

Heteropoly Problems

A look at heteropoly anions, long used in science and industry, shows big gaps in the dossier

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Heteropoly anions, known for more than a century, play a variety of roles in both science and industry. But despite their long history, says Charles H. Kline of Climax Molybdenum, we know relatively little of the chemistry of these compounds and probably have just scratched the surface of their industrial potential.

Molybdenum, tungsten, and vanadium are perhaps the best understood "poly" elements, followed by niobium, tantalum, and uranium. These six can combine in many different ways with more than 30 different "hetero" elements to form a very large class of compounds, Kline told the symposium on heteropoly anions of the Division of Physical and Inorganic Chemistry.

Molecular weights ranging to above 4000, extraordinary solubility in water and often in polar organic solvents, and other unusual properties make heteropoly anions quite useful in pure science. Studies of their structure have done much for theoretical inorganic chemistry, and a number of analytical procedures are based on them. Heteropoly anions have long served as reagents and precipitants in biochemistry, and recent work suggests that phosphomolybdates and silicomolybdates form the activating groups in molybdenum-bearing enzymes.

Heteropoly anions find their biggest industrial use as precipitants for basic dyes in making color lakes. In 1956 this outlet will take an estimated 300,000 pounds of contained molybdenum (phosphomolybdates) and 250,000 pounds of contained tungsten (phosphotungstates). And heteropoly complexes may take a big part in the growing trend toward multicomponent catalysts in petroleum refining and synthetic organic chemicals production.

► **Structures Solved.** These compounds form excellent crystals, so their structure is best studied by x-ray diffraction and crystal structure analysis. Howard T. Evans, Jr., of U. S. Geological Survey has used these methods to solve the structure of $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24}\text{H}_6\text{TeO}_6 \cdot 7\text{H}_2\text{O}$ and two other molybdotellurates. He finds that all three contain the heteropoly ion $(\text{TeMo}_6\text{O}_{24})^{-6}$, according to Stanley Block of National Bureau of Standards (speaking in Evans' absence); also, the complex consists of a TeO_6 octahedron surrounded by six MoO_6 octahedra, condensed into a disk-shaped molecular group.

Little enough is known of molybdate and tungstate structure, but vanadates are even worse off. However, Evans finds by crystallographic studies of $\text{K}_6\text{V}_{10}\text{O}_{28} \cdot 9\text{H}_2\text{O}$ and three similar compounds that polyvanadate ion contains 10 vanadium atoms. And the metavanadates, KVO_3 and $\text{KVO}_3 \cdot \text{H}_2\text{O}$, are now known to contain infinite chains of vanadium-oxygen polyhedra. In KVO_3 the polyhedra are tetrahedrons, while in $\text{KVO}_3 \cdot \text{H}_2\text{O}$ they are trigonal bipyramids. Thus vanadates are apparently unlike molybdates and tungstates, whose structures are based on octahedra.

Many possible heteropoly anions probably have never been observed, but Louis C. W. Baker of Boston University and Thomas P. McCutcheon of University of Pennsylvania have found four of them: 12-tungstodicaltoate, 12-tungstocobaltocobaltiate, 12-tungstocobaltoate, and 12-tungstocobaltiate. These compounds have unique features and are quite unlike the molybdocobaltiate or other known heteropoly complexes in structure, chemical behavior, and valence interrelationships of the hetero atoms.

Proposed structures of these compounds rest on a combination of chemical evidence and the crystallographic

symmetry concept. In solution, 12-tungstodicaltoate apparently contains one oxidizable cobaltous atom at the center of a CoO_6 octahedron enclosed in a "basket" of 12 WO_6 octahedra. The other cobaltous atom is at the center of a CoO_6 octahedron which is outside the basket. This exterior cobaltous atom cannot be oxidized, but acidic action or cation exchange resin can strip it from the complex. However, the interior cobalt apparently can be oxidized, as in 12-tungstocobaltocobaltiate, giving the unusual situation of two cobalt atoms existing in the same complex in different oxidation states.

How molybdate and other complexes form in solution is not entirely clear, but Leslie H. Jenkins of Oak Ridge National Laboratory, and S. Y. Tyree, Jr., University of North Carolina, have learned something about several systems; the most definitive results are on molybdates. They use light-scattering techniques, which are ideal for the purpose, Tyree says, because they neither change the system when measurements are taken nor depend on the degree of dissociation or activity of the species present.

► **Molybdate Discovery.** Their main molybdate discovery is that when sodium molybdate solution is acidified progressively, molybdate ion goes to paramolybdate $(\text{Mo}_7\text{O}_{24})^{-6}$. Ingvar Lindqvist of Institute of Chemistry, Uppsala, Sweden, previously had suggested both this reaction and one in which octamolybdate, $(\text{Mo}_8\text{O}_{24})^{-4}$, is formed. The light-scattering work confirms the first suggestion and weakens the second.

Lindqvist himself asks several basic questions: What factors govern the formation of heteropoly anions in the solid state and in solution? What factors govern the structure of heteropoly anions? And what are the reduction products of heteropoly anions? He suggests, to avoid duplication of research on these and related questions, that a voluntary, informal committee of two or three be set up. These people would find out, by correspondence or otherwise, who in the world is working on heteropoly anions, and what they are doing. The main purpose here, he believes, would be to keep all interested scientists up to date in this potentially fruitful field.