complexes, and revealed everywhere the same pattern—topotactic transformation with preserved outer shape and size of original crystals, but with internal densification, resulting in the formation of TiO_2 nanoparticles with an anatase core structure (Fig. 4).

In the cases where salts, featuring oligonuclear oxo-alkoxide cation and halogeno-metalate anion, were subjected to humidity or contact with water, the observed result was exactly the same [49]. To the best of our knowledge, there are actually very few alkoxides featuring resistance to water, such as $\text{Re}_4\text{O}_2(\text{OMe})_{16}$ or its higher oxidation state analog $\text{Re}_4\text{O}_6(\text{OMe})_{12}$ [50]. It is worth noting that this latter paperbag compound forms on thermal condensation of a true cluster $\text{Re}_2\text{O}_3(\text{OMe})_6$, demonstrating that denser packing in a bigger molecule may offer better stabilization than a metal-metal bond. However, the origin of the hydrolytic stability of these rhenium species is not the cluster nature, but the dense packing of molecules rendering it hydrophobic, impenetrable for water. The structures that are not accessible to water would apparently not be reactive in photoelectrochemical water splitting (see, for example, [51]). In many cases, the reported results directly indicate the transformation to surface-modified titania, as in the case where different salicylate substituted titanium oxo-alkoxides have all demonstrated exactly the same photoelectrocatalytic activity (originating supposedly from formation of the same kind of salicylate-capped anatase) [52].

In summary—there is a challenge: in all cases, where transformations of these so-called oxo-alkoxide “clusters”

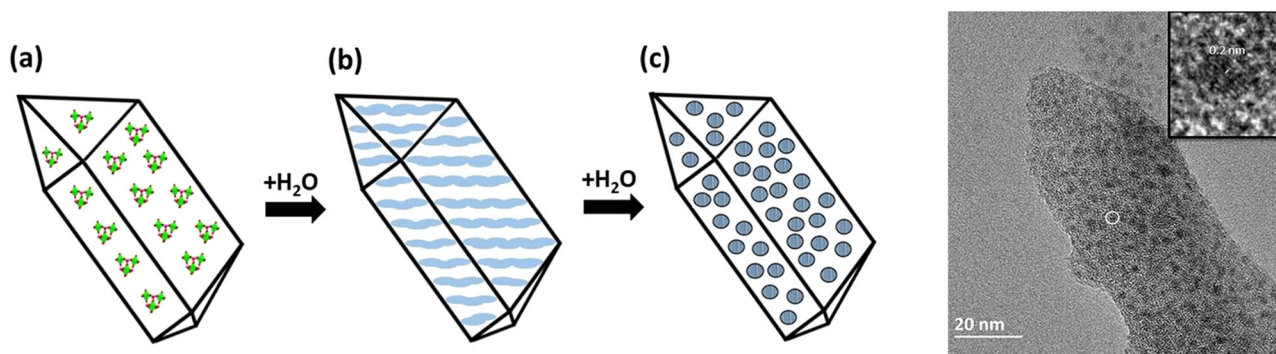


Fig. 4 Transformation of an (oxo) alkoxide crystal to crystalline anatase particles on topotactic hydrolysis in water: Addition of water to the molecular precursor crystal **(a)** causes hydrolysis and contraction of the crystal structure, leading to densification with formation of the amorphous lamellar structures **(b)**. Randomly scattered crystalline (anatase) nuclei emerge in the disordering amorphous phase upon further hydrolysis **(c)**. Reprinted with permission from ref. 35

have actually been followed, they resulted in formation of (surface-capped) nano titania, which was apparently responsible for the catalytic properties. In my opinion, the Sol-Gel and, more broadly, Inorganic Chemistry community needs to reflect on this in two ways. One reasonable measure is to require the authors in all cases, where preserved or “partly condensed” structure of an oxo-alkoxide oligonuclear complex is postulated [53], to provide convincing high-resolution microscopy (TEM, AFM) and/or structure-sensitive X-ray spectroscopy evidence for the nature of their material after contact with aqueous medium. This, however, will not be sufficient. Something needs to be done with the misuse of the word “cluster” itself. In English, this (for a non-native-English speaker) beautifully sounding word, has a rather clear meaning, evoking an image of a cluster of grapes or a cluster of wheat—a structure bound on the inside by connections and branches. In a molecule, these are metal-metal bonds. For structures emerging not due to internal bonding, but as a result of external molecular (self-)assembly forces such as dense packing and minimization of the surface energy, we need a different term with an unequivocal everyday life image to relate to. A different kind of object needs a different name. My proposal would be a “paperbag” (Fig. 5).

The need for a separate term lies in the expectations for the behavior. Both clusters and paperbags can have different stability, but naming something a cluster induces expectation of a stable cluster behavior. Naming an object a paperbag will work as an apparent alarm for avoiding the pitfalls described above.

Oligonuclear oxo-alkoxide complexes and poly-oxo-metalates, not behaving as clusters and generally not being good subjects of study in photo electrochemical behavior, are however excellent instrument for providing insights into the surface chemistry of oxide nanoparticles, and are especially valuable for understanding of the mineral nanoparticle interactions with biologically active species such as

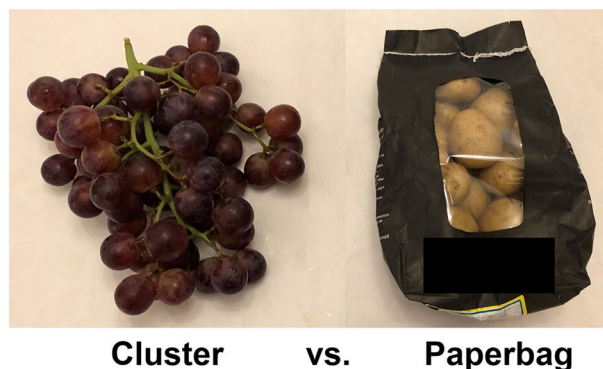


Fig. 5 Visual references for the classic term cluster and the new complementing one—paperbag

medicines and bio-molecules, phospholipids, peptides and nucleotides. Analysis of structure and bonding in the paperbag species provides a strong background for theoretical modeling of mineral nanoparticle—biomolecule interaction, such as, for example, strong specific binding to viral proteins, potentially contributing to anti-viral activity [54].

4 Conclusion

Oligonuclear complexes without metal-metal bonding are behaving similarly to a bag of paper filled with potatoes or apples. As far as external forces remain the same—the content stays in it. If the conditions change—we can pour over a part of the content or contents of several bags into a new one. If we put a bag with potatoes into a bucket of water—it will crack and offer us a densely packed pile on the bottom—a reasonable visual analogy of a metal oxide nano crystal. The paperbag chemistry is exciting and can enable us to learn a lot about oxide nanoparticles. However, it is not cluster chemistry and, in my opinion, should not be treated as such.

Acknowledgements This work was supported by the grant of the Swedish Research Council (Vetenskapsrådet) 2018-03811.

Funding Open access funding provided by Swedish University of Agricultural Sciences.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Cotton FA, Haas TE (1964) A molecular orbital treatment of the bonding in certain metal atom clusters. *Inorg Chem* 3:10–17
- Chisholm MH (2008) Frank Albert cotton. *Biogr Mem Fell R Soc* 54:95–115
- Bertrand JA, Cotton FA, Dollase WA (1963) The metal-metal bonded, polynuclear complex anion in CsReCl_4 . *J Am Chem Soc* 85:1349–1350
- Kamiguchi S, Mori T, Watanabe M, Suzuki A, Kodomari M, Nomura M, Iwasawa Y, Chihara T (2006) Retention of the octahedral metal framework of Nb and Mo halide clusters in catalytic decomposition of phenyl acetate to phenol and ketene. *J Mol Catal A Chem* 253:176–186
- Pinkard A, Champsaur AM, Roy X (2018) Molecular clusters: nanoscale building blocks for solid-state materials. *Acc Chem Res* 51:919–929
- Hoffmann R (1971) Interaction of orbitals through space and through bonds. *Acc Chem Res* 4:1–9
- Maillet JB, Boutin A, Buttefey S (1998) From molecular clusters to bulk matter. I. Structure and thermodynamics of small CO_2 , N_2 , and SF_6 clusters. *J Chem Phys* 109:329–337
- Schubert U (2003) Sol-gel processing of metal compounds. In: McCleverty, J.A., Meyer, T.J. (eds.) *Comprehensive coordination chemistry II*, Pergamon, Oxford, 7: 629–656
- Caruso J, Hampden-Smith MJ, Rheingold AL, Yap G (1995) Ester elimination versus ligand exchange: the role of the solvent in tin-oxo cluster-building reactions. *J Chem Soc Chem Comm* 1995:157–158
- Caruso J, Roger C, Schwertfeger F, Hampden-Smith MJ, Rheingold AL, Yap G (1995) Solvent-dependent ester elimination and ligand exchange reactions between trimethylsilyl acetate and tin(IV) tetra-tert-butoxide. *Inorg Chem* 34:449–453
- Turova NY, Kessler VG, Kucheiko SI (1991) Molybdenum and tungsten(VI) bimetallic alkoxides. Decomposition accompanied by dialkyl ether elimination. *Polyhedron* 10:2617–2628
- Kessler VG, Nikitin KV, Belokon' AI (1998) A new argument in favor of ether elimination mechanism. *Polyhedron* 17:2309–2311
- Pazik R, Tekoriute R, Håkansson S, Wiglusz R, Streck W, Seisenbaeva GA, Gun'ko YK, Kessler VG (2009) Precursor and solvent effects in the non-hydrolytic synthesis of complex oxide nanoparticles for bio-imaging applications by the ether elimination (Bradley) reaction. *Chem Eur J* 15:6820–6826
- Rominger KM, Nestor G, Eriksson JE, Seisenbaeva GA, Kessler VG (2019) Complexes of Keggin POMs $[\text{PM}_{12}\text{O}_{40}]^{3-}$ (M = Mo, W) with GlyGly peptide and arginine – crystal structures and solution reactivity. *Eur J Inorg Chem* 2019:4297–4305
- Kessler VG, Spijksma GI, Seisenbaeva GA, Håkansson S, Blank DHA, Bouwmeester HJM (2006) New insight in the role of modifying ligands in the sol-gel processing of metal alkoxide precursors: A possibility to approach new classes of materials. *J Sol-Gel Sci Tech* 40:163–179
- Cheng K, Chhor K, Brinza O, Vrel D, Kanaev A (2017) From nanoparticles to bulk crystalline solid: nucleation, growth kinetics and crystallisation of mixed oxide $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ nanoparticles. *CrystEngComm* 19:3955–3965
- Cheng K, Chhor K, Kanaev A (2017) Solvent effect on nucleation-growth of titanium-oxo-alkoxy nanoparticles. *Chem Phys Lett* 672:119–123
- Seisenbaeva GA, Kessler VG (2014) Precursor directed synthesis – “molecular” mechanisms in the Soft Chemistry approaches and their use for template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures. *Nanoscale* 6:6229–6244
- Veith M, Mathur S, Lecerf N, Huch V, Decker T, Beck HP, Eiser W, Haberkorn R (2000) Sol-gel synthesis of nano-scaled BaTiO_3 , BaZrO_3 and $\text{BaTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ oxides via single-source alkoxide precursors and semi-alkoxide routes. *J Sol-Gel Sci Tech* 15:145–158
- Seisenbaeva GA, Gohil S, Kessler VG (2004) Influence of heteroligands on the composition, structure and properties of homo- and heterometallic zirconium alkoxides. Decisive role of thermodynamic factors in their self-assembly *J Mater Chem* 14:3177–3190
- Kessler VG (2013) Single source precursor approach. hydrolysis mechanisms in organic media. In: Schneller, T.; Waser, R.; Kosec, M.; Payne, D. (eds.) *Chemical Solution Deposition of Functional Oxide Thin Films*, Springer-Verlag, Wien, 71–92
- Bradley DC, Holloway H (1962) Metal oxide alkoxide polymers. PART V. The Hydrolysis of some Alkoxides of Tin (IV), Cerium (IV), and Uranium (V) *Can J Chem* 40:1176–1182
- Chisholm MH, Huffman JC, Kirkpatrick CC, Leonelli J, Foiling K (1981) Metal Alkoxides—Models for Metal Oxides. 1. Preparations and Structures of Hexadecaalkoxytetratungsten Compounds, $\text{W}_4(\text{OR})_{16}$, Where R = Me and Et, and Octaoxotetraisopropoxytetrapyridinotetramolybdenum, $\text{Mo}_4(\text{O})_4(\text{mu-O})_2(\text{mu}_3\text{-O})_2(\text{O-i-Pr})_2(\text{mu-O-i-Pr})_2(\text{py})_4$. *J Am Chem Soc* 103:6093–6099
- Chisholm MH, Foiling K, Huffman JC, Rothwell IP (1982) Metal Alkoxides: Models for Metal Oxides. 2.1 Addition of Ethyne, Propyne, and 2-Butyne to $\text{Mo}_2(\text{OR})_6$ ($\text{M} \equiv \text{M}$) Compounds (R = t-Bu, i-Pr, and Ne). Characterization of μ -Alkyne and μ - C_4H_4 Adducts and an Evaluation of Their Role in Alkyne Oligomerization Reactions. *J Am Chem Soc* 104:4389–4399
- Chisholm MH, Foiling K, Hoffman DM, Huffman JC (1984) Metal alkoxides-models for metal oxides. 4. alkyne adducts of ditungsten hexaalkoxides and evidence for an equilibrium between dimetallatetrahedrane and methylidyne metal complexes: $\text{W}_2(\text{mu-C}_2\text{H}_2) \rightleftharpoons 2\text{W} \equiv \text{CH}$. *J Am Chem Soc* 106:6794–6805
- Campana CF, Chen YW, Day VW, Klemperer WG, Sparks RA (1996) Polyoxotitanates join the Keggin family: synthesis, structure and reactivity of $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^+]_{17}$. *J Chem Soc Dalton Trans* 1996:691–702

27. Turova NY, Turevskaya EP, Kessler VG, Yanovskaya MI (1994) Oxoalkoxides—True precursors of complex oxides. *J Sol-Gel Sci Tech* 2:17–23
28. Coppens P, Chen Y, Trzop E (2014) Crystallography and properties of polyoxotitanate nanoclusters. *Chem Rev* 114:9645–9661
29. Galkina OL, Ivanov VK, Agafonov AV, Seisenbaeva GA, Kessler VG (2015) Cellulose nanofiber–titania nanocomposites as potential drug delivery systems for dermal applications. *J Mater Chem B* 3:1688–1698
30. Galkina OL, Önnby K, Huang P, Ivanov VK, Agafonov AV, Seisenbaeva GA, Kessler VG (2015) Antibacterial and photochemical properties of cellulose nanofiber–titania nanocomposites loaded with two different types of antibiotic medicines. *J Mater Chem B* 3:7125–7134
31. Seisenbaeva GA, Melnyk IV, Hedin N, Chen Y, Eriksson P, Trzop E, Zub YL, Kessler VG (2015) Molecular insight into the mode-of-action of phosphonate monolayers as active functions of hybrid metal oxide adsorbents. Case study in sequestration of rare earth elements. *RSC Adv* 5:24575–24585
32. Mezy A, Vardanyan A, Garcia A, Schmitt C, Lakić M, Krajnc S, Daniel G, Kořak A, Lobnik A, Seisenbaeva GA (2021) Long-chain ligand design in creating magnetic nano adsorbents for separation of REE from LTM. *Sep Purif Technol* 276:119340
33. Turova NY, Turevskaya EP, Kessler VG, Yanovskaya MI (2002) *The Chemistry of Metal Alkoxides*. Springer, New York
34. Kessler VG (2003) Molecular structure design and synthetic approaches to the heterometallic alkoxide complexes (soft chemistry approach to inorganic materials by the eyes of a crystallographer). *Chem Comm* 2003:1213–1222
35. Svensson FG, Daniel G, Tai CW, Seisenbaeva GA, Kessler VG (2020) Titanium phosphonate oxo-alkoxide “clusters”: solution stability and facile hydrolytic transformation into nano titania. *RSC Adv* 10:6873–6883
36. Spijksma GI, Seisenbaeva GA, Bouwmeester HJM, Blank DHA, Kessler VG (2009) The molecular composition of non-modified and acac-modified propoxide and butoxide precursors of zirconium and hafnium dioxides. *J Sol-Gel Sci Tech* 51:10–22
37. Spijksma GI, Seisenbaeva GA, Bouwmeester HJM, Blank DHA, Kessler VG (2013) Zirconium and hafnium tert-butoxides and tert-butoxo- β -diketonate complexes – isolation, structural characterization and application in the one-step synthesis of 3D metal oxide nanostructures. *Polyhedron* 53:150–156
38. Bradley DC, Chakravarti BN, Chatterjee AK, Wardlaw W, Whitley A (1958) Niobium and tantalum mixed alkoxides. *J Chem Soc* 1958:99–101
39. Kessler VG, Turova NY, Yanovsky AI, Belokon’ AI, Struchkov YT (1991) The structure of $Nb_8O_{10}(OEt)_{20}$ and the nature of the crystalline oxoalkoxides. *Russ J Inorg Chem* 36:938–944
40. Boyle TJ, Sears JM, Perales D, Cramer RE, Lu P, Chan RO, Hernandez-Sanchez BA (2018) Synthesis and characterization of tris(trimethylsilyl)siloxide derivatives of early transition metal alkoxides that thermally convert to varied ceramic–silica architecture materials. *Inorg Chem* 57:8806–8820
41. Bakker TMA, Mathew S, Reek JNH (2019) Lindqvist polyoxometalates as electrolytes in p-type dye sensitized solar cells. *Sustain Energy Fuels* 3:96–100
42. Seisenbaeva GA, Baranov AI, Shcheglov PA, Kessler VG (2004) Isolation, X-ray single crystal and theoretical study of quinquevalent metal oxoisopropoxides, $Nb_6O_8(^iPrO)_{14}(^iPrOH)_2$ and $Re_4O_6(O^iPr)_{10}$. *Inorg Chim Acta* 357:468–474
43. Turova NY, Kozunov VA, Yanovskii AI, Bokii NG, Struchkov YT, Tarnopolskii BL (1979) Physico-chemical and structural investigation of aluminium isopropoxide. *J Inorg Nucl Chem* 41:5–11
44. Artner C, Czakler M, Schubert U (2015) New zirconium and zirconium–titanium oxo cluster types by expansion or metal substitution of the octahedral Zr_6O_8 structural motif. *Inorg Chim Acta* 432:2028–212
45. Artner C, Koyun A, Schubert U (2015) A heterobimetallic copper–titanium oxo cluster with a new structural motif. *Monatsh Chem* 146:1777–1780
46. Schubert U (2021) Titanium-Oxo Clusters with Bi- and tridentate organic ligands: gradual evolution of the structures from small to big. *Chem Eur J* 27:11239–11256
47. Seisenbaeva GA, Ilina E, Håkansson S, Kessler VG (2010) A new concept for titanium oxo-alkoxo-carboxylates’ encapsulated biocompatible time temperature food indicators based on arising, not fading color. *J Sol-Gel Sci Tech* 55:1–8
48. Svensson F, Seisenbaeva GA, Kessler VG (2017) Mixed-ligand titanium “oxo clusters”: structural insights into the formation and binding of organic molecules and transformation into oxide nanostructures on hydrolysis and thermolysis. *Eur J Inorg Chem* 2017:4117–4122
49. Fu MY, Wang HY, Zhai HL, Zhu QY, Dai J (2021) Assembly of a titanium-oxo cluster and a bismuth iodide cluster, a single-source precursor of a p-n-type photocatalyst. *Inorg Chem* 60:9589–9597
50. Seisenbaeva GA, Shevelkov AV, Kloos L, Gohil S, Tegenfeldt J, Kessler VG (2001) Homo- and hetero-metallic rhenium oxo-methoxide complexes with a $M_4(\mu-O)_2(\mu-OMe)_4$ planar core—a new family of metal alkoxides displaying a peculiar structural disorder. Preparation and X-ray single crystal study. *Dalton Trans* 2001:2762–2768
51. Zhu BC, Hong QL, Yi XF, Zhang J, Zhang L (2020) Supramolecular co-assembly of the Ti_8L_{12} cube with $[Ti(DMF)_6]$ species and Ti_{12} -Oxo cluster. *Inorg Chem* 59:8291–8297
52. Zhang K, Du SW (2021) Studies of high-nuclearity lanthanide–titanium oxo clusters: Structure and properties. *Inorg Chim Acta* 528:120621
53. Ge CY, Hou JL, Zhou ZY, Zhu QY, Dai J (2022) A cyclic titanium-oxo cluster with a tetrathiafulvalene connector as a precursor for highly efficient adsorbent of cationic dyes. *Inorg Chem* 61:486–495
54. Agback P, Agback T, Dominguez F, Frolova EI, Seisenbaeva GA, Kessler VG (2022) Site-specific recognition of SARS-CoV-2 nsp1 protein with a tailored titanium dioxide nanoparticle – elucidation of the complex structure using NMR data and theoretical calculation. *Nanoscale Adv* 4:1527–1532
55. Gumerova NI, Rompel A (2020) Polyoxometalates in solution: speciation under spotlight. *Chem Soc Rev* 49:7568–7601
56. Bradley DC, Hursthouse MB, Rodesiler PF (1968) The structure of a crystalline niobium oxide ethoxide, $Nb_8O_{10}(OEt)_{20}$. *Chem Comm* 1968:1112–1113