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INVITED PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

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

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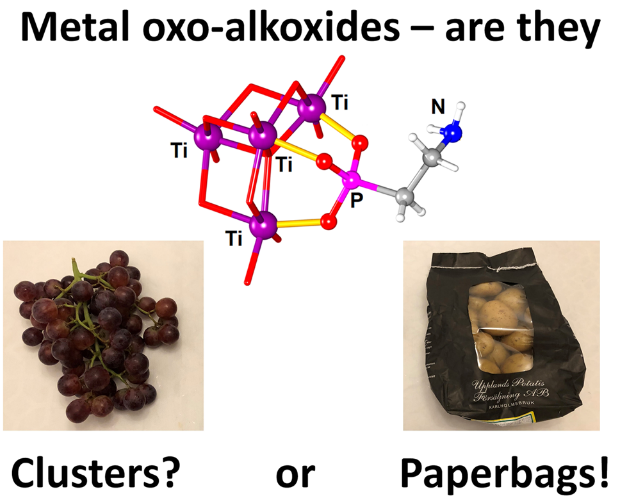
Abstract

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



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

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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 $Re_3Cl_9(H_2O)_3$ 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, $[Mo_6Cl_8]^{4+}$ 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 $(CO_2)_{13}$ [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 retransform 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 $[PW_{12}O_{40}]^{3-}$ in MilliQ water was found to be 6.96×10^{-3} s giving the reaction halftime of 100 s—a seemingly quick reaction [14].

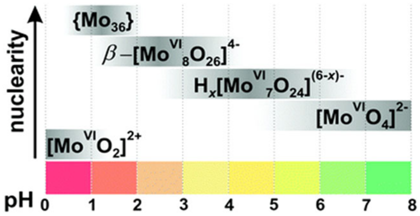

Fig. 1 Phase diagram for isopoly-molybdate compounds' formation in solution with Mo concentration in the range 0.1–0.4 M. Reprinted with permission from [55]

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 $[BaZr(OH)(O^iPr)_5(^iPrOH)_2]_2$, 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 $Ba(O^tBu)_2$ with the industrially available $Zr(O^tBu)_4$. Then, it was hydrolyzed by a stoichiometric amount of water and later subjected to ligand exchange with an excess of ^iPrOH [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 ^nPrOH. Toluene was purified via distillation over lithium aluminum hydride.

2.1 Preparation and synthesis

Niobium n-propoxide, $Nb_2(O^nPr)_{10}(l)$, 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-smeared 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, $Nb_2(OEt)_{10}(l)$, 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 $Nb_2(O^nPr)_{10}(l)$.

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 2Theta range 2.68–50.05° using graphite-monochromated MoKα radiation (sealed tube), $\lambda = 0.71073$ Å. Integration of the data was performed with Bruker SAINTPLUS and data reduction with the Bruker SADABS program. $\mathbf{C_{60}H_{140}Nb_8O_{30}}$, M = 2084.99 Da, Orthorhombic, Space group Pbca, $a = 22.314(4)$, $b = 17.157(3)$, $c = 24.459(4)$ Å, $V = 9364(3)$ Å^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 > 2sigma(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 spontaneous formation of oxo-substituted species has actually been proved for Nb(V) alkoxides earlier [38, 39].

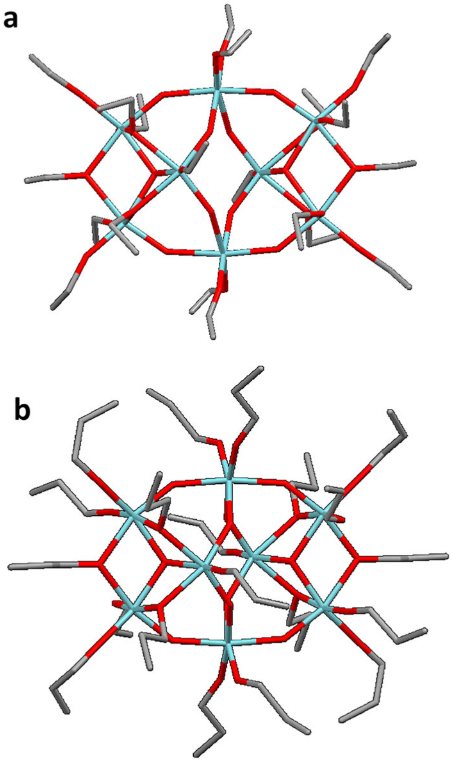

Fig. 2 Molecular structures of $Nb_8O_{10}(OEt)_{20}$ (**a**) [39, 56] and $Nb_8O_{10}(O^nPr)_{20}$ (**b**, this work)

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 $Nb_8O_{10}(OEt)_{20}$ the addition of 2 equivalents of $HOSi(SiMe_3)_3$ [40] gives $Nb_8O_{10}(OEt)_{18}(OSi(SiMe_3)_3)_2$, making a "flash" of cluster behavior, but the excess of the same ligand without heating(!) produces $Nb_6O_{13}(OSi(SiMe_3)_3)_6H_2$, 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,

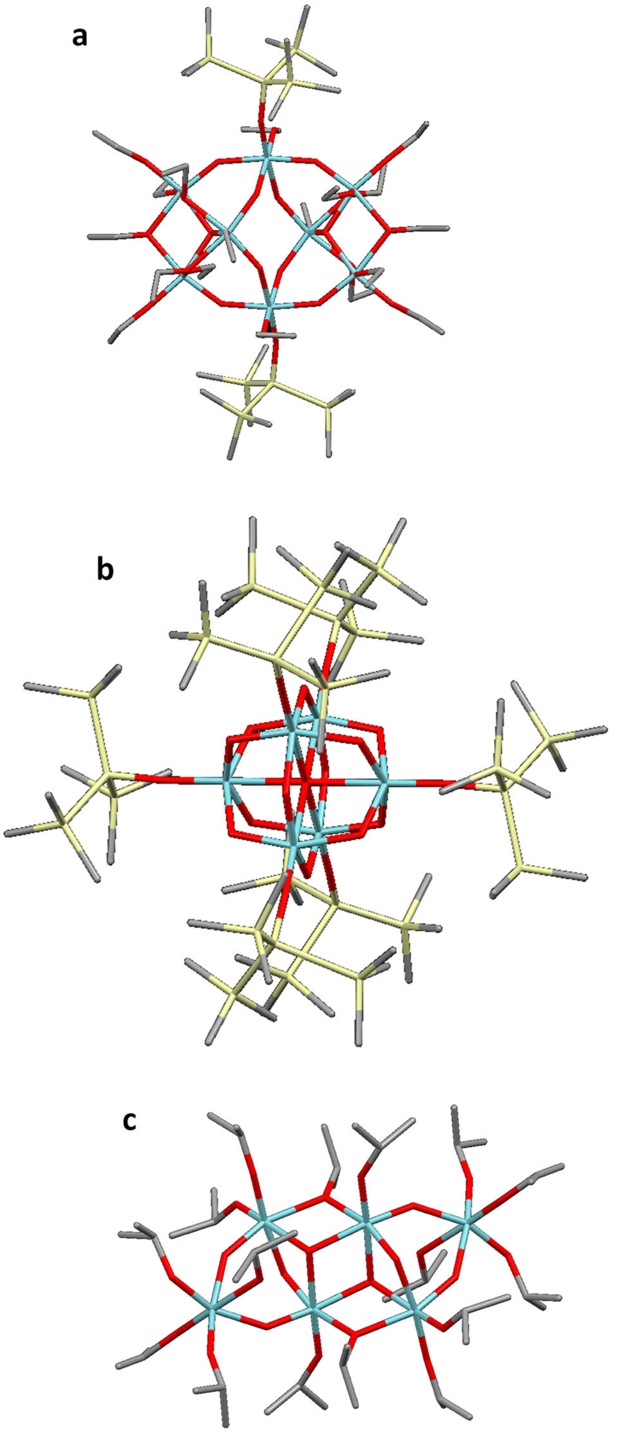

Fig. 3 Molecular structures of $Nb_8O_{10}(OEt)_{18}(OSi(SiMe_3)_3)_2$ (**a**) [40], $Nb_6O_{13}(OSi(SiMe_3)_3)_6H_2$ (**b**) [40] and $Nb_6O_8(O^iPr)_{14}(^iPrOH)_2$ (**c**) [42]

where a kinetically slow $[Al(OR)_3]_3 \rightleftarrows [Al(OR)_3]_4$ 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 $Re_4O_2(OMe)_{16}$ or its higher oxidation state analog $Re_4O_6(OMe)_{12}$ [50]. It is worth noting that this latter paperbag compound forms on thermal condensation of a true cluster $Re_2O_3(OMe)_6$, 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”

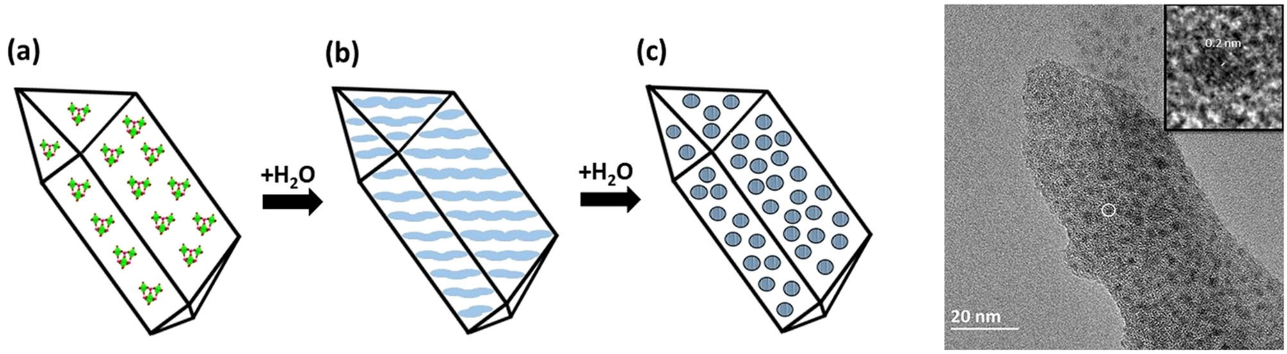

Fig. 4 Transformation of an (oxo) alkoxide crystal to crystalline anatase particles on topotactic hydrolysis in water: Addition of water to the molecular precursor crystal (**a**) causes hydrolysis and contraction of the crystal structure, leading to densification with formation of the amorphous lamellar 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-oxometalates, 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 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].

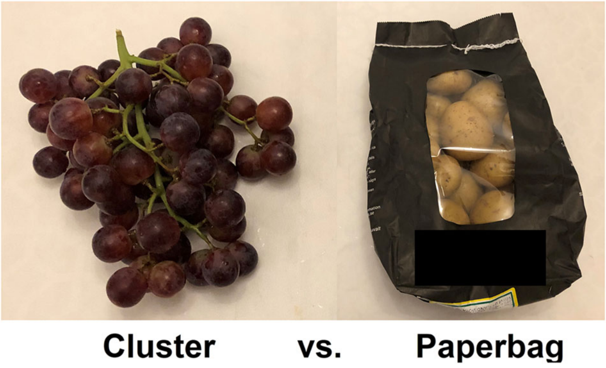
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Fig. 5 Visual references for the classic term cluster and the new complementing one—paperbag

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.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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