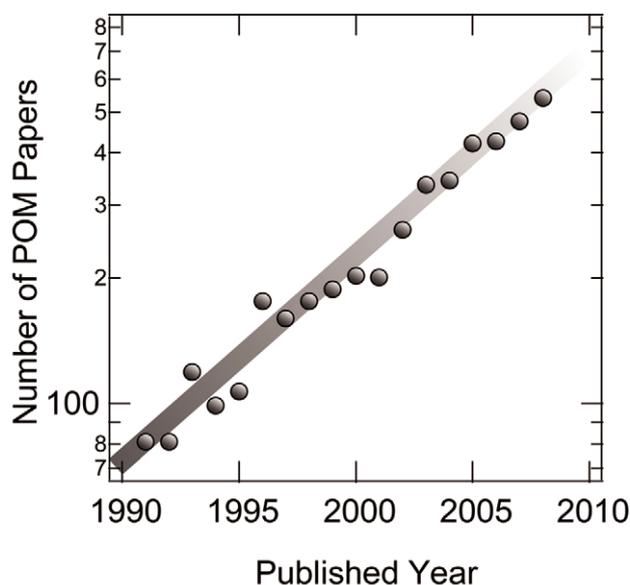


# Oxo-Metalate Building Blocks: Conceptual Competitors for Tetravalent Carbon?

In honor of Prof. Michael T. Pope for over half a century of excellent contributions to polyoxometalate chemistry

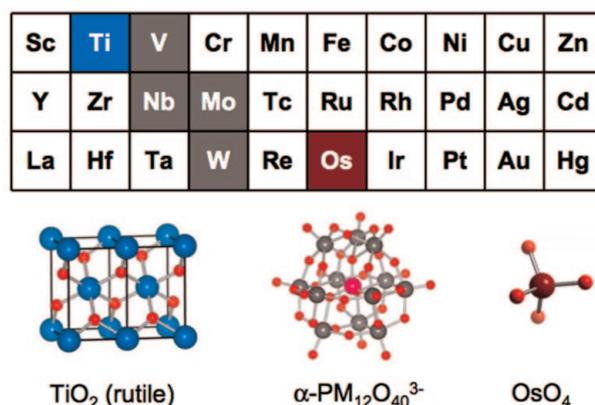
The versatility of chemistry based on tetravalent carbon is unparalleled. Small organic molecules are readily modifiable by traditional serial syntheses and/or combinatorial libraries, and systematically linked together by Nature; in the laboratory, polymeric structures ranging from biological macromolecules to functional solid-state materials can be generated. Meanwhile, molecular or oligomeric building blocks can be designed to self-assemble into supramolecular structures, including increasingly sophisticated “nano-reactors”<sup>[1,2]</sup> that link molecular to nano-scale worlds. When combined with metal cations, organic linkers can generate (now predictable) metal-organic frameworks (MOFs) with large and controllable pore sizes.<sup>[3]</sup> On the other hand in 1991, Pope and Müller noted in a review that metal oxide cluster anions (polyoxometalates, or POMs) “form a class of inorganic compounds that is unmatched in terms of molecular and electronic structural versatility, reactivity, and relevance to analytical chemistry, catalysis, biology, medicine, geochemistry, materials science, and topology.”<sup>[4]</sup>



**Figure 1.** Numbers of publications involving metal-oxide cluster anions (POMs) as a function of year. The linear trend, obtained by using a logarithmic scale on the y-axis, reveals two decades of exponential growth. Reproduced with permission from ref. [5].

Now, after two decades of exponential growth in publications (Figure 1),<sup>[5]</sup> we have the following situation: Discrete simple oxoanions of the early transition metals (mainly V, Nb, Mo, and W; Figure 2) in their highest ( $d^0$  or  $d^1$ ) oxidation states can be “assembled” to generate functional metal–oxygen-based polynuclear structures that come ever closer to paralleling the range of molecular, macromolecular, supramolecular, and solid-state compounds normally associated with organic and organometallic chemistry. Bridging  $O^{2-}$  (and sometimes  $OH^-$ ) ligands are responsible for the POM type cluster formations, while terminal  $O^{2-}$  ligands limit their nuclearities.

Many POMs possess a fascinating versatility of reversible redox chemistry<sup>[4]</sup> the knowledge of which, for many years, was used together with potentiometric determinations of  $H^+$  concentrations to document the formation of polynuclear species in aqueous solutions.<sup>[6]</sup> Upon reduction by one or more electrons, special POMs absorb strongly in the visible region, thereby giving rise to colors ranging from blue to red/brown which led to the early use of POMs as “stains”, for example, for several applications even in medicinal diagnosis (see also ref. [7]).

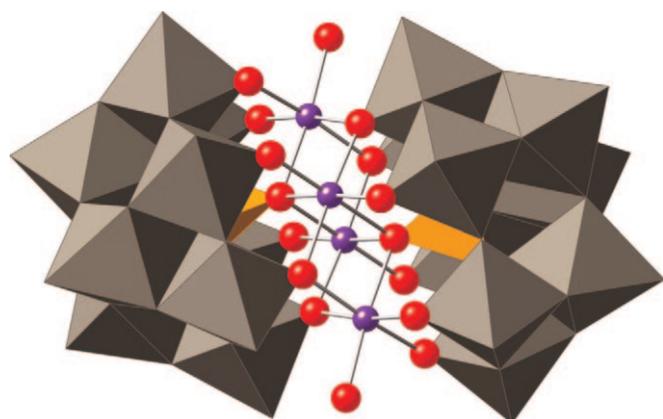


**Figure 2.** Metal-oxide structures (examples).  $TiO_2$  (rutile; bottom left), with only *bridging* oxido ligands (in red), is a refractory solid-state material with a melting point of  $1850^\circ\text{C}$ .  $OsO_4$  (bottom right), with only *terminal* oxido ligands (red), is a highly volatile solid. Metal oxide cluster anions, such as the famous  $\alpha$ -Keggin ion ( $M = \text{Mo}, \text{W}$ ; bottom center), lie between these limiting structures. They possess both bridging and terminal oxido ligands, exist as discrete species, and are formed by the elements underlined in grey.

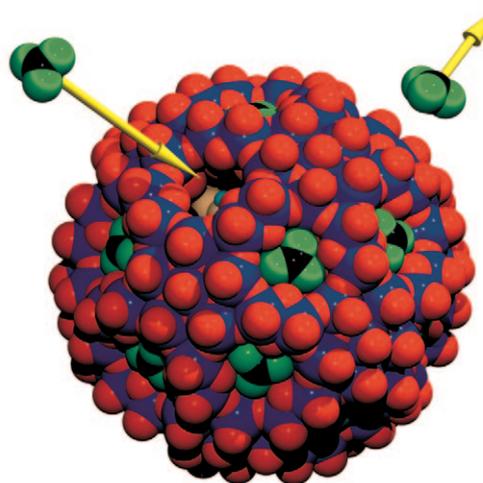
By the early 1980s, the application of NMR spectroscopy (especially in context with  $^{183}\text{W}$ ,  $^{51}\text{V}$ , and  $^{31}\text{P}$  nuclei), combined with technological advances that made single-crystal X-ray analysis faster and more accessible, led to a change with respect to how many scientists viewed the exciting metal-oxide cluster chemistry. It became increasingly apparent that this large family of molecular species could be characterized in both the solution and solid state with an ease and efficiency that had, until then, been limited to (especially) organic or organometallic compounds.

Moreover, the use of POMs as functional molecular analogues of solid-state metal oxides captured the imagination of new researchers with backgrounds in organic and organometallic chemistry, catalysis, and electronics. This inaugurated new directions in synthesis, leading to an explosion in reports of a variety of compounds for use in an expanding range of applications. This tendency was supported by the fact that POM reduction potentials, acidities, and other properties are relevant, for example, for green chemistry,<sup>[8]</sup> renewable energy (Figure 3),<sup>[9–11]</sup> or catalysis<sup>[12,13]</sup> (model compounds are also considered<sup>[14]</sup>).

Parallel to the above developments, the discovery of giant molybdenum/tungsten oxide clusters (obtained under reducing conditions according to a type of growth process) containing up to 368 metal atoms<sup>[15]</sup> was considered by the scientific community as a breakthrough because it was the route to new length scales and provided the option to discover a variety of new phenomena, including those related to processes under confined conditions. This refers especially to the porous spherical  $\text{Mo}_{132}$ -type capsules,<sup>[16]</sup> which interact specifically with the environment—for example, with different cations<sup>[17]</sup> and also larger species because of the flexibilities of the pores, as well as with themselves (see below). The capsules provide options, for example, of carrying out sphere-surface supramolecular chemistry at their 20 well-defined pores/host sites (Figure 4; see also ref. [17]),<sup>[18]</sup> and of perform-



**Figure 3.** A molecular water-oxidation catalyst comprised of two  $[\text{PW}_9\text{O}_{34}]$  ligands (grey, orange, and red) with four Co centers in between (purple); see ref. [9].



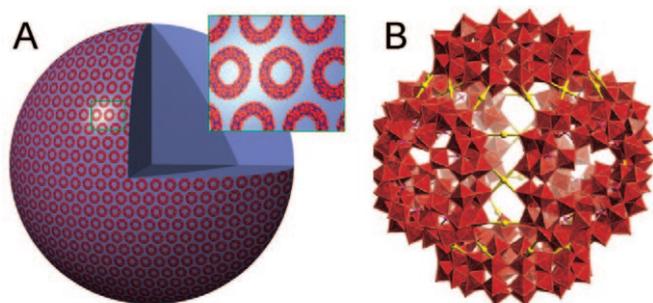
**Figure 4.** A porous metal-oxide based capsule of the type  $\text{Mo}_{132}$ . Supramolecular chemistry can be performed at the 20 flexible crown-ether type pores (hosts) with, for example, guanidinium cations (guests, in green/black); Mitra et al. ref. [18].

ing coordination chemistry in their cavities (ca. 2.5 nm diameter) as well as in and above their pores.

Importantly, the aforementioned giant complex inorganic macromolecules are stable, flexible,<sup>18</sup> and highly soluble in water, wherein they maintain their structure and functionality so that chemical reactions can be performed at specific sites, rendering them singularly equipped for the study of basic transport processes under confined conditions and to mimic biological processes; these materials “bring inorganic chemistry to life”.<sup>[19]</sup> Generally speaking, giant molybdate clusters exhibit an extraordinarily rich behavior pertinent to many additional aspects of contemporary chemical research.

Presently, there is ongoing research also in other directions, for example, in context with the self-assembly of the molybdenum-oxide based macroions to form a new type of hollow vesicles (Figure 5A),<sup>[20,21]</sup> and in the construction of increasingly sophisticated framework structures (e.g., with 1 nm diameter entrance pores and ca.  $7\text{ nm}^3$  cavities; Figure 5B).<sup>[22]</sup> Furthermore, combining POMs as building blocks<sup>[23]</sup> with cationic surfactants leads to the construction of interesting materials, like liquid crystals—this refers not only to the above-mentioned giant molybdenum-oxide based clusters (see, for instance, refs. [5], [23–26]). Three further topics of interest related to POM chemistry are: molecular magnetism,<sup>[27]</sup> nucleation processes in protein cavities,<sup>[28]</sup> and the fascinating aesthetic aspects.<sup>[29]</sup>

Molecule-by-molecule assembly is clearly an important challenge. Based on that, recent advances in metal-oxide cluster science provide new options for the design of self-assembling systems that can be controlled to provide a spectrum of increasingly larger and more complex structures, that is, from molecular- to (non-classical molecular



**Figure 5.** A hollow vesicle, ca. 90 nm diameter, formed by self-assembly of the molybdenum-oxide based  $\text{Mo}_{154}$  rings (A), and a section of an open-framework structure based on the linking of  $\{\text{W}_{48}\text{P}_3\}$  units (B).

type) micrometer-scale size domains. The metal-oxide based structures result from sophisticated control over reactions based on the simplest tetrahedral oxoanions of the type  $\text{MO}_4^{n-}$  or on larger ones like the important pentagonal building blocks.<sup>[30]</sup> These developments offer options for controlling structure and function—in principle analogous to activities in organic chemistry.

This is nicely demonstrated by the contributions included in this special issue, entitled, “Frontiers in Metal Oxide Cluster Science”. Although the number of articles included here is small relative to the many groups currently active in POM research, the present contributions provide authoritative perspectives on a number of important lines of research currently underway in this diverse and rapidly growing field.



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Guest Editor



Achim Müller

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