INTRODUCTION TO POLYOXOMETALATE CHEMISTRY

M.T. POPE *

Department of Chemistry
Georgetown University
Washington, DC 20057-1227, U.S.A.

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1. Introduction

To an Inorganic Chemist, the high abundance of oxygen in the Earth’s Crust (55 atom%) is largely manifested in the solution chemistry of aquo-, hydroxo-, and oxo-ions and in the solid-state realm of silicates, clays, and metal oxides. The role of (di)oxygen in the biosphere is of course also not insignificant, but that is another story.

The inorganic aqueous solution chemistry of oxygen can be organized in terms of Brønsted acid-base behavior, e.g.:

\[
\text{Al(H}_2\text{O)}_6\text{]}^{3+} + \text{OH}^- \leftrightarrow \text{[Al(H}_2\text{O)}_5(\text{OH})]^{2+} \cdots \text{[AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+} \cdots \text{Al(OH)}_3^n
\]

\[
\text{[HVO}_4\text{]}^{2-} + \text{H}_3\text{O}^+ \leftrightarrow \text{[H}_2\text{VO}_4\text{]}^- \cdots \text{[H}_2\text{V}_{10}\text{O}_{28}]^{4-} \cdots \text{V}_2\text{O}_5
\]

Although the ultimate products of such acid-base processes are generally the insoluble neutral oxides or hydroxides, equilibria involving intermediate polyoxo or hydroxo ions such as 1 and 2 are established prior to the precipitation of the neutral (hydr)oxides. For reasons discussed below polyoxoanions have a more developed and extensive solution chemistry than do polyoxocations.

With the notable exception of the silicates, minerals containing discrete polyoxoanions, as opposed to mixed metal oxides, are not common. Most of these contain polyvanadates, e.g. pascoite (Ca₃[V₁₀O₂₈]), hewettite (Ca[VO₆O₁₆]) and sherwoodite (Ca₄.₅[AlV₁₂O₄₀]), although two, mendoza-
vilite, Na(Ca,Mg)$_2$Fe$_6$(PO$_4$)$_2$(PMo$_{11}$O$_{39}$)(OH,Cl)$_{10}$·33H$_2$O, and paramendozavilite, NaAl$_4$Fe$_7$(PO$_4$)$_5$(PMo$_{12}$O$_{40}$)(OH)$_{16}$·56H$_2$O, have been formulated to contain molybdophosphate anions. It seems likely that if these formulas are confirmed, the polyanions had been produced by surface oxidation/hydrolysis processes.

Polyoxoanions with three or more non-oxo atoms are found in two regions of the Periodic Table, the early transition metals (V, Nb, Ta, Cr, Mo, W) and certain p-block elements (B, Si, Ge, P, As, Sb, Te, I), see Figure 1. These two groups have little chemistry in common other than a general formula $M_xO_y^{n-}$, and it is the transition elements, especially V, Mo, and W, which generate the enormous variety of complexes known as heteropolyanions and isopolyanions, or in general, polyoxometalates [1]. This behavior can partly be ascribed to coordination preferences. Polyoxoanions of B, C$^{IV}$, Si, P$^{V}$, and As$^{V}$ invariably exhibit coordination numbers of four, whereas the remaining nine elements can also accommodate 5, 6, or occasionally even 7 oxo ligands. These differences can be rationalized by the usual arguments based on size, see Figure 2. The commonest coordination number exhibited by all the transition metals except C$^{VI}$, and by Sb$^{V}$, Te$^{VI}$, and I$^{VII}$, is six. The availability of vacant $d$-orbitals in the transition metal complexes allows significant $p\pi$-$d\pi$ overlap, and this accounts for a lengthening of the bond trans to the $M$-$O_{terminal}$ bond, and for the $cis$ and $fac$ arrangement of the terminal oxygen atoms in dioxo and trioxo complexes. In contrast, the p-block elements show very weak trans influences, see Figure 3 (note the $mer$ arrangement of terminal oxygens in [H$_3$IO$_6$]$^{2-}$). Unlike the polyoxometalate anions, which are typically “closed” structures bounded by surfaces of weakly nucleophilic oxygens, the (terminal) oxygen atoms of oxoanions of the p-block elements are susceptible to protonation and condensation processes that lead to further oligomerization and “open” one-, two-, or three-dimensional structures.

![Figure 1. Polyoxoanion-forming elements.](image)

Polyoxometalates, therefore, incorporate atoms of V, Nb, Ta, Cr, Mo, or W as the primary constituents (these have been termed “addenda” atoms), but by far the largest number of examples are those containing Mo, W and V. The limited numbers of polyniobates, -tantalates, and -chromates is often attributed to