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Introduction: Polyoxometalates—Multicomponent Molecular Vehicles To Probe Fundamental Issues and Practical Problems

Early transition metal oxygen anion clusters (polyoxometalates or POMs for convenience) are a large and rapidly growing class of compounds. The first report of what we term a polyoxometalate dates back to Berzelius (1826).

These compounds presented significant conceptual and experimental challenges to Werner and the founding fathers of coordination chemistry and to many investigators since. It has only been with the advent of modern high-resolution and sophisticated instrumentation that the fundamental chemistry of these compounds has moved rapidly forward. Most POM molecular science (chemistry, physics, biology, and materials science) has been reported in the past few years.

Few, if any, other classes of compounds can be so extensively modified. Virtually all molecular properties that impact the utility of a class of compounds in catalysis, medicine, and materials science can be altered in POMs, many by methods that are now rational and defensible.

These properties include molecular composition, size, shape, charge density, redox potentials (ground and excited state), acidity, and solubility. (POMs can be rendered soluble in nearly all media from H_2O to hydrocarbons by choice of countercation(s) and/or by other approaches.)

The extreme variability of the accessible POMs derives in good measure from the point that most of the elements in the periodic table can be incorporated into the structural framework of these compounds, and a growing repertory of synthetic reactions exists for the substitution of one or more metal centers (p-, d-, or f-block), organic functions, or organometallic groups into a parent POM structure.

It is this remarkable degree of molecular tunability that has made POMs useful probes of fundamental structural and dynamic issues in chemistry and practically useful entities. Some of the fundamental problems addressed in recent research on POM systems include aspects of self-assembly and the genesis of metal oxides, magnetic interactions in large multicomponent systems, electron transfer in solution and at metal oxide interfaces, reactivity and selectivity in oxidation processes, modulation and catalysis of interfacial redox chemistry, mixed-valence chemistry/physics, excited-state processes in metal oxide-like materials, molecular recognition by multicenter inorganic species, and the interplay of solute−biomacromolecule association selectivity and the time- and dosing-dependent loss of chemotherapeutic agent efficacy (drug resistance).

On the utilitarian front, several catalytic processes involving POMs in both homogeneous and heterogeneous modes have recently been commercialized. In addition, other processes or technologies based on POM derivatives are in serious development.

In this volume we have endeavored to obtain a collection of articles that provides an in-depth coverage of selected topics of current intellectual or technical significance and simultaneously defines the breadth of the research now impacted by these clusters. While a few topics are not explicitly covered in depth, such as the "heteropoly blues and browns" and other reduced POMs, nearly all such topics are addressed indirectly in one or more of the reviews. One invited article that did not make this issue and is only sparingly covered in the articles is the thermodynamic speciation of POMs in solution. An up-to-date review of this timeless information is needed as no recent comprehensive one exists and it impacts several aspects of POM research.

The first two articles, appropriately, deal with the history and the nomenclature of POMs. Baker has the longest history of current U.S. investigators working with these compounds, and Baker and Glick agreed to cover the early and recent history of POM chemistry. Jeannin authors the second article on POM nomenclature, updating his earlier treatment. The third article by Gouzerh and Proust covers the sizable literature on the organic and organometallic derivatives of POMs. In the fourth article, Weinstock reviews electron-transfer reactions in POM systems in considerable depth, a subject area heretofore characterized by many conflicting, incomplete, or otherwise compromised reports. This article and the background material set up the reader for the next three articles on different aspects of POM catalysis. Article five by Kozhevnikov addresses catalysis by heteropoly acids, a major subset of POMs, for selected

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liquid-phase reactions. Much of the early (pre-1980) Russian literature on this topic is covered here. Article six by Mizuno and Misono focuses on the heterogeneous catalysis by POMs, and article seven by Sadakane and Steckhan focuses on the electrochemistry and electrocatalysis of these compounds.

The next three articles address structural aspects and materials chemistry associated with POMs. Müller and Peters in Germany, Pope in the United States, and Gatteschi in Italy coauthor an up-to-date account of the rapidly moving area of giant POMs including clusters of POMs and related supramolecular species. Next Coronado and Gómez-García review POM-based molecular materials, a area of recent genesis and development. Klemperer and Wall follow with a report on POM surface chemistry with an emphasis on the applications of scanning probe microscopy.

Yamase reviews the photochromism and electrochromism of POMs in article eleven. Rhule et al. (Hill, Judd, and Schinazi, coauthors) then cover the interface of POMs and biology, a literature dominated by antiviral studies (cell culture, molecular biology, and some enzymology). In the final article, Katsoulis rises to the considerable challenge of making sense of the voluminous patent literature on the applications of POMs to a host of problems.

I thank all the authors for their attempts not just to obtain comprehensive coverage of the target subjects but to bring some critical analysis to their respective articles. It is the hope that this volume will function as a useful reference base for this burgeoning subarea of chemistry for some time to come and provide creative stimulation and a modicum of enjoyment to old and young investigators alike.

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