



### Polyoxometalate Nanostructures, Superclusters, and Colloids: From Functional Clusters to Chemical Aesthetics\*\*

Paul Kögerler and Leroy Cronin

It has often been stated that polyoxometalates (POMs) represent a class of molecules of almost unrivaled versatility, which results from their enormous structural diversity, range of sizes, tunable redox properties, and fascinating catalytic activity. These properties were very much in evidence at a recent four-day “International Symposium on Nano-structures and Physicochemical Properties of Polyoxometalate Superclusters and Related Colloid Particles” in Kanagawa (Japan), organized by T. Yamase, M. T. Pope, and A. Müller with the support of the JSPS, CREST, the Rigaku Corporation, and the Chemical Society of Japan. The previous conference in this series had taken place in 1999 at the Universität Bielefeld (Germany). POMs represent unique polymerizable entities that are often based on common structural fragments, or building blocks. This research area has

undergone an important transition from classical structural and coordination chemistry towards the chemistry of “smart”, “functional” materials, which may even have properties of artificial cells/porous capsules. There has been a dramatic increase in the number of interdisciplinary projects in a reasonably short period of time. The field also continues to surprise with new findings at a fundamental scientific level which open avenues for future research.<sup>[1–7]</sup>

The diverse and exciting nature of this field became apparent immediately from the opening lecture of F. Sécheresse (Université Versailles St-Quentin, France), who described interesting developments in the synthesis of discrete polyoxomolybdates and polyoxotungstates. In particular the careful use of simple, directing building blocks based on Mo<sup>V</sup> dimers of the form [Mo<sub>2</sub>O<sub>2</sub>(μ-E)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> (E = S or O) to produce an impressive array of larger cluster structures was demonstrated.<sup>[1]</sup> Sécheresse then described effectively how POM-based building blocks (this time lanthanide-functionalized ε Keggin anions) can be taken to the next level by linking complete molecular cluster anions with carboxylate ligands to networks of different topologies and dimensionalities, as well as strategies for the formation of “superclusters” by carefully considering how POM-based building blocks can be connected geometrically and chemically.

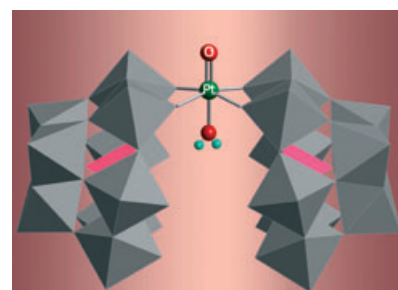
This concept was also a focus of M. T. Pope’s (Georgetown University, USA) review of general routes to ever larger POMs by using lacunary fragments. Pope also proposed the development of large clusters based on reduced polytungstate moieties, thereby applying concepts that are successfully used in polyoxomolybdate chemistry.<sup>[2]</sup> P. Gouzerh (Université Pierre et Marie Curie, France) extended the discussions on polytungstate-based moieties by presenting the special abilities of the hexavacant {P<sub>2</sub>W<sub>12</sub>} anion. This species readily cocondenses with 3d cations to form large and symmetrical assemblies of {P<sub>2</sub>W<sub>12</sub>} fragments that are supported by a {M<sub>4</sub>O<sub>6</sub>} core (M = Fe<sup>III</sup>).

The self-assembly of a range of polytungstate clusters was also explored by U. Kortz (Universität Bremen, Ger-

many), who showed some exciting new approaches to polytungstate systems by using novel linking groups, including a polyoxotungstate wheel [[β-Ti<sub>2</sub>SiW<sub>10</sub>O<sub>39</sub>]<sub>4</sub>]<sup>24-</sup>. In this case the use of Ti<sup>4+</sup> to connect the {W<sub>10</sub>}-based building blocks is key.<sup>[3]</sup> Recent developments in polyoxoniobate chemistry were presented by M. Nyman (Sandia National Laboratories, USA), who demonstrated how this field could be expanded from the {Nb<sub>6</sub>O<sub>19</sub>} Lindqvist ion to a variety of Keggin-based compounds, despite the considerable challenges faced in determining the correct conditions for the formation and isolation of these materials.

In one of several highlights of the conference C. Hill (Emory University, USA) presented a route to break through the “oxo wall” and stabilize a single (H<sub>2</sub>O)Pt=O moiety by using electron-withdrawing {PW<sub>9</sub>} building blocks as ligands to sandwich the Pt=O moiety. The resulting complex is the first discrete metal–oxo complex of a late transition metal (Figure 1).<sup>[4]</sup> Because such species are thought to represent intermediates in O<sub>2</sub> activation at platinum surfaces, this finding is of significant consequence and will surely spark extensive follow-up work.

The nanoscopic nature of POM-based clusters and their great potential as mesoporous materials were discussed by T. Yamase (Tokyo Institute of Technology, Japan), who showed how the photoreduction-induced self-assembly of molybdenum blue type polyoxomolybdates can be controlled by the incorporation of different Ln<sup>3+</sup> ions into the reaction system. This process leads to the formation of nanowheel structures



**Figure 1.** The structure of [O=Pt<sup>IV</sup>(H<sub>2</sub>O)(PW<sub>9</sub>O<sub>34</sub>)]<sup>16-</sup>. The [PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> ligands are represented by gray polyhedra (Pt green, O red, H blue-green).<sup>[4]</sup>

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of the type described by Müller and co-workers, but also mediates the self-assembly of nanotubes comprised of stacked  $\{\text{Mo}_{154}\}$  wheels, as well as the self-assembly of ellipsoidal Japanese-rice-cake-shaped nanorings.<sup>[5]</sup> The formation of Mo-based nanotubes is extraordinary, and the possibility of generating very long tubes from solution is tantalizing. The development of multifunctional and nanoporous materials was also explored in some detail (Hill, Yamase, Sécheresse, Errington, Aida), as well as the development of sophisticated catalysts (Hill, Mizuno).

The utilization of POM-based building blocks in the area of hybrid, conducting, and magnetic materials was discussed; it was illustrated how POMs can be very effectively incorporated into hybrid architectures with organic donors, such as tetrathiafulvalene, nitroxide radicals, and organometallic units (Ouahab). A notable development in this field was presented by E. Coronado (Universidad de Valencia, Spain) in the form of a hybrid material that demonstrates metallic conductivity down to 2 K and comprises a complex of the organic radical bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) and the  $\{\text{BW}_{12}\}$  Keggin anion. This result certainly shows the potential the field of POM-based hybrid materials holds for novel material properties.<sup>[6]</sup> In a further discussion L. Cronin (University of Glasgow, UK) presented several new POM architectures and routes to hybrid materials. Some of these POMs may be used in the development of POM-based components for molecular electronics and functional nanoscopic systems.

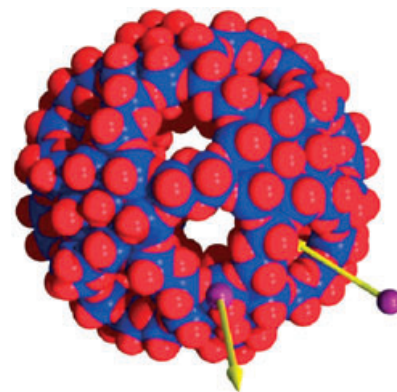
Polyoxometalates also serve as versatile frameworks for the generation of large and sometimes highly symmetrical spin arrays. Indeed, the interest in functionalized POMs that serve as novel magnetic molecules and materials is growing rapidly. P. Kögerler (Iowa State University and Ames Laboratory, USA) presented the latest developments in understanding the complex and rich magnetic behavior associated with, for example, magnetically substituted keplerate clusters, such as  $\{\text{Mo}_{72}\text{Fe}_{30}\}$ . H. Nojiri (Tohoku University, Japan) expanded on this topic and described the manipulation of the mag-

netic states of spin-frustrated clusters by pulsed magnetic fields.

The development of POM-based colloids and nanoparticles was also an important theme, as many of the participants are already able to synthesize molecular metal-oxide-like fragments effectively; POM-protected nanoparticles were also described (Tong, Cronin). T. Liu (Brookhaven National Laboratory, USA) suggested that the aggregation of cluster anions to giant vesicles in aqueous solution represents a “second solute state”. He has examined the assembly of giant molybdenum blue type wheels as well as keplerate spheres to partially monodisperse anionic spherical vesicles containing approximately 1000 monomers.<sup>[7]</sup> This phenomenon will certainly attract much attention in the future. In surface studies of POM clusters there have also been developments; indeed, the structure, stability, and stoichiometry of transition-metal oxides on surfaces is a tremendously interesting research area (Klemperer, Errington, Tong, Cronin), which is central to understanding many chemical processes.

The complex and demanding general structural analysis of nanometer-sized POMs by crystallographic techniques was described by H. Bögge (Universität Bielefeld), who outlined the various approaches to determine the structure of these sometimes protein-sized molecules. M. Henry (Université Louis Pasteur, France) expanded on the area of structural studies by discussing structural, computational, and NMR spectroscopic studies. The examination of confined water clusters and patches was also an important topic (Müller, Henry, Ozeki). Henry, inspired by the dramatically beautiful functional clusters of Müller, summed up some of the perspectives and expectations for this field in what must be the quote of the conference, with the phrase: “... these clusters exist in the hyper-super-supra-molecular-bio-nano-world of polyoxometalates!” A. Müller (Universität Bielefeld), whose research group produced, for example, the giant wheels (molybdenum blue), the  $\{\text{Mo}_{368}\}$  nanohedgehog, and nanosized porous spherical clusters (keplerates), took the audience through an inspiring, colorful, and sometimes philosophical journey in describing

how these ring species and the keplerates can serve as comparatively stable platforms for chemistry at the level of nanoparticles: For example, control over the molecular porosity of keplerates enables the stabilization of water clusters of different sizes inside these spherical polyoxomolybdate hosts. He then suggested that the keplerates could be described as artificial cells<sup>[8]</sup> and outlined perspectives for nanotechnology (Figure 2). The related POM



**Figure 2.** Schematic space-filling representation of the temperature-dependent reversible equilibrium of  $\text{Li}^+$ -ion binding observed for a keplerate species, a model of an “artificial cell” (Mo blue, O red, Li purple).<sup>[8]</sup>

chemistry allows access to different areas of chemistry that were simply not available before, such as the generation of protein-sized clusters, the formation of inorganic “cells”, and the examination of confined molecules in porous nanometer-sized capsules; a new type of “super-supramolecular chemistry” that can be extended down many avenues is also now possible.

The most satisfying aspect of this conference was the truly diverse and interdisciplinary nature of the work presented, yet almost all topics discussed were unified by the themes of utilizing POM-based building blocks and the quest to design architectures to produce functionality. It was also interesting to see how conceptual cross-fertilization in polyoxotungstate and polyoxomolybdate chemistry is providing inspiration. POM chemistry is an extraordinary area of science which touches an almost unprecedented number of other fields of chemistry and has provided many highlights in the past, both in the

academic and the public arenas. Based on this symposium, the future of polyoxometalate chemistry as a multifaceted and interdisciplinary subject shines bright, and is sure to deliver further inspiration and highlights.

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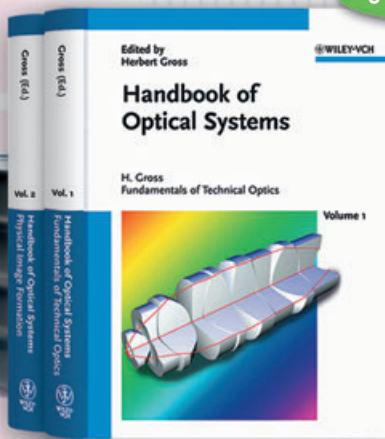
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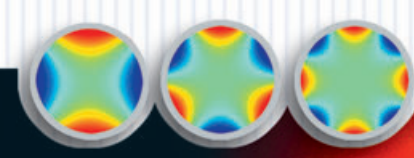
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