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Present General Status of Understanding of Heteropoly Electrolytes and a Tracing of Some Major Highlights in the History of Their Elucidation

Louis C. W. Baker* and Diana C. Glick

Department of Chemistry, Georgetown University, Washington, D.C. 20057

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The free acids and salts of heteropoly anions constitute a large, distinct fundamental category of compounds,[1−3] having high potential for theoretical contributions and for practical applications. This paper will first describe (section A) the present general understanding of these compounds and then (section B) trace main points in the history of elucidating the field up to 1970. Isopoly complexes, although closely related, will not in general be treated, to keep the paper's scope within reasonable limits. The post-1970 contributions of those who were most active prior to 1971 will be summarized (section C, part 1), and the areas of accomplishments of various groups established after 1970 will be mentioned (section C, part 2).

Louis C.W. Baker was born in New York City in November 1921. He obtained the bachelor's degree in chemistry from Columbia in 1943 and the M.S. (1947) and Ph.D. (1950) in inorganic chemistry from the University of Pennsylvania. In 1988 Georgetown University awarded him the D.H.L. honoris causa. During World War II he, as coinventor of a high thermal efficiency airplane engine, was codirector of a high priority war research project (1942–1945). Simultaneously, he served at Pennsylvania (1943–1951) as Assistant Instructor in Chemistry, then Instructor, and then Associate in Chemistry. Also simultaneously (1945–1948) he served as parttime Instructor in the Pennsylvania Area Colleges (college-level programs for returning veterans, state-run in high school buildings at night). In 1951 he transferred to the Boston University faculty, becoming head of the Inorganic Division. Eleven years later (1962) he transferred to Georgetown as Chemistry Department Chairman. He refused reelection as Chairman in 1984, remaining as Professor. In 1992 he became emeritus but remained active in research. Biographical listings include American Men and Women of Science and Who's Who in the World (Marquis). Professor Baker is a Guggenheim Fellow (1961 to present), spoke at Gordon Conferences (1956 and 1967), and was lead-off Plenary Lecturer at the 1973 International Conference on Coordination Chemistry (Moscow). He has some 100 refereed publications and has given invited lectures at numerous international conferences, universities, and professional meetings, as well as invited lecture series in the USSR, Romania, Spain, and Poland. In 1973 he received the Tchugaev medal (Inorganic Chemistry) from the USSR Academy of Sciences. In 1974 he was appointed scientific member of the visiting committee to evaluate and advise on improvement of Ferdowsi University, Mashad, Iran. From 1974 to 1978 he served as Chairman, National Academy of Sciences' Committee on Recommendations to the US Army for Basic Scientific Research. In 1984 he was awarded the Georgetown University President's Medal for Distinguished Service. Avocations have included sailing, piano, tennis, and old English folk dancing.

Diana Carbonneau Glick, a native of New Hampshire, received her bachelor's degree in chemistry from Western New England College in 1987. She completed her graduate studies involving the NMR elucidations of isomeric mixtures of fluoro-substituted heteropolytungstates under Dr. Louis C. W. Baker from Georgetown University in 1995. She was awarded the ARCS fellowship in 1992. Dr. Glick is currently a Visiting Assistant Professor at Georgetown University.

A. Present General Understanding of the Field

The following fairly comprehensive overview is necessarily abbreviated and consequently, in places, somewhat oversimplified. More detailed treatments of some subjects will be found in refs 1−3.

A classical heteropoly anion contains numerous oxygen atoms, sometimes hydrogen atoms, and atoms of at least two other elements in positive oxidation state(s). Heteropoly anion structures resemble discrete fragments of metal oxide structures of definite sizes and shapes.[1−3] These complexes generally represent thermodynamically relatively stable arrangements, although, especially in the case of polytungstates, their formation is often under kinetic control rather than thermodynamic control. They characteristically maintain their identities in aqueous and nonaqueous solutions as well as in ionic crystals. Examples are: $[PW_{11}O_{39}]^{7-}$, $[((OH)_2Co^{3+}O_4)_2Mo_{10}O_{26}]^{6-}$ (optical isomers), $[\eta^5\text{-}C_5H_5Ti^{3+}PMo_{11}O_{39}]^{5-}$, $[SiW_{11}O_{39}Co^{3+}(\text{pyrazine})Co^{2+}SiW_{11}O_{39}]^{11-}$, dl-$\alpha_1$-$[(H_2O)Mn^{3+}O_5H_2F_6NaW_{17}O_{50}]^{8-}$.

Typically, a heteropoly complex contains a high atomic proportion of one kind of atom in positive oxidation state ("addenda atoms") and much smaller proportion(s) of the other kind(s) of atom(s) in positive oxidation state(s) ("heteroatoms"). W, Mo, and V, in their highest oxidation states, function as addenda atoms in a great many heteropoly anions. A few additional atomic species (e.g., Nb^{5+}, Ta^{5+}, Re^{7+}, I^{7+}) can, less commonly, fulfill that role. Over 60 other elements, including most nonmetals and transition metals, can function as heteroatoms.

The atoms that can function as addenda are those that (1) change their coordination with oxygen from 4 to 6 as they polymerize in solution upon acidification and (2) have high positive charges and are among the smaller atoms that fall within the radius range for octahedral packing with oxygens. The ability to act as addenda is greatly enhanced if the atoms are able to form double bonds with unshared oxygens of their MO_6 octahedra, by $p\pi{-}d\pi$ interaction. The formation of a heteropoly complex involves the polymerization of addenda polyhedra around a heteroatom as the solution is acidified.

Distortions of the Addenda Octahedra

Typically, two potent factors act to displace each addendum atom far off-center in its MO_6 octahedron toward the complex's unshared (exterior) oxygen atoms: (1) the formation of double bonds between addenda and unshared oxygens and (2) the greater polarizability of the octahedrons' unshared oxygens toward the addenda. This situation not only explains most of the unique nonredox properties of heteropoly complexes but accounts for their very existence as discrete species.

The highly charged addenda atoms produce strong ion-induced dipole attractions for adjacent unshared oxygens of their octahedra. The oxygens on the exterior of the complex exert by far the strongest attractions because they are the most polarizable toward the addenda atoms. The other oxygens of the complex, being interior or between addenda, are much less polarizable in any given direction.

The most typical addenda (W, Mo, V) form double bonds with the unshared (exterior) oxygens. The two factors that move the addenda atoms toward the unshared exterior oxygens are, of course, strongly symbiotic. The more the double bond shortens the addendum−oxygen distance, the greater is the polarization and the stronger the ion-induced dipole attraction. The more the latter moves the addendum toward the unshared oxygen, the shorter and stronger is the double bond. For example, the *differences* in W−O distances for interior oxygens versus peripheral oxygens are commonly 0.7 to 1.0 Å. (An I^{7+} addendum, which cannot form a double bond, nevertheless shows, on the basis of polarization differences, a marked shortening of the exterior oxygens' distance from the I^{7+}. That shortening is about 40% as great as that for the corresponding Mo−O distance in an isomorphous molybdo complex.[4])

Effects of the Distortions of the Addenda Octahedra

Thus the typical heteropoly complex has an exterior layer of oxygen atoms that are unusually strongly polarized toward the interior of the complex. Beneath that layer is a layer of addenda atoms strongly attracted toward and attracting the outer layer of oxygens. This combination forms a sort of shell within which there is space, and interior atoms are subject to less than average forces. Thus interiors of isomorphous heteropoly complexes can often accommodate a variety of heteroatoms.

The oxygens in the exterior layer, being strongly polarized toward the interior of the complex, present relatively positive sides toward the exterior. They therefore attach hydrogen ions only extremely weakly, and free heteropoly acids are characteristically strong (pK's of ∼0−2).

Crystalline free heteropoly acids are thus commonly salts of solvated proton cations. Furthermore, the exterior oxygen atoms form only very weak H bonds or none at all. Consequently the big complexes' hydrodynamic radii, as shown by viscosity and diffusion measurements, frequently coincide with their crystallographic radii,[5] and solvation energies of heteropoly species are typically essentially negligible.

Crystalline heteropoly salts frequently have between the big complexes large interstices which accommodate sizable numbers of waters of crystallization as well as the counterions. These waters, often being essentially unattached to the complexes (although H-bonded together), are frequently zeolytic and often not in crystallographically defined positions. Sometimes some or all of the counterions are in defined positions, but often not all of them are.

Why Heteropoly Species Exist

Polymerization of the addenda species requires a mechanism involving attachment of protons to oxygens. Once the stage of the heteropoly species is reached, the strong inward polarization of the exterior layer of oxygens terminates any further polymerization. This accounts for the existence of relatively small discrete heteropoly complexes rather than insoluble extended solid matrixes.

Lattice Energies, Volatility, and Solubilities

Crystals of heteropoly electrolytes typically have very low lattice energies. The anionic negative charge is spread over numerous atoms. The large size of heteropoly complexes places their charge centers at relatively large distances from the cations in the crystal structures of their salts or free acids, thus greatly diminishing electrostatic attractions. The fact that the exteriors of heteropoly anions consist largely or entirely of oxygen atoms that are very strongly polarized toward the addenda, and therefore not polarizable in other directions, creates a condition where one might expect van der Waals attractions between the complexes to be essentially nonexistent if they involve species having only exterior oxygen atoms that are adjacent to addenda atoms only. The expected lack of ability of species coated with nonpolarizable, nonbasic oxygens to form H bonds that even approach average strength contributes to the picture for typical heteropoly complexes of appropriate structure. One consequence is that salts of near spherical or ellipsoidal heteropoly species are frequently somewhat volatile. For example, a K salt of a Keggin structure 12-heteropoly complex (Figure 1a, nearly spherical with a diameter >10 Å) can be sublimed (probably as ion pairs) at about 1 Torr and 300 °C.[6]

Solubility depends on the balance between lattice energy, solvation energy, and interactions between solvent molecules. For a typical heteropoly electrolyte both the lattice energy and the complex's solvation energy are very low. Solubility therefore depends on the solvation energy of the cation. Thus

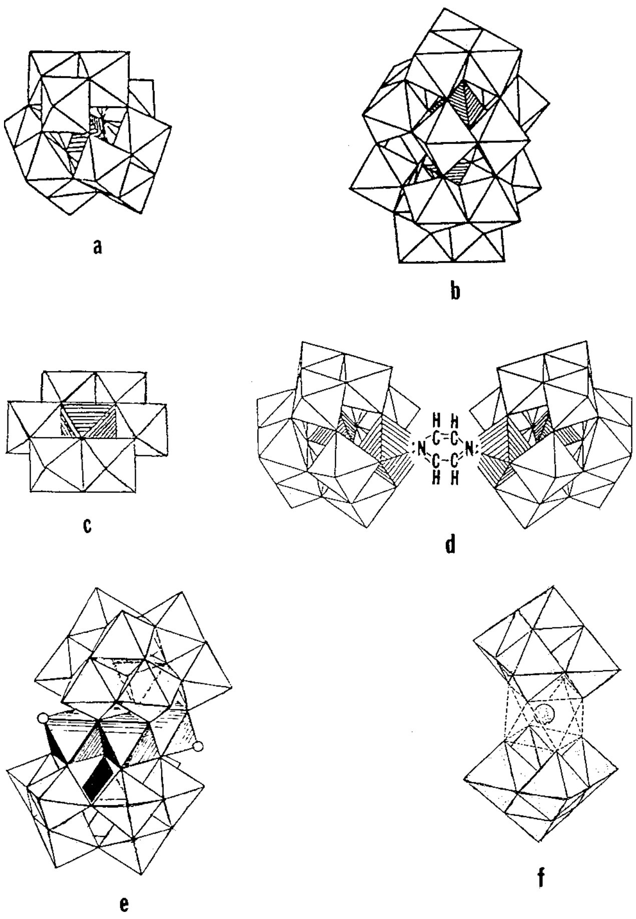

Figure 1. Some structures of heteropoly anions. Each vertex locates the center of an oxygen atom. An addendum atom is within each white octahedron, displaced toward the unshared oxygen(s). The heteroatoms are within the hatched polyhedra: (a) the α-Keggin 12-heteropoly structure (i.e., containing 12 addenda atoms per heteroatom); (b) the α-Wells–Dawson 18-heteropolydiphosphate or -diarsenate structure; (c) the Anderson–Evans 6-heteropoly structure; (d) $[SiW_{11}O_{39}Co^{3+}(pyrazine)Co^{2+}SiW_{11}O_{39}]^{11-}$ (a "dumbbell" complex; two Keggin-like heteropoly units, each containing a Co substituted for a W and with the units joined by each Co's coordination to a pyrazine bridge); (e) $[PW_9O_{27}(Ni_4{}^{2+}O_{14}(H_2O)_2)PW_9O_{27}]^{10-}$ (the circles locate coordinated H_2O molecules; the PO_4 central tetrahedra (largely hidden) are indicated); and (f) $[W_5O_{18}M^{n+}W_5O_{18}]^{(12-n)-}$.

free heteropoly acids are extremely soluble in water and numerous salts are relatively soluble, while salts of cations having decidedly organic natures, such as tetrabutylammonium salts, are characteristically soluble in nonaqueous solvents but insoluble in water.

The Effects of Relative Rigidities

Factors that affect the rigidity of heteropoly structures have a profound effect on their lability and stability, and thus on the maximum pH at which they are stable.

All heteropoly species are degraded by base if it is concentrated enough. The mechanism of the degradation involves attack by OH^- ions and change of addenda's coordination number. This, as well as exchange of addenda atoms with the solution, is more facile as the flexibility of the complex increases. For example, the isomorphous complexes $[X^{3+}(OH)_6Mo_6O_{18}]^{3-}$ wherein $X^{3+} = Cr^{3+}$, Co^{3+}, Al^{3+}, or Fe^{3+}, all have the Anderson–Evans 6-heteropoly structure (Figure 1c). (The nonacidic six H's are on the six O's that surround the heteroatom.[7]) The d^3 Cr^{3+} and d^6 Co^{3+} have strong crystal field stabilization energy (CFSE) to maintain compact and rigid heteroatom octahedra and thereby markedly stiffen their complexes. These two complexes are resistant to degradation, do not decompose upon boiling, and exchange Mo with labile paramolybdate, $[Mo_7O_{24}]^{6-}$, 2 orders of magnitude more slowly than do the d^0 Al^{3+} or d^5 Fe^{3+} complexes, which have no CFSE stiffening.[8] The latter two complexes decompose in solution above 60 °C.

Mo^{VI} and W^{VI} are both d^0 and, owing to the lanthanide contraction, are generally listed with the same ionic radii. Nevertheless, it is generally observed that polymolybdates (like polyvanadates) are labile while polytungstates are inert and much more stable.[9,10] This may be attributed to the slightly larger force constant of the W–O attachment as compared to that of the Mo–O attachment. Although that difference is small in itself, the cumulative effect over the many bonds in the polyanion produces a relative stiffening of the polytungstate framework which sizably reduces the complex's reactivity. The differences in lability and stability are striking, as illustrated[10] by $[Ni^{2+}(OH)_6Mo_6O_{18}]^{4-}$ and its isomorph $[Ni^{2+}(OH)_6W_6O_{18}]^{4-}$. A striking stiffening effect is also observed for all the heteropoly blue species,[11] as discussed below.

Lacunary Species, Mixed Addenda, Metal Ions Substituted in Addenda Sites, Organic Derivatives, Fluoride Substitutions, and Bridged Complexes

Many variations of structure have been prepared. (1) Controlled treatment of many heteropoly species with base can produce so-called "lacunary" heteropoly species wherein one or more addenda atoms have been eliminated from the structure along with the oxygens those addenda were not sharing with other atoms. Lacunary species generally react readily with any potential addenda or with a wide variety of octahedrally coordinating metal ions to refill the vacant sites. (2) Many distinct species containing mixtures of addenda have been prepared. (3) Many customarily octahedrally coordinated metal ions can be substituted for between one and three adjacent addenda.[12–14] (4) The unshared coordination position of a substituted metal ion is available for coordination to H_2O or to many other ligands. This produces complexes that are hybrid between heteropoly species and coordination complexes.[15] (5) The coordination of organic ligands to the unshared coordination sites of metals substituted into heteropoly complexes produces one important type of organic derivative.[15] (6) Another large class of organic derivatives has carbon atoms from the organic part directly bonded to a nonmetallic heteroatom.[16] These may be formed, for example, by polymerizing addenda species directly onto oxyanions (such as phosphinates or phosphonates) that have bonds between carbon atoms and central atoms of such oxyanions. (7) Still a third important type of organic derivatives has organic groups bonded to the heteropoly anion through exterior oxygen atoms of the latter. (8) Fluoride ions, being isoelectronic with oxide ions, can be substituted for interior oxygens of heteropoly species.[17] In contrast with oxygen ions, fluoride ions are nonpolarizable and are loath to form double bonds. Consequently species that contain fluoride ions substituted for exterior oxygens have not been identified in aqueous solutions. Perhaps they may form in nonaqueous media. (9) Two heteropoly moieties can be joined by coordination to various bridges. One sort of bridge consists of a ligand (e.g., pyrazine) that can coordinate at two positions, linking two heteropoly units through coordination to metal ions that have been substituted into the heteropoly structures (Figure 1d).[18] Another sort of bridge (Figure 1e) links two trivacant lacunary species via their attachment to each side of a planar layer of four octahedrally coordinated divalent cations (Zn, Co, Cu, Cd, Ni, Mn).[19] A third type of bridge consists of a single large eight-coordinate atom[20] (e.g., Th^{4+}, Ce^{4+}) simultaneously tetracoordinated to monovacant lacunary sites in two heteropoly or isopoly[20,21] moieties. Several other types of bridges exist for particular compounds.[1] All of these structural variations produce compounds having properties which may be inferred from their constituents and the principles given in the previous sections.

Isomerisms

There are a great many obvious possibilities for geometrical isomerisms for these complexes. One type, unique to heteropoly species, may be described. Keggin and Wells−Dawson structures (Figure 1a,b) and their numerous derivatives are among the most common heteropoly species. The Keggin structure contains four M_3O_{13} addenda groups, and a Wells−Dawson complex contains two. Each of these M_3O_{13} groups can be rotated 60° about its 3-fold axis and reattached. For example, the structure illustrated in Figure 1a is the α configuration of the Keggin structure. Rotation of one or two of its M_3O_{13} groups produces the β and γ forms, respectively.[15]

Enantiomorphic forms are fairly common, with the asymmetry depending upon overall arrangements of the polyhedra rather than on any given atom. However, separation into optical isomers is very rare owing to insolubility of diasterioisomeric combinations with resolving agents. One complex, $[Mn^{4+}O_6Mo_9O_{26}]^{6-}$, has been resolved by picking of asymmetric crystals.[22] The optically active $[((OH)_2Co_4)_2Mo_{10}O_{26}]^{6-}$ complex has been resolved by classical diastereoisomer formation.[23] Others have had optical activity demonstrated by mutarotation experiments.[24]

Heteropoly Blues and Other Reduction Products

Heteropoly complexes are generally fairly strong oxidizing agents. In the cases of complexes that do not contain any addenda that have just one unshared oxygen, reduction usually disintegrates the complex, forming species containing lower oxidation states of the addenda.

An octahedrally coordinated d^0 addendum atom with a double-bond attachment to just one unshared oxygen atom has a vacant nonbonding orbital. Many heteropoly complexes have several or all of their adjacent addenda in this condition.[25] Such complexes are readily reversibly reduced by addition of various specific numbers of electrons depending upon the pH and the potential employed. The reduction products, which typically retain the general structures of their oxidized parents, are characteristically deep blue in color and comprise a very large group of complexes known as the “heteropoly blues”. The added (“blue”) electrons are “delocalized” according to various time scales over certain atoms or regions of the structures. Heteropoly blues correspond to class II systems in the Robin and Day classification[26] of mixed-valence compounds.

The electron delocalization is viewed as operating through two mechanisms: (1) a thermally activated electron hopping (commonly $\sim 10^{10}$ to 10^{11} s^{-1} at room temperature) from one addendum atom to the next and (2) a ground-state delocalization presumably involving π bonding through bridging oxygens from the reduced metal atom to its neighbors. The existence of the ground-state delocalization is required to account for intervalence charge-transfer optical absorption bands[27,28] and evident increased negative charge on oxygens.[11] Whenever a polytungstate contains an even number of blue electrons their spins are firmly spin paired, although the added “blue” electrons are frequently not on adjacent addenda at a given instant.

Heteropoly blue structures in which adjacent atoms that can receive the blue electrons are arranged in unbroken circles, exhibit ring currents corresponding to the diameters of the circles and the numbers of blue electrons in them.[29]

The interatomic distances in a heteropoly blue complex differ by only very small amounts from those in the oxidized parent complex, the result of a very small expansion of the blue framework plus a small influence toward changes in expected directions for increasing those addenda-oxygen orbital overlaps which facilitate intracomplex electron exchange.[11] However, the thermal displacement parameters for all of the atoms in the blue complex are markedly reduced relative to those in the oxidized parent, while the displacement parameters for atoms not in the complex remain unchanged.[11] This suggests the importance of a ground-state delocalization mechanism involving partial “blue” electron residency in molecular orbitals that involve oxygen atoms. There are therefore additional energy terms tending to hold atoms in the blue complexes in optimal locations for transfer of electrons between adjacent addenda.

The increased resistance to atom displacements in heteropoly blue complexes relative to the condition in the oxidized parents implies a decided stiffening of the blue structure and explains why heteropoly blues are more resistant than their parents to substitution reactions and degradation by base.[11]

Which addenda atoms participate in exchanging blue electrons can depend upon the geometry of the complex. In a Keggin structure (Figure 1a) all 12 addenda sites are equivalent, so all the addenda participate in the blue electron hopping process. In an 18-tungstodiphosphate Wells–Dawson structure (Figure 1b), for example, addition of one or two blue electrons involves hopping among only the 12 belt addenda. Whether the high magnetic fields, used in the NMR or ESR determinations of which W's receive hopping blue electrons, force the delocalized electrons into the larger diameter ring currents of the belt addenda or whether the electrons are delocalized only there in the absence of the magnetic field, has not been determined. Mo^{6+} is more easily reduced than W^{6+}; so, if one cap is Mo_3O_{13} while the rest of the framework is tungstate, the blue electrons remain delocalized only in that cap. If an Mo^{6+} is substituted for one of the W's in the 18-tungsto Wells–Dawson framework, the first added electron remains localized on the Mo, and a second added electron is delocalized over belt W's.

Further reduction of heteropoly blue complexes frequently leads to formation of so-called heteropoly brown anions. These are species that retain the gross structures of the parent complexes but wherein the addenda in some or all subunits (e.g., M_3O_{13} groups) are reduced by two electrons apiece. The added electrons in heteropoly browns are not delocalized.[30]

Peroxy Derivatives

H_2O_2 is catalytically activated by some heteropoly species for highly selective oxidations of organic compounds. However, relatively few peroxy heteropoly complexes have been isolated, and of these, only three, recently reported, are peroxy complexes based on traditional highly condensed heteropoly structures.[303,777,857] Preliminary evidence indicates the existence of heteropoly superoxide derivatives.[31]

Potentialities and Uses

Heteropoly complexes have proven to be enormously valuable industrial catalysts, the subject of a large patent literature and offering important scope for further fundamental work.[32] Because most attention has centered on relatively few heteropoly structures, abundant possibilities exist for future work. Besides heterogeneous applications, frequent solubility in nonaqueous solvents offers opportunities for homogeneous catalysts.[32,33] Essentially the complexes resemble metal oxides subdivided on a molecular level, thus offering enormous effective surface. Many transition metal ions in various structural combinations can be incorporated into the exposed surfaces of the complexes.

Heteropoly complexes provide a variety of specialized oxidizing agents. Recently their usefulness in bleaching wood pulp via oxidative delignification has been reported.[33b,856]

The heteropoly blues provide important potentialities, almost unexplored, as specialized reducing agents, with a wide range of controllable reduction potentials. Since a complex can release a specific number of its blue electrons between specific potentials, complexes can be one-electron, two-electron, or specific multielectron reducing agents which can reduce other compounds to specific products instead of mixtures.[34] A potentially important extension of this is their use as electroreduction catalysts. By fixing the potential, one fixes the heteropoly blue species involved and thus controls the number of electrons per reduction event.

There is a large and growing area of heteropoly photochemistry[35] and photocatalysis.[35,36,829,842]

Medical applications of heteropoly species are of potential major importance.[32] Since heteropoly species adhere to different tissues with varying tenacity, the polytungstates are valuable as electron microscope stains. Specificity is enhanced by attachment of particular organic side chains.[35d,e] Most heteropoly molybdates and tungstates are of relatively low toxicity. Heteropoly magnetic resonance imaging agents, based on incorporation of appropriate rare earth atoms, may prove useful. Important possibilities attach to demonstrations of potent antitumor and antiviral (including HIV and herpes) action of various polytungstates and polymolybdates.[32] Selection of the compounds is still at the Edisonian level, but striking results have been achieved in vivo as well as in vitro.[32,37] Other applications have been cited,[32,33,49] and the pace of research continues to grow.

Exploration and explanations for numerous major effects of counterions on heteropoly preparations and chemistry have scarcely been investigated.[17c,37,887,888] The possibilities of nonaqueous heteropoly chemistry are ripe for further development. Multinuclear NMR elucidation of structure and bonding is making striking progress.[38] Heteropoly complexes and heteropoly blues are especially valuable for studies of important areas of current interest including (a) intermolecular and intramolecular electron transfer,[39–41] (b) atom transfer reactions,[30a,42,43] (c) mixed metal oxide conductivity,[39] (d) various types, mechanisms, and pathways for mixed-valence electron delocalization,[39] and for extensive d-electron spin delocalization,[44] (e) theory of multinuclear NMR chemical shifts,[38,45] (f) electron spin couplings,[46] and (g) isolated paramagnetic spin-coupled systems.[46,47,112] A few specific insoluble heteropoly salts have long been used as ion exchangers, but there is room for expanded attention.[48] Soluble salts of giant heteropoly anions (e.g., mol wt > 41 500) are the subject of current research as are photochromism and electrochromism.

B. Some Major Highlights in the History of Heteropoly Complexes up through 1970

In 1826 Berzelius[50] published the first account of a compound that we now call a heteropoly salt. This was ammonium 12-molybdophosphate, “the yellow precipitate”, which, beginning with the work of Svanberg and Struve[51] (1848), became famous in analytical chemistry as the eventual basis for both gravimetric and volumetric determinations of phosphorus.

Dualistic Theory

Berzelius was the propounder of the “dualistic theory” of compounds, which held sway until the advent of the theory of ionization in 1887. The dualistic theory was based on the extensive electrolysis experiments of Sir Humphrey Davy in the first three decades of the nineteenth century. Berzelius postulated that every atom contained both positive and negative electric charges with the positive predominating in some kinds of atoms (e.g., metals) and the negative in other kinds. Thus some elements were liberated at the cathode and others at the anode. Various extents of the predominance of charges accounted for the different voltages required to liberate different elements. Atoms with a net positive charge joined with atoms having net negative charge to form binary compounds. The fact that compounds had definite atomic compositions presented a challenge to the reasoning, which was met by adoption of a phrase, it being said that the attachment was by "partial mutual saturation" of the opposite charges, so that the resulting binary entity retained a (smaller) net charge itself, the sign of which depended upon the numbers of its constituents and the extents of their charges. Those binary entities could join with other binary entities of opposite net charge or with appropriate single atoms. For example: Potassium (very electropositive) could join with oxygen (electronegative) to form K_2O in which positive charge predominated. This oxide could form a simple solution when added to water. Sulfur could form SO_3 wherein three electronegative oxygens combined with a not very positive sulfur atom. The resulting SO_3 molecule retained a net negative charge. When a solution of K_2O was added to a solution of SO_3, a very exothermic reaction resulted and $(K_2O)^+(SO_3)^-$—(that is, K_2SO_4)—could be isolated from the solution. A similar sequence of reactions would produce $(Cr_2O_3)^+(3SO_3)^-$. Overall positiveness would predominate in $K_2O{\cdot}SO_3$ owing to two very positive K's while overall negativeness predominated in the chromium compound owing to the three negative SO_3 groups. $K_2O{\cdot}SO_3{\cdot}Cr_2O_3{\cdot}3SO_3{\cdot}24H_2O$ (potassium chrom alum) could be isolated from a mixture of the solutions. The yellow precipitate was formulated $3(NH_4)_2O{\cdot}P_2O_5{\cdot}24MoO_3{\cdot}aq$. (Actually, the yellow precipitate as used in quantitative analysis contains HNO_3 of crystallization: $(NH_4)_3[PMo_{12}O_{40}]{\cdot}HNO_3{\cdot}aq$.)

Especially for salts of oxyacids, the dualistic theory provided ready rationalizations. It was valuable for predicting products of electrolysis and the relative strengths of most oxyacids, but it predicted little else. Until the widespread acceptance of the ionic theory, the dualistic formulation was used for most of the heteropoly compounds reported. It conveyed essentially no structural information, but at least it expressed the results of quantitative analyses of the compounds, yielding the relative atomic proportions of the elements present.

If the dualistic formula for a compound contained more than one kind of acidic oxide, the compound was classified as a heteropoly species. If more than one unit of the *same* acid anhydride was in the formula, the compound was an isopoly species.

Individual heteropoly compounds continued to be reported in increasing numbers. In 1854 Struve[52] reported polymolybdates based on some metal heteroatoms, including the 6-molybdates of Al^{3+}, Cr^{3+}, and Cu^{2+}. In 1862 Marignac[53] made an extensive study of the tungstosilicates, and greatly improved pertinent analytical techniques.

In the 1860s the concept of constant valences of elements (i.e., numbers of bonds to a given kind of atom) proved enormously successful in explaining the structures of organic compounds, which led to numerous attempts to apply such reasoning to the structures of inorganic compounds. This was only partially successful, rationalizing the formulas, if not the structures, of so-called "valence compounds", but failing in attempts to explain the "molecular compounds", i.e., salts of what we now recognize as coordination complexes.[54]

No one proposed structures for the heteropoly and isopoly species until 1892 when Blomstrand suggested chain and ring configurations, e.g., of MoO_3 units.[55] This idea quickly proved indefensible.

Werner's Coordination Theory

In 1893 Alfred Werner proposed his monumental theory of coordination complexes.[56] The first paper was interpretive and theoretical, reporting no new experimental evidence. It did not receive universal acceptance quickly. The remainder of Werner's career at the ETH, Zurich, was spent accumulating irrefutable and elegant experimental evidence in support of his theory and its ramifications. The first two experimental papers,[57] unequivocally supporting the new proposals and demolishing important counter arguments of Jörgensen, were produced in collaboration with Arturo Miolati, an ETH colleague who was knowledgeable about conductivity measurements, and an enthusiastic supporter of Werner's ideas.

Later in 1893 Miolati returned to Italy, where he continued extensive work, independent of Werner, on coordination complexes and, in 1902, became the first professor of electrochemistry in Italy.

Early Attempts at Rationalization of Isopoly and Heteropoly Structures

In 1906 Copaux[58] proposed that heteropoly complexes are essentially similar in structure to isopoly anions, the latter, he assumed, being based on H_4O_2 units (formed from two water molecules) acting in place of the heteroatom acid anhydride. This idea was never substantiated, but it provided the nucleus for Rosenheim's explanation of isopoly complexes 13 years later.

By this time Werner's coordination theory had gained wide acceptance and generated much enthusiasm among those contemplating research in inorganic chemistry. In 1907 Werner himself tried his hand at explaining 12-heteropoly structures.[59] For potassium 12-tungstosilicate, for example, he postulated a central SiO_4^{4-} tetrahedron attached by "primary valence" to four $MW_2O_6^+$ groups (M = a unipositive ion) and with the whole surrounded by two $K_2W_2O_7$ groups attached by "secondary residual valence". This appeared to fit those 12-heteropoly species that are based on central tetrahedra containing quadrivalent heteroatoms, but it failed for other species.

Miolati's Suggested Structure

By 1908 approximately 750 heteropoly compounds had been reported and analyzed by over 250 authors,[60] among the most active of whom were P. Chrétien, H. Copaux, H. von Euler-Chelpin, C. Friedheim, W. Gibbs, R. D. Hall, E. Marckwald, O. Pufahl, A. Rosenheim, E. F. Smith, and H. Struve. Rosenheim and Jaenicki[60b] reviewed this early work.

As a result of these efforts it had been widely noted that heteropoly species containing a 6:1 or 12:1 atomic ratio of addenda to heteroatoms were the most common. In 1908 Miolati[61] combined this observation with the fact that Werner coordination numbers were most commonly six, to suggest, tentatively, a structural hypothesis based on the coordination theory.

The suggested hypothesis eventually evolved as follows. One first considered the most common acid of the heteroatom in the observed oxidation state. Then H_2O's were added to that formula until it contained six oxygen atoms, which Miolati presumed formed an octahedron about the heteroatom. This produced the "hypothetical parent acid." Then the oxygens of that parent acid could be progressively replaced by MoO_4^{2-}, $Mo_2O_7^{2-}$, WO_4^{2-}, or $W_2O_7^{2-}$ coordinated to the heteroatom. Thus

$$\begin{array}{lccc} H_3P^{5+}O_4 + 2H_2O \rightarrow & & & \\ & H_7[PO_6] & \rightarrow & H_7[P(Mo_2O_7)_6] \\ & \text{hypothetical} & & \text{12-molybdophosphoric} \\ & \text{parent acid} & & \text{acid} \end{array}$$

6-molybdophosphoric acid became $H_7[P(MoO_4)_6]$. Complexes wherein all of the six oxygens of the hypothetical parent had been replaced were called "limiting" or "saturated" species. If not all of the oxygens had been replaced, the complexes were "unsaturated", e.g., $H_7[AsO(Mo_2O_7)_5]$.[62] Unsaturated anions (often lacunary species in modern terms) usually reacted readily with excess molybdate, tungstate, or vanadate to form saturated species.

It is notable that, despite the subsequent widespread acceptance of these ideas of Miolati's about heteropoly structures, he never again published on the subject. He was generally very conservative about publishing speculations.

The Miolati–Rosenheim Theory

Arthur Rosenheim had been working in the heteropoly field for about 14 years when Miolati's proposal appeared. Rosenheim took to it with great enthusiasm and for the next 24 years he was the leader in research efforts to prove it and to interpret many sorts of heteropoly species and properties in terms of that theory. Thus the "Miolati–Rosenheim Theory" of heteropoly and isopoly complexes became the dominant view and held sway in many areas into the 1950s. A detailed exposition of the field in terms of the Miolati–Rosenheim theory was presented in Rosenheim's review article[63] in 1921.

Arthur Rosenheim

Early Rosenheim contributions to the body of Miolati–Rosenheim interpretations included the following:

(1) The concepts were extended to cover essentially all isopoly complexes[64] by postulating a "hypothetical aquo acid", $H_{10}[H_2O_6]$, formed from six water molecules, wherein two H^+ ions played the role of heteroatom while the oxygens could be progressively replaced by addenda radicals. Far-fetched as this sounds and eventually proved to be in most cases, it is ironic that metatungstate anion, which has the Keggin structure (Figure 1a), has actually turned out to be based on a central tetrahedron of O's containing two H atoms: $[H_2W_{12}O_{40}]^{6-}$.

(2) A more extensive examination of "unsaturated" complexes was made.[65] To rationalize some of the compounds, polynuclear complexes involving various bridging groups had to be postulated, and some complexes with addenda-to-heteroatom ratios of less than 5 had to be assigned tetrahedral central groups.[66]

(3) Polyvanadates, including mixed addenda complexes, were brought into the theory by postulating attachments of VO_3^- or $V_2O_6^{2-}$ in place of some or all of the O's in the hypothetical parent acids.[67]

Efforts to Confirm the Miolati–Rosenheim Theory

Rosenheim set out to find experimental evidence that supported the Miolati–Rosenheim formulations. The efforts took several directions.

1. Dehydration Experiments. Since the Miolati–Rosenheim formulas for the heteropoly acids indicated large numbers of replaceable hydrogens, most heteropoly salts had to be formulated as acid-salts (e.g., $K_3H_4[P(Mo_2O_7)_6]\cdot nH_2O$), and most had several waters of crystallization. One line of attack was dehydration experiments, designed to show that waters of crystallization were easily expelled from crystals at moderate temperatures (<200 °C), but the appropriate numbers of constitutional water molecules (e.g., two in the case of $K_3H_4[P(Mo_2O_7)_6]$) were expelled only at much higher temperatures accompanied by the disintegration of the complexes. (In many cases upon changing the heating technique, such experiments yield a variety of results.)

2. Titrations. Free acids were titrated, using indicators. Some, especially the important compounds $H_7[P(Mo_2O_7)_6]$ and $H_7[P(W_2O_7)_6]$ appeared to yield the desired number of replaceable hydrogens. (These acids, for example, are really tribasic, e.g., $H_3[PW_{12}O_{40}]$, but the higher the charge on the heteroatom the lower the pH at which Keggin 12-heteropoly species hydrolyze to form lacunary 11-heteropoly complexes. That hydrolysis, occurring for these 12-heteropoly phosphate species, produces H^+ in just about the right proportion to make the overall titration appear to be that of a heptabasic acid.) In other cases, it was difficult or impossible to obtain the characteristically very soluble (and therefore not cleanly recrystallizable) heteropoly acids free of traces of the low molecular weight acids used in their metathesis preparations. Because the molecular weights of the heteropoly acids are so large, a very small impurity of a low molecular weight acid provided a relatively significant amount of additional H^+.

3. Conductivity Experiments. Conductivity titrations, such as those on "$H_7[P(W_2O_7)_6]$" (really on its hydrolysis product $H_7[PW_{11}O_{39}]$) appeared to confirm the heptabasic formula of the former. After the acceptance of heptabasic formula for what is really tribasic 12-tungstophosphoric acid, and using its conductivities as reference, the conductivities of several other polybasic heteropoly acids (with basicities indicated by their Miolati−Rosenheim formulas) appeared well supported.

4. Attempts to Prepare Normal Salts. Since most of the known heteropoly salts were acid-salts according to their Miolati−Rosenheim formulations, a considerable search was undertaken to find cations that would precipitate heteropoly anions as normal salts, with all of the indicated H's replaced. Precipitates that were said to have normal salt formulas were reported in a few instances.[68] In the case of the 12-heteropoly phosphates it is likely that the precipitates were salts of the heptabasic 11-heteropoly lacunary complexes formed as hydrolysis products, with perhaps some occlusion of the other product(s) of the hydrolyses (isopoly species). This gave the illusion of a normal salt of the Miolati−Rosenheim heptabasic 12-heteropoly structure. Other cases probably involved precipitation of other decomposition products of the original heteropoly species. The few cases of reports of normal salts involved precipitations by silver, mercurous, thallous, cesium, and guanidinium cations.

An early objection to the Miolati−Rosenheim formulas was the fact that there is no evidence for the independent existence of $Mo_2O_7^{2-}$ or $W_2O_7^{2-}$ species. In response, it was pointed out that Mo and W are in the same periodic group as Cr, and $Cr_2O_7^{2-}$ certainly exists. It was postulated that $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$ were stabilized by their coordination to other elements.

Sometimes Miolati−Rosenheim formulas had to become rather complicated. For example, the complex $[P_2Mo_{18}O_{62}]^{6-}$ that actually has the Wells−Dawson structure (Figure 1b) had to be formulated with a bridge linkage as shown in Figure 2a. Its lacunary 17-tungstodiphosphate derivative, $[P_2Mo_{17}O_{61}]^{10-}$, was formulated as shown in Figure 2b. It must be remembered that these formulations predated ideas of the electronic bases of valency.

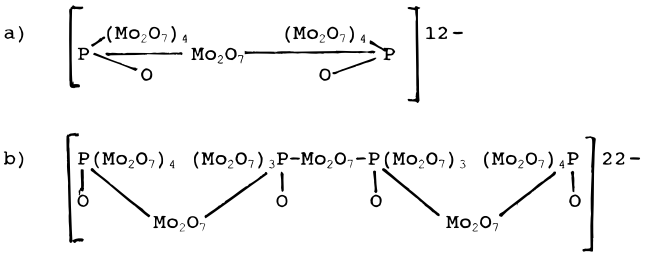

Figure 2. Miolati−Rosenheim structures: (a) 18-molybdodiphosphate (actually $[P_2Mo_{18}O_{62}]^{6-}$ having the Wells−Dawson structure, Figure 1b); and (b) 34-molybdotetraphosphate (actually $[P_2Mo_{17}O_{61}]^{10-}$, a lacunary Wells−Dawson species).

Perspective

The Miolati−Rosenheim Theory placed the correct positive-valent atoms in the complex anion in the correct proportions. It brought unity to the heteropoly (and isopoly) field, creating a framework by which it was possible to rationalize and categorize essentially any polyoxoion formula no matter what its atomic ratios. It thus provided numerous subfields and targets for the corrective efforts of later workers. The theory placed heteropoly chemistry squarely in the realm of coordination complexes, a position it was to lose in the 1930s and 1940s as an interpretation based mainly on mixed-oxide structure took precedence, until later work on transition metal derivatives took the field back into coordination chemistry.

Although, as we shall see, all of Rosenheim's theoretically proposed structures and formulations eventually were proven incorrect, still Rosenheim and his students carefully and capably did and described a very large amount of preparative and descriptive chemistry, which remains valuable and generally very reliable. The whole episode also illustrates the dangers involved in working to establish a preconceived interpretive framework.

Pauling's Proposals

A major breakthrough in the structural chemistry of heteropoly anions resulted from the proposals of Linus Pauling[69] in 1929. In 1927 Pauling[70] had drawn together a set of principles, partly original and partly based on the work of Goldschmidt[71] and others, for rationalizing and predicting the structures of complex ionic crystals. In his 1929 paper[69] Pauling proposed that these "rules for the structures of complex ionic crystals" [72] should also apply to the internal structures of heteropoly anions. There are four rules: (1) negative atoms pack around positive atoms in geometries governed by their radius ratios; (2) the resulting structures must be those that maintain local electrical neutrality insofar as possible; (3) polyhedra of negative ions surrounding positive ions share corners, edges, and/or faces, but corner sharing is strongly preferred over edge sharing, which is strongly preferred over face sharing (owing to increased electrostatic repulsions between the positive ions in the latter cases); and (4) in a structure containing cations of different kinds, those with large charge and small coordination number tend to be as far apart as possible, their polyhedra not sharing polyhedral elements with one another.

In the 1929 paper Pauling (1) accepted the Miolati−Rosenheim formulas and structures for the 6-heteropoly species, e.g., $[Cr^{3+}(MoO_4)_6]^{10-}$; (2) proposed structures for 12-heteropoly species and their isomers, and (3) proposed structures for 9-heteropoly and 2:18 heteropoly species.

As with some other of Pauling's seminal insights that started workers in various chemical areas on correct paths, each of his detailed heteropoly structural proposals proved to be incorrect, but the approach and the *sort* of structures it envisioned have been most useful. Closest to correct was Pauling's proposed structure for 12-heteropoly species. It correctly placed the heteroatom in an XO_4 tetrahedron at the center, surrounding it, in accordance with his second rule, by 12 addenda octahedra sharing only corners. This required a total of 58 oxygens. All 36 of the exterior unshared oxygens then had to attach a hydrogen to drop the total negative charge down to the correct value. This meant that every 12-heteropoly salt had to have at least 18 constitutional waters. Numerous stable hydrates were soon discovered that contained fewer waters than were required for the Pauling formulas.

Keggin Structure

In 1933 Keggin reported an X-ray crystallographic study[73] of cubic "$H_3[PW_{12}O_{40}]\cdot 5H_2O$". (A more recent detailed X-ray and single-crystal neutron diffraction study[76] has made it clear that the crystal is actually a hexahydrate of formula $(H_5O_2)_3[PW_{12}O_{40}]$.) Determination of the anion structure (see Figure 1a) was an X-ray tour de force for its day, being derived from only 17 powder X-ray lines. Only the positions of the W's could be directly determined, but the interatomic W−W distances made the general locations of the anion's oxygens unambiguous. The complex's structure was confirmed by a second powder X-ray study of $H_3[PW_{12}O_{40}]\cdot 29H_2O$.[74] Signer and Gross[75] confirmed by matching powder X-ray patterns that several other 12-heteropoly complexes as well as metatungstate anion, $[H_2W_{12}O_{40}]^{6-}$, have the Keggin structure.

The Keggin structure involves four 3-fold W_3O_{13} groups. Each WO_6 octahedron therein is sharing two edges with other WO_6's and the four W_3O_{13} groups are attached to one another by corner sharing. The total assemblage contains 40 close-packed oxygens and has a tetrahedral pocket in its center for the heteroatom.

Coefficients of Diffusion, Dialysis, and Electrodialysis

Beginning in the mid-1920s and extending into the mid-1940s, G. Jander and his students undertook to elucidate the condition and formulas of polyanions in solution.

He believed it logical to investigate first the polymerizations of the isopoly systems of pure molybdate, pure vanadate, and pure tungstate before progressing to the heteropoly systems. Such a choice can be disadvantageous because heteropoly species are usually of greater thermodynamic stability than the isopoly species and involved in fewer equilibria over greater ranges of pH and concentration. Jander chose as his investigative tool measurement of diffusion coefficients, from which he deduced ionic weights by means of "Rieke's Law" [77] (which was a solution analogue of Graham's Law of Gaseous Diffusion):

$$Dz\sqrt{(\text{ionic weight})} = \text{constant}$$

where D stands for the diffusion coefficient and z, the specific viscosity (i.e., $\eta_{\text{soln}}/\eta_{\text{water}}$). The method requires the choice of a reference ion of supposedly known ionic weight. In the 1930s Brintzinger[78] modified the method by substituting dialysis coefficients and then electrodialysis coefficients for the experimentally more challenging diffusion coefficients.

Elaborate multistep sequences of isopoly polymerization reactions were worked out for molybdates, vanadates, and tungstates.[78−80]

By 1960 some 150 papers had appeared purporting to deduce ionic weights and formulas from diffusion, dialysis, or electrodialysis data or using previous deductions from such data to advance various chemical interpretations. Detailed treatments continued to appear in advanced textbooks on inorganic chemistry. Some of the results were occasionally criticized on various grounds,[81] including precision of experimental techniques, choice of reference ions, degrees of solvation assumed, lack of chemical homogeneity of solutes, probable equilibrium shifts caused by concentration gradients, nonuniformity of membrane pore size, and neglect of variations in ionic shapes and charges. Most such criticisms, however, held to the central idea that molecular or ionic weights as such are related to diffusion or dialysis coefficients in liquids, and might be estimated if the complicating factors could be empirically incorporated into some relationship or made similar for the reference solution and the solution under investigation.

When Jander turned his attention to heteropoly species, little difference in diffusion coefficients was found between the behaviors on acidification of pure molybdate and acidification of molybdate in the presence of a heteroacid. The same was found for vanadates and for tungstates. This led Jander to conclude that heteropoly acids are actually only molecular complexes of Mo_6, W_6, or V_8 polyacids with the heteroacid. For example,[82] 12-molybdophosphoric acid was formulated

$$H_7\begin{bmatrix} H_3Mo_6O_{21} \\ H_3PO_4 \\ H_3Mo_6O_{21} \end{bmatrix}$$

He also erroneously concluded that heteropoly acids are extensively dissociated into polyion fragments in solution.

Modern theories of diffusion in liquids predict that molecular or ionic weights per se will play no role whatever in determining rates of diffusion. For a given solvent only the size and shape of the diffusing species, plus the magnitude of its interactions with adjacent particles, will affect the diffusion coefficient. The rate-determining process for the diffusion of a large solute species is the movement of the solvent molecules around it, by means of a succession of jumps into holes of dimensions comparable to a solvent molecule.[83] (Valid empirical relationships connecting molecular weight and diffusion rate can sometimes be devised for particular groups of large solute species. These equations apply between solute particles having the same (1) shape, (2) interaction with solvent molecules, and (3) internal density within the diffusing species. Such methods introduce the molecular weight only inasmuch as it depends upon the molecular volume and hence often involve an inverse proportion between diffusion coefficients and cube root of the molecular weights.)

In 1960 Baker and Pope[84] ended the use of diffusion and dialysis coefficients for deducing ionic weights of polyion species by showing that the $[SiW_{12}O_{40}]^{4-}$ ion (ionic wt = 2875) and its isomorph $[SiMo_{12}O_{40}]^{4-}$ (ionic wt = 1820) diffuse at identical rates. Since the literature concerning polyion chemistry contains numerous chemical interpretations and formulations based directly or indirectly on “ionic weights” deduced from dialysis or diffusion data, and it is often not obvious that such is the case, the need for care in reading is apparent.

The Anderson–Evans Structure

In 1937 Anderson[85] suggested a structure, in accord with the Pauling principles, for 6-molybdoperiodate ion, $[I^{7+}Mo_6O_{24}]^{5-}$, and other anhydrous 6-heteropoly species that form normal salts with the expected number of monovalent cations. The Miolati–Rosenheim formula for such species envisioned six $MoO_4{}^{2-}$ tetrahedra coordinated to the heteroatom. The structure Anderson proposed (Figure 1c) consists of six coplanar MoO_6 octahedra arranged in a ring sharing edges. This leaves an octahedral pocket in the center of the ring for the heteroatom.

Anderson's proposal went without experimental verification until 1948 when Evans[86,87] confirmed it by a single-crystal X-ray determination of the positions of the central heteroatom and the molybdenums in ammonium and potassium normal salts of $[Te^{6+}Mo_6O_{24}]^{6-}$.

Pure Heteropoly Acids and Determinations of Anionic Charges

The difficulties inherent in attempts to obtain free heteropoly acids of sufficient purity for reliable titration were mentioned above in discussing efforts to substantiate the Miolati–Rosenheim theory. The advent of the strong acid synthetic ion-exchange resins, properly conditioned and washed, made it possible, in 1950, to prepare, in solution, pure heteropoly acids from recrystallized moderately soluble salts.[88] The free acid solutions could be potentiometrically titrated with base to reveal acid strengths and the correct numbers of replaceable H's, thereby fixing the negative charge on each heteropoly anion.[89,90]

In most cases the p*K*'s for the successive replaceable H's are so close in value that no inflections are shown in the H^+ neutralization portions of the potentiometric titration curves. In a typical case, the titration curve for the neutralization is followed by a plateau corresponding to degradation of the heteropoly complex by base into $MoO_4{}^{2-}$ (or $WO_4{}^{2-}$) and the product expected for the heteroatom at the pH involved. The plateau indicates the pH above which the complex is degraded. The number of moles of base represented by the distance between the first (neutralization) inflection point and the final (degradation) inflection provides a sensitive internal check on the purity of the acid.

Other 6-Heteropoly Species

Into the 1950s the 6-heteropoly complexes of trivalent and divalent heteroatoms continued to be represented by Miolati–Rosenheim formulas,[91] e.g., $K_3H_6[X^{3+}(MoO_4)_6]\cdot 7H_2O$. Construction of a model of such an anion, using equal size spheres for O atoms, reveals severe crowding of the oxygens that would impose an unlikely low symmetry. Titrations of the free 6-molybdo acids wherein X = Cr^{3+}, Co^{3+}, Fe^{3+}, and Al^{3+}, as described in the previous two paragraphs, showed that all of those acids had just three replaceable H's.[90] Contrary to Rosenheim's 1914 report,[92] all of the water could be expelled from the salts below 200 °C, and the anhydrous residues so obtained immediately dissolved in water to re-form the complexes completely.[93] This work ended the last remnant of the long reign of the Miolati–Rosenheim theory.

In 1960 the preparation of 6-tungstonickelate(II) salts and free acid were reported, and a single-crystal X-ray study of the sodium salt located the Ni and W atoms.[3a,94] This proved that the anion is monomeric, and has the Anderson–Evans structure involving 24 oxygen atoms. The acid is tetrabasic. These results require that the anion contain six H atoms, so the sodium salt, e.g., is $Na_4[Ni^{2+}W_6O_{24}H_6]\cdot 16H_2O$. This conclusion was important because this was the first heteropoly complex proven to contain H atoms. The availability of more O atoms (one for each two H's included in a complex) opens greater arrays of structural possibilities for heteropoly anions.

In the following year, 6-molybdonickelate(II) complex was shown[3a,8] to be isomorphous with the 6-tungsto species, and the 6-molybdo complexes of Cr^{3+}, Co^{3+}, Fe^{3+}, Al^{3+}, and Rh^{3+} were shown, by fused $Na_2SO_4\cdot 10H_2O$ cryoscopy, to be very stable and monomeric in solution at room temperature.[8] Since any reasonable structure must have at least 24 oxygens, these results showed that each of these complexes probably contained six H atoms also. A consideration of the possible locations for these H's placed them, almost certainly, on the six O's surrounding the heteroatom in an Anderson–Evans structure. That assignment was later confirmed, in 1966, by a particularly accurate X-ray crystal structure[7] for $Na_3[Cr(OH)_6Mo_6O_{18}]\cdot 8H_2O$, in which the locations of all the O's were directly determined and the positions of the complex's six H's could be confidently assigned on the basis of the H-bonding pattern.

Persulfate oxidation of blue $[Ni^{2+}(OH)_6W_6O_{18}]^{4-}$ leads to a black solution from which black crystals of $(Na,K)_8[Ni^{4+}W_6O_{24}]\cdot 12H_2O$ could be separated.[94,95] In 1970 an X-ray crystal structure located all of the atoms.[95] The Ni^{4+} complex has the Anderson–Evans structure, but, unlike the 6-heteropoly species based on divalent or trivalent heteroatoms, the Ni^{4+} complex, like the 6-molybdotellurate(VI), contains no hydrogen. It thus appears that when the oxidation state of the heteroatom is +4 or higher, the 6-heteropoly complexes contain no H, but when that oxidation state is +3 or lower, there is an H atom on each of the six O's surrounding the heteroatom.

The Wells–Dawson Structure

In 1915, Rosenheim and Traube[96] reported preparation of dimeric ammonium 9-molybdophosphate(V) (i.e., 18 molybdodiphosphate). In 1920 the anion was extensively studied by Wu,[97] who used Miolati−Rosenheim formulations and who showed that the preparation produces two geometrical isomeric forms of the anion (presently designated by α and β). A. F. Wells, in 1945, suggested a detailed structure[98] for the tungsten isomorph, the dimeric (2:18) 9-tungstophosphate anion (Figure 1b), based on Pauling's principles and the structure Keggin had shown for the 12-tungsto complex. In 1952, the formula indicated for the tungstate complex by Wells's proposed structure, $[P_2W_{18}O_{62}]^{6-}$, was established for the molybdo complex by Tsigdinos.[99] Dawson, in 1953, determined by a single-crystal X-ray study[100] that the positions of the W atoms in $[P_2W_{18}O_{62}]^{6-}$ were as postulated by Wells. Strandberg[101] in 1975 and D'Amour[102] in 1976 reported complete and accurate X-ray crystal structures of α-$[P_2Mo_{18}O_{62}]^{6-}$ and α-$[P_2W_{18}O_{62}]^{6-}$. These show that the molybdo complex is chiral because of displacements of the Mo atoms within their MoO_6 octahedra. In 1978 Garvey and Pope[24] demonstrated by mutarotation that the chirality exists in solution also. The tungsten complex shows no such chirality,[24,101,102] which is probably related to the greater rigidity of the tungstate framework. Possible reasons for the chirality and its effects on the numbers of blue electrons the molybdo complex will accept, have been discussed by Pope.[103] In 1979 Acerete[104,105] proved by ^{183}W NMR that the β geometrical isomer of $[P_2W_{18}O_{62}]^{6-}$ differs from the α isomer (see Figure 1b) by a 60° rotation of one W_3O_{13} cap.

The Distortions of Addenda Octahedra

Prior to 1959, all of the structural X-ray crystallographic studies of discrete heteropoly complexes determined only the positions of the heavier atoms. Locating by X-ray the low atomic number oxygen atoms in the presence of the high atomic number addenda was at that time a very challenging problem. The X-ray crystal structure of $K_5[Co^{3+}W_{12}O_{40}]\cdot 20H_2O$, determined in 1959, was the first to locate directly all of the oxygen atoms in a heteropoly complex.[3a,106,107] Their positions revealed the important distortions of the WO_6 octahedra, described in the first section of this paper, which are of fundamental importance in explaining the properties of heteropoly compounds. The central $Co^{3+}O_4$ tetrahedron is Jahn−Teller distorted by the weak forces involved in removing degeneracy in the e_g orbitals, which emphasizes the ease of moving central O atoms in the Keggin structure. The distortion of the $Co^{3+}O_4$ tetrahedron and the regularity of the $Co^{2+}O_4$ tetrahedron in the cobaltous isomorph was later confirmed by accurate magnetic measurements by Simmons[108] and, independently, by spin-density distribution studies, calculated from NMR data by Acerete et al.[44] Many subsequent structural X-ray determinations have confirmed the sorts of striking off-center displacements of addenda atoms toward unshared oxygens of their octahedra. In cases where two unshared oxygens are part of an addendum's octahedron, the addenda atom is displaced toward the midpoint between the unshared oxygens, as first shown by Perloff.[7]

Some Important Tungstocobaltates

In 1956 Baker and McCutcheon[109] reported the preparation of four interrelated tungstocobaltates, now formulated:[110,111]

$$\begin{tikzcd}
{[(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]^{8-}} \arrow[r, "H^+"] \arrow[d, shift right=1, "\text{ox.}"'] & {[Co^{2+}O_4W_{12}O_{36}]^{6-}} \arrow[d, shift right=1, "\text{ox.}"'] \\
{[(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}]^{7-}} \arrow[r, "H^+"] \arrow[u, shift right=1, "\text{red.}"'] & {[Co^{3+}O_4W_{12}O_{36}]^{5-}} \arrow[u, shift right=1, "\text{red.}"']
\end{tikzcd}$$

These were early examples of large heteropoly species based on d-transition-metal heteroatoms, and, as such, contributed to reestablishing the field as an area of coordination chemistry. The dicobalt derivatives eventually proved to be examples of an important major new category of complexes[111] wherein a different, lower-valent metal atom replaces an addendum atom in the heteropoly structure. The monocobalt derivatives have the Keggin structure,[3a,110] the Co^{3+} complex providing the first example of a d^6 ion in a tetrahedral site.[110] The spectra proved that the oxidizable Co is in a tetrahedral site and the other Co in an octahedral site.[107d,108] The magnetic properties of the $Co^{2+}Co^{3+}$ complex exemplify a new type of magnetic behavior,[108,112] wherein a wide span of energy states leads to gradual transition between the low- and high-temperature Curie law limits and hence to a broad temperature range (>200 °C) wherein the susceptibility changes very little. (The dicobalt complexes were initially misformulated as 12-tungstates, with one (oxidizable) Co at the center of each and the other Co coordinated to the outside. The latter, octahedral, Co was immediately expelled by acid, yielding an undoubted 12-tungsto complex. In the X-ray structure of the dicobalt complexes, all 12 of the Keggin W positions were occupied by substantial electron density and the octahedral Co had disappeared (attributed to its being coordinated to the exterior of the complex and disordered over several equivalent positions). Actually, the octahedral Co replaced a Keggin structure W and that Co was crystallographically disordered over the 12 possible W positions. The analytical difference was so small (11:1 = 12:1.09) that the 11-tungsto and 12-tungsto formulas could not be unambiguously distinguished by any analysis or measurement except, eventually, by X-ray density versus measured density. In that case a W atom is heavy enough to prove conclusively that the dicobalt complexes (and the other complexes with analogous substitutions of addenda) are 11-tungstates.)

Complexes Wherein a Lower-Valent Octahedral Metal Ion Replaces an Addendum Atom

Although the dicobalt derivatives described in the previous paragraph were actually species wherein Co^{2+} had replaced a W atom in a Keggin structure, that was not realized until 1966. The preparation of the $Co^{2+}Co^{2+}$ species involves adding pink Co^{2+} solution to boiling colorless neutral tungstate. The solution quickly becomes the deep green of the Co^{2+}-Co^{2+} complex. In 1961 Simmons was carrying out that familiar preparation, using colorless “Na_2WO_4” crystals that had been recovered from tungstate residues by an undergraduate. The boiling solution turned a deep red instead of the expected often-observed green! (The procedure for recovering Na_2WO_4 involved precipitating metal hydroxides with base, filtering, and precipitating tungstic acid with HCl. The undergraduate had left the strongly basic solution on the steam bath overnight. Enough glass from the beaker had dissolved to produce colorless $[SiW_{12}O_{40}]^{4-}$ when the solution was acidified, and its Na salt was crystallized and delivered as “Na_2WO_4”.) The ammonium salt of the new red complex was crystallized and analyzed.

This was the first heteropoly complex containing two different elements as heteroatoms. Simmons reported this at the 1962 (Stockholm) International Conference on Coordination Chemistry (I.C.C.C.).[113a]

The structure of the red complex was reported at the 1966 (St. Moritz) I.C.C.C.[113b] It was an 11-tungstosilicate wherein one W of the Keggin structure had been replaced by Co^{2+}. The structure of that complex and four other analogous ones was established by Baker et al.[12] in 1966. Two of the four complexes reported had, like metatungstate, H_2^{2+} in place of the central atom, while Co^{3+} or Ga^{3+} replaced one W in the Keggin-like structure. Subsequently, Weakley and Malik[12,13] and then the Tournés,[14] Ripan and Puscasu,[114] and Fournier, Massart, and Souchay,[115] and many others reported preparations of a large number of 11-tungsto, 17-tungsto, 11-molybdo, and 17-molybdo complexes with various central heteroatoms and various lower-valent octahedral metal atoms substituted for a W or Mo in a Keggin or Wells−Dawson structure.[116]

Species Hybrid between Heteropoly and Conventional Coordination Complexes

In 1970 Figgis[117] established that the unshared position on the substituted lower-valent metal atom, described in the previous section, was generally occupied by a water molecule coordinated to that metal, and the water molecule could be displaced by a wide variety of other ligands or removed entirely by heating the crystals. The latter procedure yielded very reactive five-coordinate species. A ligand with two coordination sites could link two heteropoly units together.

Porphyrin-like Nature of M-Substituted Keggin Structures

Landis[18] was the first to state that metal-substituted Keggin structures show many analogies to porphyrin complexes. As in porphyrin chemistry, the lower-valent metal atom is coordinated about its equator into an electron-conducting structure, with the identity of the group at one pole of its octahedron (i.e., the central tetrahedron) very much affecting the coordination properties of the other polar species (at the exterior of the heteropoly anion). The analogy to porphyrins was expanded upon by Pope[42,118,119], Hill,[797,830] and several other groups and is a basis for various catalytic uses.

Octahedral Trans Effect

The identity of the central heteroatom accordingly can have a pronounced effect on ligands coordinated to a substituted lower-valent metal atom in 11-tungstates, most obviously with respect to their lability. This suggests analogies to vitamin B chemistry. For example, Bezas[120] and later Landis[18] found that when the 11-tungsto heteropolies' central atoms were H_2^{2+} or B^{3+}, ligands attached to substituted octahedral Co^{3+} were surprisingly labile, but when the central heteroatom was Si^{4+} or P^{5+} those ligands were inert.

Heteropoly Complexes Based on Icosahedral Heteroatoms

In 1953, it was shown[89] that the pure free acid of 12-molybdocerate(IV) is octabasic, so neither that complex, $[Ce^{4+}Mo_{12}O_{42}]^{8-}$, nor its Th^{4+} isomorph can have the Keggin structure. In 1968 Dexter and Silverton[121] determined a complete X-ray structure, which showed the large Ce heteroatom to be in a regular CeO_{12} central icosahedron. Surrounding the Ce are six Mo_2O_9 groups, each of which is composed of two face-sharing MoO_6 octahedra. The Mo_2O_9 groups are linked together by corner sharing. This was the first case of face sharing by addenda polyhedra and the first case of icosahedral coordination of a heteroatom. Subsequently, it was found that 12-molybdo complexes of Ce^{3+}, U^{4+}, U^{5+}, and Np^{4+} are isomorphous with the Ce^{4+} and Th^{4+} derivatives. In 1979 a complete X-ray structure was also determined for the U^{4+} complex.[122]

Isotope Exchanges

The results of Spitsyn and Torchenkova[9a] (1954) and of Ripan and Marcu[123] (1959) appeared to indicate that radioactive W^{185} exchanges very slowly between 12-tungstosilicate or metatungstate ($H_2W_{12}O_{40}{}^{6-}$) and the solute(s) in a solution prepared by acidifying Na_2WO_4 solution to pH = 1. At pH 4.5 $[SiW_{12}O_{40}]^{4-}$ exchanges its W rapidly, but at pH 6.8 the exchange is very slow.[9d] (Possibly the degradation of the complex to 11-tungstosilicate was essentially complete at the latter pH and exchange with that species is slow.)

In 1961, Tsigdinos[3a,8] reported studies of exchange of Mo^{99} between paramolybdate ion, $Mo_7O_{24}{}^{6-}$, and (a) $[Cr^{3+}(OH)_6Mo_6O_{18}]^{3-}$ and (b) its isomorph $[Fe^{3+}(OH)_6Mo_6O_{18}]^{3-}$. At 29.5 °C and pH's in the range 2.5−4.5, the exchange was complete in each case in time of mixing (<0.5 min.); but at 0 °C and pH = 2.5 the exchange with the Cr^{3+} complex had a half-time of 35 min while the exchange rate with the Fe^{3+} complex was 2 orders of magnitude faster. The exchange rates increased as pH increased. Tsigdinos also determined exchange rates of Cr^{51} between $[Cr^{51}(H_2O)_6]^{3+}$ and $[Cr^{3+}(OH)_6Mo_6O_{18}]^{3-}$. At 29.5 °C and pH = 1.06 half-times ranged from 4.3 to 22 min. The exchange was faster at lower pH. This 6-molybdo species was therefore the first example of a chromic complex that exchanges its Cr rapidly. Consequently, it was proposed that the very nonlabile Cr−O bonds were not breaking but that CrO_6 was exchanging as a unit. The Fe^{3+} and Cr^{3+} 6-molybdo complexes have the Anderson−Evans structure, as explained above. A detailed argument based on the geometries, kinetics, and energetics was advanced which convincingly holds that the mechanisms of the exchanges involve squeezing out of an MoO_4^{2-} group from each kind of polyanion by addition of two solvent oxygens, forming two new Mo−O bonds while simultaneously breaking two other Mo−O bonds. This interpretation strongly indicates that the faster exchange of Mo with the ferric complex would at most be only slightly dependent upon the greater ease of breaking Fe−O bonds as contrasted with Cr−O bonds, and that therefore the much slower exchange of Mo with the latter is a consequence of the CrO_6's greater compactness and rigidity, caused by crystal field stabilization energy, which results in the complex's resistance to the necessary distortion.

In 1970, Lee[10] reported conclusive proof that CrO_6 exchanges as a unit, with unbroken Cr−O bonds, between $[Cr(OH)_6Mo_6O_{18}]^{3-}$ and $[Cr(H_2O)_6]^{3+}$. The proof was based on O^{18} exchange between $[Cr(H_2O)_6]^{3+}$ and H_2O,[18] Cr^{51} exchanges between the heteropoly anion and $[Cr(H_2O)]_6^{3+}$, and three-way exchanges of O^{18} among $[Cr(H_2O)_6]^{3+}$, H_2O, and $[Cr(OH)_6Mo_6O_{18}]^{3-}$. This was the first case of an MO_x group proven to exchange as a unit.

Studies of O^{18} exchanges[10,124] between H_2O and $[Cr(OH)_6Mo_6O_{18}]^{3-}$ show that six oxygen atoms of the heteropoly exchange very rapidly, 12 exchange with a $t_{1/2}$ in tens of minutes, and six exchange extremely slowly. The latter would be those attached to the Cr, the first six those shared between two Mo's only, and the twelve would be the unshared O's, which do not exchange directly but exchange through a process of dissociation of MoO_4^{2-} and reattachment of MoO_4^{2-} in new orientations.

All of this substantially confirmed the most probable mechanism suggested by Tsigdinos,[8] which involves dissociation of MoO_4^{2-} units from the polyanion accompanied by simultaneous attack of two solvent O's per Mo expelled. Expelled MoO_4^{2-} reattaches to chromic ion or to heteropoly fragments which have been left with fewer than six Mo's.

Lee[10] also measured exchange reactions with the isomorphs $[Ni^{2+}(OH)_6Mo_6O_{18}]^{4-}$ and $[Ni^{2+}(OH)_6W_6O_{18}]^{4-}$, both of which have the Anderson−Evans structure. Ni^{63} exchanged between $[Ni(H_2O)_6]^{2+}$ and the 6-molybdonickelate(II) with $t_{1/2} = 3.9$ min at 30 °C, and the analogous exchange with 6-tungstonickelate(II) had $t_{1/2} = \sim 3$ days. H_2O^{18} and 6-molybdonickelate showed an initial fast O^{18} exchange ($t_{1/2} \cong 0.5$ min) for some of the oxygens, followed by a slower exchange of other O's ($t_{1/2} \cong 8.5$ min). H_2O^{18} and 6-tungstonickelate(II) showed an overall $t_{1/2} \cong 3$ days.

As explained in part A above, it is probable that the greatly decreased lability of most polytungstates relative to polymolybdates results from the greater rigidity of the polytungstate frameworks.

Action of Surface Active Catalysts

The presence of surface active catalysts has long been used to labilize various ligands on otherwise inert coordination complexes and to cause reaction mixtures to yield products that are different from those obtained in the absence of such catalysts. Tsigdinos[8] reported the first cases of such behavior on the part of heteropoly complexes.

Kurnakov[125] in 1900 and Friedheim and Keller[126] in 1906 had reported that a mixture of Co^{2+} in potassium paramolybdate solution, when oxidized by Br_2, formed primarily what we now formulate $K_3[Co^{3+}(OH)_6Mo_6O_{18}]\cdot aq$ with a small byproduct of a more soluble potassium salt containing 5 Mo atoms per Co^{3+} atom. This was confirmed by Tsigdinos[8] who also showed that the same product distribution resulted when various other oxidizing agents (H_2O_2, Cl_2, $NaBiO_3$, PbO_2, or $KBrO_3$) were used in place of Br_2. However, when active charcoal or Raney nickel was added to the reaction mixture, the H_2O_2 oxidation quantitatively converted all of the Co present to the 5-molybdocobaltate(III). This reaction has been used as the basis for quantitative determination of cobalt.

The charcoal and Raney nickel were ineffective when used with oxidizing agents other than H_2O_2. In fact they prevented the formation of any heteropoly species under conditions that, in the absence of catalyst, normally produced $[Co(OH)_6Mo_6O_{18}]^{3-}$ plus a little 5-molybdocobaltate. Treatment of a hot solution of $[Co(OH)_2Mo_6O_{18}]^{3-}$ with H_2O_2 plus charcoal or Raney nickel, produced complete conversion of the heteropoly complex to the 5-molybdo derivative. As with various coordination compounds, presence of the surface active catalyst apparently lets the most stable complex form. Unsurprisingly, substitution of active alumina, SiO_2, or PtO_2 for the charcoal or nickel was ineffective.

In 1956, Shimura et al.[127] interpreted the absorption spectrum of the 5-molybdocobaltate(III) as showing the presence of $Co^{3+}{-}O{-}Co^{3+}$, requiring the complex to be polymeric.

Tsigdinos[8] showed by fused $Na_2SO_4\cdot 10H_2O$ cryoscopy that the 5-molybdocobaltate(III) is a very stable dimer: $[(Co^{3+}O_6)_2Mo_{10}O_{36+n}H_{2n}]^{6-}$. Later, in 1969, Evans and Showell[128] determined the complete X-ray structure of the ammonium salt. This showed the formula to be $[(Co^{3+}O_6)_2Mo_{10}O_{38}H_4]^{6-}$. The structure may be formed by removing one Mo (and its two unshared O's) from each of two Anderson−Evans 6-molybdocobaltate(III) complexes, which produces chiral $CoMo_5$ units, and then slotting together two d-$CoMo_5$ units or two l-$CoMo_5$ units. This gives a d- or l-Co_2Mo_{10} complex with two CoO_6 octahedra sharing an edge. Four H's remain on those oxygens of the two CoO_6's which are also common to just two MoO_6's. In 1970, the complex was resolved into stable optical isomers.[23]

Isomers of the Keggin Structure

In 1862 Marignac[53] showed that 12-tungstosilicate forms two geometrical isomers, now designated α and β (see Figure 1a). These have been shown to differ by a 60° rotation of one of the W_3O_{13} 3-fold groups.[117b,129] In 1952, Strickland[130] showed that 12-molybdosilicate analogously forms α and β isomers. This sort of isomerism has also been found for the 12-tungsto complexes of Ge and H_2 and for the 12-molybdo complexes of Ge, P, and As.[131]

Fast Reversible Reductions to Heteropoly Blues

Strickland[130] also studied reductions of 12-molybdosilicate to heteropoly blues by stannous ion. He noted that the reduced species could be rapidly and quantitatively reoxidized to the parent 12-molybdosilicate under conditions in which silicate and molybdate do not combine. This led him to speculate correctly that the reduction product probably has a structure that is a slight modification of that of the parent complex, and that the similar results of Treadwell and Schaeppi[132] with 12-molybdophosphate were an analogous case. Strickland was unaware that reductions by stannous ion lead to substitution of tin atoms into the heteropoly structure.[133]

Souchay and Co-workers

From the early 1940s into the mid-1970s Pierre Souchay, his students, and co-workers at the Sorbonne investigated both isopoly and heteropoly anions, centering largely on discovery of the formulas in solution. While the most major thrust of their work relied on electrochemistry (e.g., polarography, potentiometric titration, controlled potential electrolysis), other methods were substantially utilized when appropriate (e.g., fused salt hydrate cryoscopy, classical analysis, spectrophotometry, magnetochemistry, ultracentrifugation, NMR). Possibly the group's most valuable contribution was the number of productive scientists who, through it, became interested in the field and continued research in it (such as Chauveau, Courtin, Massart, Tourné, Teyssèdre, Hervé, Fournier, Contant, Tézé, Ciabrini, Lefebvre, Faucherre, Schaal, Carpeni, Martin-Frère, Fruchart, Lourijsen, Ostrowetsky, Doppelt, Michelon, Launay, etc.).

Souchay wrote two books[2] (1963 and 1969) which summarize most of his major contributions. His 1965 21-page review,[134] "Polarographie des Polyanions", gives a somewhat more generalized summary of that aspect of his work and that of others.

His work clarified much of the confusion that had existed as a result of the quite complex sequences of reactions existing in solution. A chronological selection of some of the important contributions follows.

1943	polarography of polyanions:[135] tungstophosphates, tungstoborate, and metatungstate
1943	clarified nonexistence of various previously claimed polytungstates[136]
1945	detailed study[137a] of the system $[PMo_{12}O_{40}]^{3+}$–H_2SO_4–H_2O-diethyl ether—on the basis of the Drechsel[137b] ether extraction methods of 12-heteropoly acids
1945	polarographic study[138] of formation and degradation of various heteropoly tungstosilicates, -arsenates, -phosphates, and -borates
1946	reporting[139] tungstogermanates and molybdogermanates, and polarography
1948	absorption spectra[81] of various tungstophosphates and molybdophosphates
1949	clarification of the confused status of molybdomanganate(IV) showing only 9-molybdomanganate(IV) exists and the isomorphous 9-molybdonickelate(IV) is reported[140]
1951	the solution chemistry of the molybdophosphates;[141] species exist with P:Mo ratios of 1:1, 2:5, 1:12, 1:11; cryoscopic, polarographic, potentiometric measurements elucidate conditions for each
1951	applications of cryoscopy in fused salt hydrates[142]
1951	use of solubility measurements to determine degrees of condensation of polyions;[143] relations between potentiometric and cryoscopic titration curves (see also ref 144)
1959	elucidation of some vanadotungstates[145]
1959	studies of decomposition of heteropoly species by acid[146]
1960	structure of molybdenum blue[147]
1961	electrolytic reductions of α-$[SiMo_{12}O_{40}]^{4-}$ to 2e and 4e heteropoly blues, both being extractable into ethyl acetate; oxidation of the 6e blue gives the β isomer of the parent oxidized complex[148]
1962	reduction of metatungstate at Hg electrode[149] leads to the complex's uptake of 21, 26, 31, and 36 electrons; reoxidation regenerates $[H_2W_{12}O_{40}]^{6-}$
1963	preparation and study of 2e and 4e heteropoly blues of α-12-molybdosilicate, and preparation of their crystalline free acids[150]
1963	polarographic study of α- and β-$[SiMo_{12}O_{40}]^{4-}$; two, four, and six electron reductions, leading to preparation of pure β isomers[151]
1963	vanadotungstates and vanadomolybdates of type $[W_5VO_{19}]^{3-}$ and $[MoVO_{19}]^{3-}$, etc.[152]
1964	$[SiMo_{12}O_{40}]^{4-}$ electrolytically reduced in two 2e steps. Formulas of products and isomers determined by spectrophotometric, potentiometric, and conductometric methods[153]
1964	preparation of three V-substituted complexes[154] from $[PMo_{12}O_{40}]^{3-}$
1965	polarographic reduction of $[SiW_{12}O_{40}]^{4-}$ shows four waves; preparation of 1e and 2e heteropoly blues of 12-tungstosilicate by controlled potential electrolysis[155]
1966	evidence for polyions of V and W with various V:W ratios; polyanions containing various ratios of V(IV):V(V); disproportionations[156]
1966	heteropoly anions fixed on an ion-exchange resin as a new type of electron-exchange resin[157]
1966	study of V substituting into $[PMo_{12}O_{40}]^{3-}$ structure;[158] only one V^{4+} can substitute in, but more V^{5+}, can go in

1967 polarography of heteropoly tungstates and molybdates[159] of Si, P, As, and Ge: numbers of electrons for various reduction steps under particular conditions; tabulation of $E_{1/2}$ values; distinguishing and quantitating isomers.

1967 controlled potential electrolytic reductions of $[PMo_{12}O_{40}]^{3-}$ and $[AsMo_{12}O_{40}]^{3-}$ yield complexes reduced by two, four, and six electrons; stability ranges of the reduced acids greater than their parents; polarographic and spectrographic exams of parents and reduction products show α and β isomers[160]

1967 isomers detected by polarography and voltammetry[161] for the α- and β-$[P_2Mo_{18}O_{62}]^{6-}$

1967 the preparation of heteropoly blues by controlled potential electrolysis[162]

1967 identification and properties of three new reduction products of $[SiW_{12}O_{40}]^{4-}$ produced at pH ~10; seven, 12, and 14 electron reduction products[163]

1968 in reducing heteropoly molybdates using Sn^{2+}, Cr^{2+}, or Ti^{3+} as reductants, the metal replaces one or two Mo's in the heteropoly structure[164]

1968 behavior of molybdovanadophosphoric acids in acid medium[165]

1968 electrolytic reduction of $[PMo_{12}O_{40}]^{3-}$ reveals α and β isomers; reduction in M $HClO_4$–50% dioxane yields α isomer; β isomer obtained in aqueous M $HClO_4$; two, three, four, five, and six blue electron reduction products of α and two, three, four, and five electron reduction products of β; p*K*'s of these derivatives determined[166]

1969 preparation of $K_6[Cr^{3+}W_{11}O_{38}H]$ reported; polarogram shows reversible two and four electron reductions and a further reduction (4 or 6e)[167]

1969 $[V^{2+}W_5O_{19}]^{4-}$ and $[HV_2^{4+}W_4O_{18}]^{3-}$ prepared, properties[168]

1969 2e blue of $[SiW_{11}O_{39}]^{8-}$ made by controlled potential electrolytic reduction at 0 °C urder inert atmosphere;[160] slowly converts to $[SiW_{12}O_{40}]^{6-}$; $[PW_{11}O_{39}]^{7-}$ behaves analogously; reduction of $[P_2W_{17}O_{61}]^{10-}$ gives $[PW_{17}O_{61}]^{12-}$ and the $[P_2W_{17}O_{61}]^{14-}$

1970 preparation and formulation of tungstoantimonate(III) and tungstobismuthate(III) as $[X^{3+}W_{11}O_{38}H]^{6-}$; potentiometric titration of their acids prepared by ion exchange[170]

1970 2e heteropoly blues of 11-tungstosilicates containing Al^{3+}, Fe^{3+}, and Cr^{3+} substituted into the Keggin structure's 12th W position were made[171]

1970 preparation of $K_5[PV_6(\text{Mo or W})_6O_{38}]$ and $K_7[PV_{10}(\text{Mo or W})_2O_{37}]$[172]

1971 preparation and properties of 4e reduced molybdostannisilicates[173]

1971 electrolytic reduction of α-$[GeMo_{12}O_{40}]^{4-}$ gives α-2e and α-4e blues, which are stable at pH 6–8; in 0.5 M HCl, the α-4e isomerizes to β-4e, reoxidation of which gave β-2e and then oxidized β (this being the only means of preparing the latter); in 0.5 M HCl, β-2e disproportionates to β-4e and oxidized β[174]

1971 tungstoantimonate(III) and tungstobismuthate(III) were reduced by controlled potential electrolysis at 0 °C; the reduction products are unstable at room temp; polarographic study discussed[175]

1972 study of kinetics and mechanisms of reactions of VO_2^+ with $[SiW_{12}O_{40}]^{4-}$ and with $[PW_{12}O_{40}]^{3-}$ to yield $[XVW_{11}O_{40}]^{n-}$ [176]

1972 preparation of α and β 12-tungstosilicates and 12-tungstogermanates; preparations and interconversions of 11-tungsto and 12-tungsto derivatives (both α and β); preparation of α and β $[MW_{11}(\text{Si or Ge})]^{n-}$ complexes[177]

1973 preparation and properties of $H_8[As_4Mo_{12}O_{50}]$[178]

1973 preparations of $[SiW_{11}M^{2+}(H_2O)O_{39}]^{6-}$; stabilities decrease in the order (for M^{2+}): Co > Ni = Fe > Zn > Cu > Mn; $H_5[SiW_{11}Cr(H_2O)O_{39}]$ was crystallized; the stability constant for $[SiW_{11}Fe^{3+}(H_2O)O_{39}]^{5-}$ was determined; in basic solution the Fe^{3+} complex forms a dimer; $K_6[SiW_{11}Fe^{3+}(OH)O_{39}]\cdot nH_2O$ was isolated[179]

1974 changes in the polarography and absorption spectra with time during the alkaline hydrolysis of α- and β-$[SiW_{11}O_{39}]^{8-}$ indicated the formation of α and β isomers of a 9-tungstosilicate; the α isomer was isolated as its Cs salt[180]

1974 IR and Raman spectra of solid 12-molybdo- and 12-tungstophosphates and -silicates and of solutions of those complexes in O-containing solvents confirm that $[X(\text{Mo or W})_{12}O_{40}]^{n-}$ complexes exist in solution[181]

1974 reduction of α- and β-$[SiMo_{12}O_{40}]^{4-}$ was studied by polarography and voltammetry and reduction by Sn^{2+}, Cr^{2+}, and Ti^{3+} was studied; a general reduction scheme shows two series of derivatives with different chemistry and redox behaviors[182]

1974 for $[SiMo_{12}O_{40}]^{4-}$ and related complexes, progressive electrochemical reduction forms redox reversible very mobile systems;[183] redox and chemical properties (stability and disproportionations) and relations between α and β isomers; for higher reduction stages, the derivatives form new series with different properties; members of each series are in redox reversible equilibrium with each other, but not with members of the other series

1974 preparation of 12-tungsto isopoly species containing one and two F atoms; polarography and reduced species; preparation of free acids and K salts; degree of condensation checked by ultracentrifugation[184]

1974 peroxy salt $Cs_4[Nb_2W_4O_{19}(O_2)]\cdot 3H_2O$ prepared; reduction gave $Cs_3H[Nb_2W_4O_{19}]\cdot nH_2O$[185]

1974 $NH_4[Sb_2W_5O_{20}]\cdot 8H_2O$ protected mice against Friend- and plasma variant-induced leukemias and delayed appearance of tumors in newborn mice inoculated with Moloney murine sarcoma virus; the compound did not induce interferon and had no effect on a grafted leukemia[186]

1975 kinetics and mechanisms for decomposition of $[H_2W_{12}O_{40}]^{6-}$ in alkaline buffers; effects of nature of buffer and of added LiCl, NaCl, and KCl[187]

1975 kinetics of decomposition of $[GeMo_{12}O_{40}]^{4-}$ in strongly acidic media[188]

Ripan and Co-workers

After 20 years of research on other inorganic problems, Raluca Ripan of the Babes-Bolyai University and the Romanian Academy of Sciences Chemistry Laboratory in Cluj, took up research in 1947 on polyanions. From then to 1972 she published over

70 papers on heteropoly research and some 25 on isopoly anion chemistry. Much of her heteropoly focus was on the status of 12-heteropoly species in solution under various conditions, starting from an acceptance of Miolati−Rosenheim formulations and progressively modifying them over the years to support her results and the modern structural ideas. Most of her major conclusions over the years were substantiations of those made earlier by others and were interpreted in terms of formulations that were becoming obsolete at the times.

Ripan made extensive use of conductometric, potentiometric, photometric, and polarographic techniques and combinations thereof.[189−212] Ripan originated, developed, and extensively applied the techniques of paper chromatography, paper electrochromatography, and, later, paper radiochromatography for elucidating structures and reaction mechanisms of heteropoly anions.[213−226] In 1957 she reviewed the preparations of silicomolybdates.[227] From 1959 to 1961 Ripan et al.[228−230] undertook cryometric titrations of the free acids of 12-tungstophosophate, and -silicate, and 12-molybdophosphate and -silicate with NaOH in fused $Na_2SO_4{\cdot}10H_2O$ (i.e., saturated Na_2SO_4 solution). These confirmed the correct basicities of the free acids and indicated various stages of the degradation of the complexes. Results with metatungstic and 12-tungstoboric acids were inconclusive.

She studied insoluble heteropoly salts as packings in electron exchange columns,[231−233] and, in 1960, wrote a summary of previous studies on iso- and heteropoly compounds of W.[234] Beginning in 1960, Ripan was active in applying radioactive isotopes to heteropoly chemistry: measuring isotope exchange rates under various conditions, establishing formulas, and following chromatography.[235−237] She reported[238,239] several new related compounds, being salts (especially of cobaltammine cations) of $[Cu^{3+}(IO_6)_2]^{7-}$, $[Ag^{3+}(IO_6)_2]^{7-}$, and $[Au^{3+}(IO_6)_2]^{7-}$. Having elucidated the formation and stability of $[TeMo_6O_{24}]^{6-}$ in solution,[16] Ripan and Calu demonstrated[240] the formation and stability of its isomorph $[TeW_6O_{24}]^{6-}$.

From 1966 to 1970 Ripan, Todorut, and Botar[241,242] reported the preparations and properties of a new heteropoly complex, $[U^{4+}W_8O_{28}]^{4-}$, but in the following year Weakley et al.[243,244] showed that an isomorph of the complex was really $[CeW_{10}O_{36}]^{8-}$. The structure (Figure 1f) consists of two W_5O_{18} units (a $W_6O_{19}{}^{2-}$ complex with one WO removed) coordinated to a central atom. Complexes of this structure have been prepared with the following central atoms: U^{4+}, Ce^{4+}, Th^{4+}, Zr^{4+}, Ce^{3+}, Y^{3+}, La^{3+}, and most trivalent rare earths.[245]

In 1971, Ripan and Botar[246,247] reported preparation and properties of salts and free acid of $[UThW_{18}O_{61}]^{6-}$.

In 1963, Ripan reinvestigated[248] the system of polytungstocobaltates, arriving at the same conclusions that had been put forward by Baker in 1956,[109] including the misformulation of the dicobalt complexes as 12-tungstates. In 1966, in accordance with the structures proposed by Baker[109] in 1956 for "$[Co^{2+}Co^{2+}W_{12}O_{42}]^{8-}$", and "$[Co^{2+}Co^{3+}W_{12}O_{42}]^{7-}$" Ripan et al.[249] reported the preparation and properties of "$[ZnZnW_{12}O_{42}]^{8-}$", "$[Ni^{2+}ZnW_{12}O_{42}]^{8-}$", and "$[Ni^{2+}Fe^{3+}W_{12}O_{42}]^{7-}$" and, in confirmation of Agarwala,[94] the preparation of $H_4[Ni(OH)_6W_6O_{18}]$. The following year (1967) radioelectrophoresis and radiochromatographic studies[250] as functions of pH confirmed Baker's 1966 conclusions[111] about the chemistry and interrelations of the tungstodicobaltates. The 1966 observation[111] that only by comparison of measured and X-ray densities could it be unambiguously proved that the bimetallotungstate anions are 11-tungstates and not 12 tungstates was confirmed.[251]

Following the 1966 formulation[252] of Simmons's $[Co(H_2O)O_5SiO_4W_{11}O_{30}]^{6-}$ complex as an 11-tungstate with the Co^{2+} replacing one W of the Keggin structure, and the 1966 paper by Baker et al.[111] establishing the class of complexes wherein a lower valent metal is substituted for an addendum in a Keggin structure, Ripan et al. reformulated their $NiZnW_{11}$, $NiFeW_{11}$, and $ZnZnW_{11}$ complexes[251,253] and reported preparation of $K_6[NiSiW_{11}O_{40}H_2]{\cdot}nH_2O$ and $K_5[NiPW_{11}O_{40}H_2]{\cdot}nH_2O$ by a cation exchange method.[254] Magnetic susceptibility[255] showed the Ni to be octahedral in $NiZnW_{11}$ and absorption spectra[256] showed the same for $NiFeW_{11}$. DTA, thermogravimetry, X-ray, and IR proved that $K_6[(H_2O)NiSiW_{11}O_{39}]{\cdot}nH_2O$ could be completely dehydrated at 570 °C without destruction of the structure.[257] 1971 saw thermogravimetric, DTA, X-ray, IR, and spectrophotometric studies of 12-vanadophosphate.[258] Thermal decompositions of some heteropoly tungstates with transition metal heteroatoms were studied in 1972.[259]

Chauveau and Co-workers, through 1970

A former student and long-time co-worker with Souchay, Francoise Chauveau's extensive earlier contributions have been cited above in the listing of Souchay's papers.[146,147,153,155,166,181,185] In about 1967 she started undertaking the guidance of separate heteropoly projects, such as a spectrophotometric, cryoscopic, and paper electrophoresis study of the Keggin structure vanadomolybdophosphoric acids: $H_4[PVMo_{11}O_{40}]$, $H_5[PV_2Mo_{10}O_{40}]$, and $H_5[HPV_3Mo_9O_{40}]$.[260] Her post-1970 research, especially on fluoro-substituted isopoly species and extensive use of multinuclear NMR, will be mentioned in the next section.

Pope and Co-workers through 1970

After three papers[5b,12,84] resulted from a postdoctoral fellowship with Baker, M. T. Pope started building his own research group at Georgetown University. In 1966 Pope and Varga[261] demonstrated by ^1H NMR the presence of two central protons in metatungstate anion, $[H_2W_{12}O_{40}]^{6-}$; and fundamentals of electrolytic reduction to form heteropoly blues were reported (1966−1970).[27,262,263] In 1967, 12-niobomanganate(V) complex was reported,[264] and two years later heteropoly niobates and tantalates containing Mn(IV) were elaborated upon.[265] Potentiometric and spectrophotometric methods for determination of W and V in heteropoly complexes were elucidated[266] in 1968. Heteropoly 13-, 11-, and 4-vanadomanganates(IV) were the subject of two papers with Flynn.[267] ESR spectra of heteropoly blues were described at the 1970 International Conference on Coordination Chemistry (Krakow).[268] Some of the more important post 1970 general accomplishments of this group will be mentioned in the next section.

The Tournés through 1970

Claude Tourné and her husband, Gilbert Tourné of Université des Sciences et Techniques du Languedoc, undertook heteropoly researches in about 1966, reporting an examination of some heteropoly blues.[269] In 1968 and 1969 following the 1966 establishment by Baker et al.[111,113b] of species wherein lower-valent metal atoms substitute for a single W of a Keggin structure, and Weakley and Malik[12,13] had, in 1967, extended the concept to substitutions into Wells−Dawson structures, and Ripan et al. had reported[251,253] further examples, the Tournés reported[14,270] numerous additional examples prepared by reacting 11-tungsto, or 17-tungsto lacunary species with various cations. The crystallographic space groups adopted by the various salts were studied and categorized, and absorption spectra of the lower valent metal chromophores were interpreted. The Tournés extended the preparations to analogous molybdates, which were found to be less stable than corresponding tungstates. Post-1970 contributions of the Tournés will be mentioned in the next section.

Other Activity of Members of Souchay's Group (University of Paris) through 1970

Beginning in 1961, René Massart had coauthored a number of papers with Souchay, which have already been cited.[133,148,150,151,153,159,164,173,182,183] In the period 1968−1970 he authored seven more papers without Souchay, six of which concerned detailed studies of the successive reduction stages of α and β 12-molybdo or 12-tungsto complexes.[271−274] The seventh,[275] in 1969, reported the 11-molybdosilicate complex wherein Fe^{3+} replaces one of the Keggin structure addenda, and the isostructural 11-molybdosilicate complexes containing Co^{2+}, Mn^{2+}, and Ni^{2+} were prepared and shown to be relatively unstable compared to isomorphous tungstates or M^{+3}-substituted analogues.

Beginning in 1965, Gilbert Hervé had coauthored several papers with Souchay, which have already been cited.[155,159,163,170,177,186] In the period 1966−1970 he authored four more papers without Souchay. These involved detailed study of reductions of 12-heteropoly complexes, including the higher reduction stages, and reductions in basic media.[272,274,276]

Roland Contant had two papers in 1967 with Souchay[161,162] and two papers, 1968 and 1970, without him[274,277] concerning reduction products of molybdoarsenic acid and of 12-tungstoborate, respectively. Paul Courtin had two papers (1964 and 1970) with Souchay already cited[154,172] and one independently in 1968[278] which elucidated the preparation and properties of $H_4[PVW_{11}O_{40}]$, $H_5[PV_2W_{10}O_{40}]$, and $H_5[PV_3W_6O_{31}H]$.

Post-1970 contributions of Massart, Hervé, Contant, and Courtin will be mentioned in the next section.

Marcu and Co-workers through 1970

In 1966, Gheorghe Marcu of the Babes-Bolyai University in Cluj, Romania, wrote a review[279] of isopoly complexes and heteropoly complexes with metals or metalloids as heteroatoms, citing 96 references. In 1966−1969 he studied chromatographic separations of metals on paper impregnated with ammonium tungstosilicate.[280−282] Papers coauthored with Ripan have already been cited.[217,222,223,236−238]

Other Workers through 1970

In addition to extensive work on isopoly complexes, K. F. Jahr and J. Fuchs of the Free University of Berlin confirmed,[283] in 1966, the existence of $[H_nIMo_6O_{24}]^{(5-n)-}$.

In 1969 Radul, Polotebnova, and Bardin[284] reported the preparation and study of $H_5[AsW_{10}V_2O_{39}]\cdot nH_2O$. In the same year Spitsyn et al.[285] confirmed Pope's NMR observation of two central protons in metatungstate ion and also detected two protons in paratungstate.

1969 also saw K. H. Tytko and O. Glemser of the University of Göttingen propose[286] a very plausible reaction mechanism for the formation of isopoly tungstates containing WO_6 octahedra upon acidification of solutions containing WO_4^{2-} tetrahedra. The proposal is relevant to heteropoly complexes. In the same year Flynn and Stucky[287] reported preparations and properties of heteropoly 12-niobate complexes of Ni^{4+} and Mn^{4+} and the preparation and characterization[288] of $Na_5[Co(en)Nb_6O_{19}]\cdot 18H_2O$ and $Na_5[Cr(en)Nb_6O_{19}]\cdot 18H_2O$.

C. Selected General Developments since 1970

Since 1970 there has been a great expansion of work in the field, built on the base described in the previous section. Over 2000 papers have been published about heteropoly chemistry since 1970, not including the large number on the closely related isopoly species. In addition to reporting many new complexes exhibiting novel and intricate new structural types, the application of new and vastly improved physical techniques has greatly expanded knowledge of structure, mechanism, bonding, electron transfer, chemical reactions, and applications, especially catalytic and medicinal.

What follows is not intended to approach a complete representation of the publications of the individuals and groups cited. The effort has been merely to cite some of the more important contributions in order to provide a sense of the activities of some of the significant individuals and groups. Inevitably numerous important papers and some individuals will have been omitted, for which we apologize but plead that more complete treatment would have been an overwhelming task.

Part 1 of the following section will outline the contributions of continuing groups, whose pre-1971 efforts have been described in the previous section (Baker, Chauveau, Evans, Marcu, post-Souchay U. of Paris group, Pope, Sasaki, the Tournés, Weakley). Part 2 will sketch some of the important areas of effort for important new groups and workers (Allman and D'Amour; Chuvaev, Kanzanskii, and Spitsyn; Coronado; Day and Klemperer; Finke; Gatteschi; Glemser and Tytko; Hedman; Hill; Jameson; Knoth and Domaille; Lunk; Papaconstantinou; Pettersson; Sasaki; Shimura; Strandberg; Yamase; Zubieta).

1. Contributions of Continuing Groups

Baker and Co-workers

The foregoing sections have cited 54 references to contributions of the Baker group. He organized the first international Symposium on Structure and Properties of Heteropoly Anions (National Meeting of the American Chemical Society, Atlantic City, Sept 1956). Other significant contributions included the following.

Simmons's[108] magnetic measurements of paramagnetic exchange interactions were extended and theoretical treatment for the unique magnetic properties was presented.[112,289] The first extensive X-ray photoelectron spectroscopic study (of 6- and 12-heteropoly tungstates and molybdates) was reported,[290] yielding exceptional accuracy by introducing use of Cs^+ or Na^+ counterions as internal reference standards,[291] and correlating chemical properties.

Fourteen 11-tungsto complexes containing Co^{2+} or Co^{3+} substituted into Keggin-like structures were studied[18] in order to elucidate the "octahedral trans effect" of the identity of the central heteroatom on the lability and bonding of the ligand coordinated to the Co. The analogy of substituted 11-tungsto complexes to porphyrin complexes was noted for the first time.[18] The existence of "dumbbell" complexes (see Figure 1d) was described.

In 1979 Acerete, Hammer, and Baker[292] introduced ^{183}W NMR as a tool for structure and chemistry. ^{183}W's spin of $^1/_2$, sharp lines, chemical shift sensitivity, and 14.3% natural abundance made it valuable, while its very low sensitivity (10^{-5} that of ^1H) had made it difficult to detect. 90−100 MHz instruments often took many hours (days) for accumulation of a spectrum. Since the advent of pulsed 250−500 MHz spectrometers, ^{183}W NMR has become convenient and commonplace, possibly the most valuable tool for polytungstate chemistry. The original authors quickly used it to settle various structural controversies and to elucidate reasons for chemical shift differences.[104,105,293,294] Analysis of variable-temperature ^{183}W NMR for paramagnetic α-$[Co^{3+}W_{12}O_{40}]^{5-}$ and its Co^{2+} isomorph led to spin density characterizations, elucidating bonding and quantitation of ligand-centered dipolar shifts.[44] It was shown that ^{183}W NMR identifies which W atoms receive blue electrons in heteropoly blue complexes.[45a,295] Ring currents of blue electrons were evaluated in 1988.[29] Effects of paramagnetic and diamagnetic transition metal monosubstitutions on ^{183}W and ^{31}P NMR of Keggin and Wells−Dawson heteropoly tungstates were studied,[17a,47] and a ^{183}W 2D INADEQUATE determination was made. It was shown[40] that one-electron heteropoly blues, although paramagnetic, nevertheless give sharp NMR lines (an effect of greatly decreased correlation time resulting from very rapid electron hopping among addenda, which provides the equivalent of swift rotation). This led to determination of intra- and intercomplex electron-transfer rates.[40] Electron exchange reactions between heteropoly anions were then studied in greater detail, with a comparison of the experimental rate constants with their theoretically predicted values.[40] The rate of electron pair transfer through a bridge between two heteropoly entities was determined by NMR.[40b] This was later expanded upon to provide a general method for determining relative conductivities of various bridges.[41] ^{183}W 2D NMR studies of lacunary and α_2-vanado 17-tungstodiphosphates were reported[38] in 1991.

In 1980 an X-ray crystal structure was reported[4,296] for $[Li(H_2O)_4]_2H[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]\cdot 3H_2O$. This led to further studies of the anion[297] and preparation of other heteropoly periodates.[298]

Magnetic exchange interactions in the bridged heteropoly complexes $[M_4O_{14}(H_2O)_2(PW_9O_{27})_2]^{10-}$ (M = Co^{2+} or Cu^{2+}),[299] see Figure 1e, and the first ferromagnetic interaction in a heteropoly complex, $[Co_4{}^{2+}O_{14}(H_2O)_2(PW_9O_{27})_2]^{10-}$, were reported and treated theoretically.[46,300] Magnetic interactions within complexes containing paramagnetic atoms in various sites simultaneously with "blue" electrons delocalized over polytungstate frameworks were studied.[300,301] Salts made by TTF and magnetic clusters were described.[302] Blue electron distributions, including time percentage residencies on various W's, conduction pathways, spin coupling patterns, and ^{183}W NMR chemical shift calculations were elucidated[39] for various heteropoly blue complexes.

The X-ray crystal structures of α-$[Co^{2+}W_{12}O_{40}]^{6-}$ and its 2-e blue reduction product α-$[Co^{2+}W_{12}O_{40}]^{8-}$ revealed structural, electronic, and chemical consequences of reduction to a heteropoly blue.[11]

The first heteropoly complexes containing F atoms substituted for O atoms were reported in Baker's 1973 plenary lecture at the Moscow International Conference on Coordination Chemistry. The structure of these α_1-$[(H_2O)M^{n+}O_5H_{2+x}F_{6-x}NaW_{17}O_{50+x}]^{(11-n)-}$ (where $x = 0-2$ and $M^{n+} = Zn^{2+}$, Co^{2+}, Co^{3+}, Ni^{2+}, Mn^{2+}, or Mn^{3+}) as well as their isomorph $[H_2F_6NaW_{18}O_{56}]^{7-}$ was proven[17a,b] in 1987, by a symbiotic combination of structural X-ray, ^{183}W, ^{19}F, ^1H, and ^{23}Na NMR. The percentages and structures of seven simultaneously formed (for a given M) inseparable M-substituted 11-tungsto Keggin-like complexes based on $H_2O_2F_2$ and HOF_3 central tetrahedra were proven[17c] by combinations of ^{183}W, ^{19}F, and ^1H NMR; $M^{n+} = Zn^{2+}$, Co^{2+}, Co^{3+}, Ni^{2+}, V^{5+}.

The first peroxo complex based on a traditional highly condensed heteropoly structure, β_3-$[Co^{2+}O_4W_{11}O_{31}(O_2)_4]^{10-}$, was reported and its structure determined by X-ray crystallography.[303]

Chauveau and Co-workers

The pre-1971 contributions of Francoise Chauveau were indicated in section B. Over the period 1974−1983 Chauveau, Doppelt, Lefebvre, et al.[304−313] published a series of papers on fluoroisopolytungstate complexes, chiefly derivatives of Keggin structure metatungstate, $[H_2W_{12}O_{40}]^{6-}$, wherein F^- ions replaced O^{2-} ions. Complexes based on the following central tetrahedra were prepared: $F_2O_2H_2$, FO_3H_2, F_3OH, and F_2O_2H, and their structures were proved by combinations of elemental analysis, ultracentrifugation, Raman and IR spectroscopy, polarography, and especially ^{1}H, ^{19}F, and ^{183}W NMR. In 1981 ^{183}W NMR spectra of $[FO_3H_2W_{12}O_{36}]^{5-}$, β-$[SiW_{12}O_{40}]^{4-}$, and the previously designated "tungstate X" allowed classification of J_{W-F} couplings and showed that "tungstate X" is β-metatungstate.[310] In 1982 the blue reduction product of a fluoropolytungstate was studied.[314] In 1986 Chauveau wrote a review (74 references) of the application of ^{1}H, ^{19}F, ^{183}W, ^{31}P, ^{17}O, ^{51}V, and ^{27}Al NMR to study of polyoxometalates.[315] The $[ZrW_5O_{19}H_2]^{2-}$ complex, isomorph of $[W_6O_{19}]^{2-}$, was prepared and characterized.[316] The properties of electrodes coated with a polymer film containing imbedded 18-tungstodiphosphate were studied in aqueous and nonaqueous media.[317] It was reported that Keggin 12-tungsto- and 12-molybdophosphates are degraded by H_2O_2, forming smaller peroxy complexes which serve as active oxygen-to-olefin transfer agents. Other Keggin and Wells−Dawson tungstates were examined in an effort to explain the relationship between catalytic activity and the products formed in the HPA−H_2O_2 systems.[318] A comparative study of imaging by atomic force microscopy and scanning funneling microscopy, using $Na_6H_2[CeW_{10}O_{36}]\cdot30H_2O$ samples, showed the same molecular dimensions and arrangements by the two techniques.[319]

Howard T. Evans, Jr.

Howard T. Evans, Jr. maintained his interest in heteropoly chemistry[3b] with several papers on X-ray crystal structure determinations. The structure of sherwoodite was shown[320] to be the hydrated Ca salt of the 2e reduction product: $[AlO_6V_{14}O_{36}]^{9-}$. The anions are joined into cross-linked chains by Ca^{2+} ions, forming an open framework containing zeolytic H_2O molecules and some disordered Ca^{2+} ions. Five recent X-ray crystal structures were subjected to rigorous reinterpretation.[321] $[PV_2Mo_{10}O_{40}]^{5-}$, $[PV_3Mo_9O_{42}]^{6-}$, and "γ-$[PW_{12}O_{40}]$" were shown to exist as disordered Keggin structures in the crystals previously investigated,[322] rather than as a new type of complex. Previously deduced,[313] "$[H_4Mo_{12}O_{40}]_{0.67}{}^{4-}[MoO_4Mo_{12}O_{40}]_{0.33}{}^{4-}$" does not exist; the complexes being[321] reduced $[SiMo_{12}O_{40}]^{n-}$. The crystal structures of the triethylammonium salts of the Co^{2+}-substituted 11-tungstophosphate and 11-tungstoarsenate revealed[324] that, in the solids, the unshared coordination position on each Co is occupied by coordination to an O from the adjacent complex, linking the complexes into chains. A paper with Ortega and Pope[325] shows the structure of the new $[W_9Re^{5+}O_{32}]^{5-}$ complex is isostructural with $[W_{10}O_{32}]^{4-}$. It can be oxidized to isostructural $[W_9Re^{6+}O_{32}]^{4-}$, and $[W_9Re^{7+}O_{32}]^{3-}$ can exist in a polycrystalline solid solution in $[W_{10}O_{32}]^{4-}$. The Re is in one of the belts of the $[W_{10}O_{32}]^{4-}$ structure.[325] A paper with the Tournés and Weakley[326] confirmed the structure of the bridged complexes $[(XW_9O_{27})M_4O_{14}(H_2O)_2(XW_9O_{27})]^{10-}$ where X = P or As and M = Zn or Co^{2+} (see Figure 1e).

Marcu and Co-workers

Pre-1971 contributions of Gheorghe Marcu were indicated in section B. During the period 1971−1995 Marcu published over 60 papers on heteropoly complexes, frequently reporting in several smaller papers the components of a study of a larger subject. He devoted nineteen papers to heteropoly tungstate complexes containing U^{4+}, especially those wherein that atom acts as a bridge connecting two lacunary $(PW_{11}O_{39})^{7-}$, $(SiW_{11}O_{39})^{8-}$, or $(PMo_2W_9O_{39})^{7-}$ units, or two lacunary $(P_2W_{17}O_{61})^{10-}$, $(P_2MoW_{16}O_{61})^{10-}$, or $(As_2W_{17}O_{61})^{10-}$ units.[327] Studies of paper electrophoresis on formation and separation of heteropoly species continued.[328] Studies of heteropoly reversible dioxygen carriers were reported.[329] Preparation and properties of the free acid and salts of the mixed addenda $[SiW_{10}Nb_2O_{40}]^{6-}$ anion were described.[330] The synthesis and properties of $[(H_2O)NiO_5TiO_4W_{11}O_{30}]^{6-}$ and $[(H_2O)NiTiW_5O_{20}]^{4-}$ were reported.[331] Studies were made of the syntheses and analyses of complexes of various metal ions with cryptate $[KAs_4W_{40}O_{140}]^{27-}$ ligands[332] (see ref 1, p 100), and also complexes[333] with the cryptate ligand $[NaSb_9W_{21}O_{86}]^{18-}$ (see Michelon, Hervé, and Leyrie *J. Inorg. Nucl. Chem.* **1980**, *42*, 1583). Syntheses of several new heteropoly tungstates were reported,[334] including: tungstorhodate(III),[335] tungstoindate(III),[336] and Co^{2+} complexes with lacunary heteropoly species having mixed addenda.[337]

The Paris Group

For over three decades Pierre Souchay trained and inspired a powerful group of heteropoly chemists. After his death in the mid-1970s, the group he inspired continued as a powerful force in the field, publishing over 175 papers, which cover an impressive range of contributions. Since the large majority of these papers have multiple authors, in a great variety of combinations, it is difficult in many cases to sort out primary responsibilities for particular lines of work. Therefore we shall treat the group as a whole. The following are among the principal workers derived from the Souchay group: Roland Contant, Paul Courtin, Pascal Doppelt, Michael Fournier, Jean Fruchart, Pierre Gouzerh, Gilbert Hervé, Yves Jeannin, Jean-Pierre Launay, Jean Lefebvre, Frederic Lefebvre, Michele Leyrie, René Massart, Jeanne Martin-Frère, Monique Michelan, Claude Rocchiccioli-Deltcheff, Clement Sanchez, Andre Tézé, and René Thouvenot. Christian Brevard, the chief of Brüker Spectrospin in France, contributed significantly to the development of multinuclear NMR of heteropoly compounds. A sampling of the post-1971 contributions of the foregoing is listed below, grouped by topics and chronologically within each group. (Contributions of Francoise Chauveau, clearly also a principal worker, have already been cited.[304−319])

Heteropoly Blues

1971	preparation of blues[338]
1971	heteropoly blues[348] of $[PW_{12}O_{40}]^{3-}$ and $[BW_{12}O_{40}]^{5-}$
1971	reduced molybdostannisilicates in acidic solution[340]
1973	reduction[341] of α-$[GeW_{12}O_{40}]^{4-}$
1974	solution investigation[342] of reduction products of $[As_2Mo_{18}O_{62}]^{6-}$ and α- and β-$[P_2Mo_{18}O_{62}]^{6-}$
1974	gradual reduction of molybdosilicate[343] and related compounds

1976 electronic spectra of heteropoly blues[344]
1983 electronic delocationization in blue tungstates[345]
1983 relationship[346] between M−O−M bridges and reduction behavior of $[P_2Mo_{18}O_{62}]^{6-}$
1994 IR spectroscopic evidence for bipolaron delocalization in reduced heteropoly 12-molybdates[347]
1996 ESR and electrochemical[348] properties of heteropoly blues of α-$[XMo_{3-x}V_xW_9O_{40}]^{n-}$; X = P or Si, $x = 1-3$
1996 synthesis, structure, redox behavior[349] of γ-$[SiW_{12}O_{40}]^{4-}$

Isomerism

1974 isomerism and properties of 9-tungsto heteropoly anions[350]
1974 isomerism of 12-tungstoborate[351]
1977 formation and isomerisms[352] of $[SiW_{11}O_{39}]^{8-}$, $[SiW_{12}O_{40}]^{4-}$, $[GeW_{11}O_{39}]^{8-}$, and $[GeW_{12}O_{40}]^{4-}$
1977 relationship between structures and properties of 11-tungstosilicate isomers and some derived compounds[353]
1981 ESR of $[SiW_{11}V^{4+}O_{40}]^{6-}$ isomers[354]
1981 stereospecific preparations of new $[P_2W_{18-n}Mo_nO_{62}]^{6-}$, $n = 2, 4, 5$, complexes and related defect structures[355]
1982 comparative stabilities of isomeric α-metallo-17-tungstodiphosphates[37b]
1984 vibrational spectroscopic investigation of isomerism in Mo and W complexes related to the Keggin structure[356]
1993 reinvestigation of isomerism in Wells−Dawson structure by ^{183}W NMR; structural characterization of three new $[X_2W_{18}O_{62}]^{6-}$ complexes, X = P or As[357]
1997 synthesis and structure of tungstoborates[358]

Vibrational Spectroscopy

1974 IR and Raman spectra of α-11- and 9-tungstosilicate, metal-11-tungstosilicates, and tungstomolybdosilicate[359]
1975 comparative study of vibrational spectra of α-12-tungstates and α-12-molybdates[360]
1975 study of isomerisms of W and Mo heteropoly complexes by vibrational spectroscopy[371]
1977 IR and Raman study of modifications of the heteropoly structures when α-molybdophosphates or -silicates or α-11-tungstophosphates or -silicates complex M^{n+} ions[362]
1977 vibrational spectrosopic study[363] of $[Nb_nW_{6-n}O_{19}]^{(2-n)-}$
1979 IR evidence[364] for the structures of α$_1$- and α$_2$-$[P_2W_{17}O_{61}]^{10-}$
1982 vibrational investigation of valence force field of $[Mo_6O_{19}]^{2-}$ based on total isotopic substitution (^{18}O, ^{92}Mo, ^{100}Mo)[365]
1983 evidence for anion−anion interactions in Mo^{6+} and W^{6+} compounds related to the Keggin structure[364b]
1984 vibrational investigation of isomerisms in molybdo and tungsto complexes related to the Keggin structure[356a]
1984 valence force fields of anions related to the Lindqvist structure[356b]
1986 vibrational investigation: valence force field calculations[366] for $[NbW_5O_{19}]^{3-}$ and $[MoW_5O_{19}]^{2-}$
1994 IR spectroscopic evidence for bipolaron delocalization in reduced heteropoly 12-molybdates[347]

NMR and ESR

1977 ^{31}P NMR studies of molybdo- and tungstophosphates: correlation of structures and chemical shifts[367]
1981 ESR of $[SiW_{11}V^{4+}O_{40}]^{6-}$ isomers[354]
1983 synthesis, vis and IR spectra[368] of square pyramidal complexes of first transition row M^{2+} ions with “20-tungstodiarsenate(III)”
1991 ^{31}P NMR MAS spin−lattice relaxation as a dispersion probe[369] for active-site concentration in silica-supported $H_3[PMo_{12}O_{40}]$
1991 ^{29}Si NMR evidence for 12-molybdosilicate in silica-supported Mo catalysts[370]
1991 ^{31}P, ^{51}V, and ^{183}W NMR structural elucidation[371] of $\alpha[P_2MM^1{}_2W_{15}O_{62}]^{6-}$ M, M^1 = Mo, V, W
1991 ^{183}W NMR of $[As_2(M_1V_1W)_{18}O_{62}]^{n-}$ complexes;[372] synthesis of lacunary tungstoarsenates from $[As_2W_{18}O_{62}]^{6-}$
1992 ^{51}V solid-state NMR characterization of V in dehydrated $H_4[PVMo_{11}O_{40}]$ and $Na_{1.5}H_{2.5}[PVMo_{11}O_{40}]$ catalysts[373]
1992 synthesis and multinuclear NMR characterization[374] of α-$[SiMo_2W_9O_{39}]^{8-}$ and α-$[SiMo_{3-x}V_xW_9O_{40}]^{n-}$ $x = 1, 2$
1993 ^{183}W structural characterization[357] of three new $[X_2W_{18}O_{62}]^{6-}$ complexes, X = P or As
1993 solid-state magic-angle NMR relaxation study of silica-supoorted Keggin and Wells−Dawson structures[375]
1994 ^{31}P and ^{183}W NMR evidence for novel peroxo species in $H_3[PW_{12}O_{40}]\cdot H_2O/nH_2O_2$; synthesis and X-ray strucure of peroxo complex that is an epoxidation catalyst[376]
1994 ^{183}W structural study of inorganic cryptates[377] $[M^{n+}As_4W_{40}W_{140}]^{(28-n)-}$ and $[M^{n+}Sb_9W_{21}O_{36}]^{(18-n)-}$ M = alkali or alkaline earth
1995 oxonitrosyl complexes: $[M_5O_{18}(M^1(NO))]^{3-}$, M, M^1 = Mo, W; syntheses, vibrational, multinuclear NMR (^{14}N, ^{17}O, ^{95}Mo, ^{183}W), and electrochemical studies[432]
1996 ESR characterization[378] of V^{4+} as a counterion of $[PMo_{12}O_{40}]^{3-}$; influence of thermal treatments

Reviews

1978 a review of heteropoly compounds[379a]
1992 new trends in polyoxometalate chemistry, toward large polyanions, toward nitrosyl-substituted polyanions[379b]

Inorganic Cryptands

1978 synthesis and chemical behavior of new heteropoly tungstate: $[M^{n+}As_4{}^{3+}W_{40}O_{140}]^{(28-n)-}$, an inorganic cryptate,[380] $M^{n+} = Na^+, K^+, Ba^{2+}$
1980 synthesis and chemical behavior of $[M^{n+}Sb^{3+}W_{21}O_{86}]^{(19-n)-}$, another inorganic cryptate,[381] $M^{n+} = Na^+, K^+, NH_4{}^+, Ca^{2+}, Sr^{2+}$
1980 X-ray crystal structure[382] of $(NH_4)_{27}[NH_4As_4W_{40}O_{140}(CoOH_2)_2]\cdot{\sim}20H_2O$
1983 square pyramidal complexes of first transition row M^{2+}’s with 20-tungstodiarsenate(III)[368]
1992 alkali and alkaline earth cryptates[383] of $[Co_2(H_2O)_2As_4W_{40}O_{140}]^{24-}$
1994 ^{183}W NMR structure study of inorganic cryptates[377] $[M^{n+}As_4W_{40}O_{140}]^{(28-n)-}$ and $M^{n+}Sb_9W_{21}O_{36}]^{(18-n)-}$

Other X-ray Crystal Structures

1980	X-ray crystal structure[384] of $K_4\beta[SiMoW_{11}O_{40}]\cdot9H_2O$
1982	X-ray crystal structure[385] of $K_{12}[(H_2O)_2Cu_3As_2W_{18}O_{66}]\cdot11H_2O$
1984	synthesis and X-ray crystal structure of first Hg^{1+}-containing polytungstate: $[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]^{10-}$ having an odd open-shell structure[386]
1985	a new crown heteropoly:[387] $K_{28}Li_5H_7P_8W_{48}O_{184}\cdot92H_2O$
1991	synthesis and X-ray crystal structures[388] of $[As^{3+}Mo_3O_{15}]^{3-}$, $[As^{3+}W_3O_{15}]^{3-}$, and $[As_6{}^{3+}CoMo_6O_{30}]^{4-}$ first linear and cyclic triarsenates(III)

Biological Significance

1979	antiviral tungstoarsenates[389]
1983	correlation of structure of polytungstates and inhibitory activity on polymerases[390]
1983	polyionic complexes between polytungstates and polylysines:[391] competition with nucleic acids
1987	modification of structural and redox properties of cytochrome *c* by heteropoly tungstate binding[392]
1996	oxidation kinetics of NADH by heteropoly anions[393]

Other Reactions

1974	stopped flow study of reaction[394] between $[Co(H_2O)_6]^{2+}$ and $[SiW_{11}O_{39}]^{8-}$
1979	M ligand electron transfers in $[VW_{11}Si]^{n-}$ isomers[395]
1984	stabilities of M^{2+} and alkali metal complexes of lacunary heteropoly tungstates: influence of the heteroatoms[396]
1994	unexpected reactivity of *p*-tolyl isocyanide to α-$[PMo_{12}O_{40}]^{3-}$ [397]
1996	photochemical behavior of Keggin ions and related species[398]

Other Compounds

1971	preparation and characterization of M^{2+}-substituted heteropoly molybdates[399]
1971	V^{5+} substituted into heteropoly molybdates and tungstates[400]
1972	metalo-11-tungstoantimonate(III) and -bismuthate(III); existence of a 5-tungstobiantimonate(III)[401]
1973	preparation and characterization[402] of chromio-11-molybdosilicate complex
1974–1975	mixed molybdotungstate ions[403]
1974	preparation and study of 11-molybdo and 9-molybdo heteropoly complexes[404]
1975	characterization and properties[405] of $H_6[SiGeW_{11}O_{40}]$
1976	preparation of new pyrochlors: $W^{6+}Sb^{5+}$ acids[406]
1977	preparation and solution properties of “defect” heteropoly complexes[37b] related to α- and β-$[P_2W_{18}O_{62}]^{6-}$
1982	new V^{4+} polytungstate complexes[407]
1983	preparation[408] of $[V_2W_8O_{31}]^{4-}$
1986	synthesis, stability, and structure of the lacunary precursor[37c] of disubstituted complexes: γ-$[SiW_{10}O_{36}]^{8-}$
1987	synthesis and properties of the new heteropoly tungstate: $K_{10}[P_2W_{20}O_{70}]\cdot24H_2O$[409]
1991	synthesis of conducting polymers doped with Wells–Dawson heteropoly complexes[410]
1991	attachment of alkyl- and arylsilyl groups to trivacant tungstosilicate complex[411]
1993	syntheses of Ce^{3+} and Ce^{4+} to lacunary tungstophosphate complexes[412]
1994	syntheses and characterizations of Keggin derivatives[413] having an $Mo(NO)^{3+}$ unit: $(n\text{-}butyl_4N)_4[PMO_{11}(M(NO))]$, M = Mo or W
1995	preparation and characterization of $H_4[PVMo_{11}O_{40}]$ and its alkali metal salts[414a]
1996	synthesis of mixed organosilyl derivatives of trivacant heteropoly tungstates[414b]

Catalysis

1988	catalytic oxidation of CH_3OH by $H_4[SiMo_{12}O_{40}]$ supported on silica[415]
1988	liquid matrix effects on the ionic species desorbed via SIMS of polymolybdate or polytungstate salts[416]
1989	polyoxometalates as models for oxide catalysts;[417] UV–vis reflectance study of polymolybdates: influence of polyhedra arrangement on electronic transitions; comparisons with supported Mo catalysts
1990	evidence for an anhydride of $H_3[PW_{12}O_{40}]$ at high temperatures[418]
1990	Mo–SiO_2 catalysts prepared from hexamolybdate[419]
1990	thermal behavior of unsupported and silica-supported 12-molybdosilicic acids from IR and catalytic reactivity studies[420]
1991	influence of V^{5+} on thermal stability of 12-molybdo- or 12-tungstophosphoric acids as shown by in situ IR studies[421]
1991	catalysis by supported Keggin structures;[422] spectroscopic study of solutions used for impregnation
1991	synthesis of polypyrrole and polythiophene in aqueous solutions of Keggin complexes[423a]
1991	^{29}Si NMR evidence for 12-molybdosilicate in SiO_2-supported catalysts[423b]
1992	X-ray study of thermal stability[424] of catalysts: $H_3[PMo_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $H_4[PVMo_{11}O_{40}]$, and $H_4[PVW_{11}O_{40}]$
1992	X-ray thermal stability study of $H_{3+x}PMo_{12-x}V_xO_{40}\cdot13-14H_2O$[424]
1992	structural and catalytic properties of silica-supported 12-molybdosilicic acid; vibrational study of dispersion effect and nature of Mo species in interaction with silica support[425]
1992	influence of V^{5+} on thermal stability of 12-heteropoly phosphoric acids[423c]
1993	evolution of V-containing heteropoly acids during oxydehydrogenation of isobutyric acid[426]
1993	activity and stability of heteropolyanionic catalysts in oxydehydrogenation of isobutyric acid[427]
1994	peroxospecies as epoxidation catalysts for olefins[376]
1994	evidence for β-MoO_3 formation during thermal treatment of silica-supported 12-molybdophosphoric acid catalysts[428]
1994	role of V in oxidation catalysis by heteropoly anions[429]
1994	novel tungsten catalysts grafted on to polymeric materials; a comparison with phase-transfer catalysts[430]
1995	acid and catalytic properties of $Cs_xH_{3-x}[PW_{12}O_{40}]$[431]
1995	electrocatalysis by heteropoly–polymer systems: [433] reductionof $NO_2{}^-$ and NO

1996	catalytic oxidation of isobutyric acid[434] by vanadyl, Cu, and mixed vanadyl-Cu salts of $H_3[PMo_{12}O_{40}]$ and $H_4[PVMo_{11}O_{40}]$
1996	silica-supported $H_3[PMo_{12}O_{40}]$ catalysts; influence of thermal treatments and of Mo contents, studied by IR, Raman, X-ray, and catalytic reacivity in oxidation of CH_3OH[435]
1996	catalytic reactivity of $H_3[PMo_{12}O_{40}]$ related to thermal teatment: a comparison with $H_4[SiMo_{12}O_{40}]$[436]

Miscellaneous

1991	colloidal molybdoantimonic acids as ion exchangers[437]

Pope and Co-workers

Michael T. Pope of Georgetown University is probably most recognized for the excellent and highly regarded text,[1] *Heteropoly and Isopoly Oxometalates*, published in 1983. A comprehensive treatment of polyoxometalate chemistry, it summarizes many of the important aspects of the field with great insight and accuracy. The chapter on heteropoly blue compounds was an excellent, thorough review of reduced heteropoly species at the time,[25b] containing valuable theoretical explanations and examples.

Throughout Pope's distinguished career, his work has branched into many directions and fruitful collaborations. The compounds that his group have synthesized, chemically characterized and/or structurally elucidated cover a broad range of molybdates,[24,438−451] tungstates,[45b,325,452−473] mixed-addenda species such as tungsto/molybdovanadates,[474−483] and vanadates.[484−487] Much of Pope's earlier work focused on reduced heteropoly species,[438,447,449,455,474e,488,489] descriptions of mixed valence complexes,[25a,476,481a,490−492] and theoretical explanations of the behavior of delocalized electrons.[448,479,486,493−496] A classification of polyanion structures into Type I (addenda atoms in octahedral sites with a single unshared O atom), Type II (addenda atoms with two mutually cis unshared O atoms), and Type III (addenda atoms in both kinds of sites) was quite useful because heteropoly blue formation is restricted to complexes with Type I or III structures.[25a] Pope and co-workers also did important work with heteropoly "browns", categorizing them as Robin and Day[26] Class I mixed-valence complexes.[30]

Substantial contributions in the areas of aprotic solvent syntheses[30b,42,118,454,455,497−500] and organic derivitization[45b,439−443,445,446,451,456−458,461,468,470,501−506] by Pope and co-workers have greatly advanced these fields. The X-ray crystal structure[460] of $[NaP_5W_{30}O_{110}]^{4-}$ showed the sodium was "encapsulated" in the polyoxometalate complex, it could not be removed by conventional ion-exchange techniques. Pope and co-workers subsequently showed that the $[NaP_5W_{30}O_{110}]^{4-}$ complex is selective toward lanthanides.[466,472] It has also been shown that lanthanides occupy an internal site in the 21-tungsto-9-antimoniate heteropoly anion.[462] Synthesis and characterization of heteropoly complexes with high valent heteroatoms[325,444,459,469] has also been an important topic for Pope and co-workers; in some cases unusual heteroatom oxidation states are stabilized.[444] Many of Pope's collaborations with scientists in biochemical and medicinal fields have led to promising biochemical applications of heteropoly complexes.[507−511] Some of Pope's work over the years has focused on the many potentialities for geometric and steroisomerism in polyoxometalates.[24,456,471,482,512,513] Additionally, Pope has contributed greatly to the understanding of polyoxometalate structure, chemistry, and applications with several excellent review articles and book chapters.[1,3d,25b,119,496,501,514−520]

The Tournés and Co-workers

The pre-1971 contributions of Gilbert Tourné and his wife, Claude Tourné, have been cited.[14,269,270] In 1972, alkali and guanidium salts of $[M^{n+}(H_2O)_xZnO_4W_{11}O_{36-x}]^{(12-n-2x)-}$ were reported,[521] prepared from $[Zn(H_2O)ZnO_4W_{11}O_{35}]^{8-}$. When $M^{n+} = Co^{3+}$ or Cr^{3+}, $x = 1$; but when $M^{n+} = Al^{3+}$, Ga^{3+}, $x = 1$ or 0; and, when $M^{n+} = V^{4+}$, V^{5+}, or Mo^{6+}, $x = 0$. In the following year, $[P_2W_{19}O_{69}]^{14-}$ was prepared[522] by progressive alkalization of $[PW_{11}O_{39}]^{7-}$. The new anion attaches two divalent transition metal ions to form $M_2{}^{2+}PW_{19}$ species. $[As_2{}^{3+}W_{19}O_{67}]^{14-}$ was prepared. It also attaches M^{2+} ions.[522] The Na and K salts of $[As^{3+}W_9O_{33}]^{9-}$ and $[Sb^{3+}W_9O_{33}]^{9-}$ were prepared.[522]

$K_m[As_2{}^{3+}M_2{}^{n+}W_{19}O_{67}(OH_x)_2]$ salts were prepared[523] where $M^{n+} = V^{4+}$, $m = 10$ and $x = 0$; and where $M^{n+} = Co^{2+}$, Ni^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, $m = 10$ and $x = 2$; and where $M^{n+} = Mn^{3+}$, Fe^{3+}, Ga^{3+}, $m = 8$ and $x = 2$. The structure was discussed.[523]

In 1976, Zonnevijlle[524,116] reported a systematic study of polytungstates containing a trivalent metal atom (Fe, Al, Ga, In, Rh) substituted for a W in Keggin or Wells−Dawson frameworks. The heteroatoms involved were P, As, Si, Ge, and B. In approximately neutral solution, the Fe^{3+}-substituted 11-tungsto complexes form dimers: $[XW_{11}O_{39}Fe{-}O{-}FeW_{11}X]^{n-}$, which were isolated as solid salts. Free acids were examined as were reductions to heteropoly blues. Substitutions of some ligands on the octahedral metals were explored. Some derivatives containing octahedral M^{2+} were examined. Relative stabilities were reported.[524,116]

Potassium salts of bridged complexes of the following formulas were prepared and characterized by the Tournés:[525] $[M^{4+}(X^{n+}W_{11}O_{39})_2]^{(20-2n)-}$ where $M^{4+} = U^{4+}$ or Th^{4+}; X = P^{5+}, As^{5+}, Ge^{4+}, Si^{4+}; $[M^{4+}(X_2{}^{5+}W_{17}O_{61})_2]^{16-}$ where $M^{4+} = U^{4+}$ or Th^{4+}; X = P^{5+} or As^{5+}. $K_{13}H[U(BW_{11}O_{39})_2]$ and $K_{12}H_2[Th(BW_{11}O_{39})_2]$ were also described.[525] K and Rb salts of $[P_2W_{19}O_{69}]^{14-}$ were prepared.[526] Salts of $[(Co(H_2O))_2P_2W_{19}O_{69}]^{19-}$ were reported.[526]

The X-ray crystal structure of $Cs_{12}[U^{4+}(GeW_{11}O_{39})_2]\cdot 13{-}14H_2O$ was reported[527] in 1980, and that of $K_7[PbGaO_4W_{11}O_{35}]\cdot 16H_2O$ in 1982.[528] 2D ^{183}W NMR spectra unambiguously revealed W−W connectivities[529] and hence correct resonance assignments in $Na_7[PW_{11}O_{39}]$, $Na_8[SiW_{11}O_{39}]$, and $Na_5[PbPW_{11}O_{39}]$.

The X-ray crystal structure and ^{183}W NMR spectrum of $K_4H_2[P_2W_{21}O_{71}(H_2O)_3]\cdot 28H_2O$ were determined in 1986.[530] The anion contains two α-A-PW_9O_{34} units linked through three equatorial

WO(H_2O) units. Two of these W's are closer to, and the third is farther from, the anion's C3 axis. The H_2O on the unique W points toward the interior of the complex, H-bonded to the oxo ligand on each of the other equatorial W's.[530] Also in 1986, X-ray crystal structures were determined for $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ and its isomorph $K_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (see Figure 1e). ^{183}W NMR spectra of the Zn compounds confirmed that the same structure persists in solution.

$K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$ was prepared from $K_{10}[P_2W_{17}O_{61}]$ and from $K_7[PW_{11}O_{39}]$ in 1988, and the X-ray crystal structure of the product, a double K cryptand, was determined.[531] Its solution chemistry was studied by ^{31}P and ^{183}W NMR, revealing a reversible transformation. The first quantitative preparation of $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 22H_2O$ was described.[531]

High-yield syntheses of $[WM_3^{2+}(H_2O)_2(M^{2+}W_9O_{34})_2]^{12-}$ where $M^{2+} = Zn^{2+}$ or Co^{2+} were described[532] and an X-ray crystal structure of the Na salt of the Zn complex was determined, showing it to be isotypical with $[M_4+2(H_2O)_2(PW_9O_{34})_2]^{10-}$ (see Figure 1e).

The anions are enantiomorphic. M^{2+} atoms in the $M_3^{2+}-W$ bridge may be replaced (2 or 3 in the Zn complex, 2 only in the Co derivative) by Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+}, or V^{4+}.

The X-ray crystal structures of $Na_{11.5}Zn_{0.25}[WCu_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 48H_2O$ and $K_{12}[WZnV_2O_2(ZnW_9O_{34})_2\cdot 30H_2O$ were determined. UV−vis and ^{183}W NMR spectra were discussed.[532]

In 1994 the Tournés wrote a review[533] of polytungstophosphate and polytungstoarsenate(V) chemistry (42 references).

Timothy J. R. Weakley

Timothy J. R. Weakley is currently of the University of Oregon. Weakley's pre-1971 work has been cited.[5c,12,13,270] Along with his independent work, he has had many successful collaborations with other heteropoly chemists such as Baker, Evans, the Tournés, and Finke. Therefore, some of his post-1971 work has already been cited as well.[19a,20b,243,244,324,326,530]

A heteropoly chemist with broad interests in the field, Weakley has, in recent years, tended to concentrate on structural X-ray crystallography. Weakley has been involved with the syntheses of many new heteropoly anions, the elucidation of structures by X-ray crystallography and multinuclear NMR, and the discovery of entirely new polyoxometalate structure classes.[534−548] In 1971, Weakley showed that the lanthanides readily react with lacunary heteropoly anions to form LnL or LnL_2 complexes wherein Ln stands for a lanthanide cation and $L{=}SiW_{11}O_{39}^{8-}$.[243] In 1973 ThL_2 complexes were isolated with $L{=}PW_{11}O_{39}^{7-}$, $SiW_{11}O_{39}^{8-}$, and $P_2W_{17}O_{61}^{10-}$.[535] Also in 1973, a new structure class was discovered, $[M_4P_2W_{18}O_{68}]^{10-}$, with four edge-sharing MO_6 octahedra ($M = Co^{2+}$, Cu^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}) between two fragments of the Keggin structure.[19a] Weakley's continued interest in lacunary heteropoly species[540,548] led to a variety of interesting new complexes.

Weakley published a crystal structure of $[PNi(H_2O)W_{11}O_{39}]^{5-}$ and showed it to be isostructural with the Co^{2+} and Zn^{2+} complexes.[541] Other Keggin-type heteropoly anions with two different heteroatoms were described[324,534,537] and evidence for the replacement of the water molecule on the metal, substituting a H_2O with pyridine (see ref 117) was discussed.[534]

With Evans et al.,[326] the complex $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ where $M = Co^{2+}$ or Zn^{2+} and X = P or As was described, see Figure 1e. The structures of related complexes with the formulas $Na_{16}[Zn_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]$ and $Na_{16}[Cu_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]$ were reported by Finke and Weakley.[546] The syntheses of these interesting M_4 metal complexes with lacunary heteropolytungstates is published with Finke and coworkers in *Inorganic Syntheses*.[548]

Weakley published the structure of $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$ which has the $As_2W_{21}O_{69}(OH_2)^{6-}$ structure with a W replaced by a Co^{2+} or Zn^{2+} in square-pyramidal coordination in the equatorial belt of the complex. With Tourné et al.,[530] a related complex, $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ with two $\alpha\text{-A-}PW_9O_{34}^{9-}$ units linked through three $WO(OH_2)^{4+}$ units, was structurally characterized. Weakley also reported the crystal structures of $K_6[MnMo_9O_{32}]\cdot 6H_2O$,[536] $(NH_4)_6[NiMo_9O_{32}]\cdot 8H_2O$,[542] and $[P_5Co_9W_{27}O_{119}H_{17}]\cdot 30H_2O$.[539]

With Finke and co-workers,[543,545] a new subclass of heteropoly anion structure was formulated as $X_2M_{18}M'_6O_{77}^{n-}$,[545] and $[Zr_3(OH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{11-}$ [543] and $A\text{-}\beta\text{-}(SiW_9O_{37})_2(Ti{-}O{-}Ti)_3]^{14-}$ [545] were structurally characterized. Other collaborations with Finke[544,547] led to some interesting complexes that will be discussed later.

2. Some Important Areas of Effort of New Groups and Workers (Post-1971)

R. Allmann and H. D'Amour

In the 1970s, R. Allmann and H. D'Amour of the University of Marburg published several papers on refinements of X-ray crystal structures of various heteropoly compounds.[549] Allmann determined the structure of "paratungstate B" ($W_{12}O_{42}H_2^{10-}$).[550] Other papers included (1) the structure of the new complex[551] $[PMo_9O_{31}(OH)_3]^{6-}$, (2) $NaH_2[PW_{12}O_{40}]\cdot 12{-}14H_2O$,[552] (3) a Keggin complex with a reduced pseudosymmetry in the structure of $H_3[PMo_{12}O_{40}]\cdot 13{-}14H_2O$,[553] and (4) a refinement of the known structure[22] of $(NH_4)_6[Mn^{4+}Mo_9O_{32}]\cdot 6{-}8H_2O$.[554] In 1976, Allmann wrote a discussion of the space group of $H_3[PMo_{12}O_{40}]\cdot 29{-}31H_2O$.[555] In the same year D'Amour published accurate atomic parameters for Wells−Dawson derivatives.[556]

Vadim F. Chuvaev, Leonid P. Kazanskii, and Viktor I. Spitsyn

Viktor I. Spitsyn, member of the U.S.S.R. Academy of Sciences, Professor of Inorganic Chemistry at Lomonosov State University (Moscow), and Director of the U.S.S.R. National Academy of Sciences Institute of Physical Chemistry, maintained a strong interest in heteropoly electrolytes for many years prior to 1970. Most of his pre-1970 publications were not mentioned in the foregoing sections[3f,9a−d,122] because, being largely interpreted in terms of Miolati–Rosenheim formulations and obsolete bonding theory, they had for the most part not produced general advancement of the field. In the late 1960s and early 1970s, however, some physically oriented co-workers, among whom were Vadim F. Chuvaev, Leonid P. Kazanskii, and M. A. Fedotov, were trained up in Spitsyn's group and carried it into competitive accomplishment. From 1968 to 1994, Chuvaev published over 80 papers, more than half of which were coauthored with Spitsyn. From 1973 to 1996 Kazanskii published about 70 papers, half of which were coauthored by Spitsyn. Spitsyn's long-time collaborator, E. A. Torchenkova, was also a coauthor on a large number of the foregoing papers. A number of other workers were coauthors on smaller numbers; e.g. M. A. Fedotov, E. M. Yaroslavetseva, A. M. Golubev, S. V. Kiselev, K. I. Popov.

Chuvaev's interests have not been so much with the structure and reactions of heteropoly complexes per se as with the status and behavior of the constituents of crystals of heteropoly compounds. A number of papers were devoted to various aspects of the status of water in various hydrated crystals,[557−566] mainly investigated by ^1H NMR. EPR and NMR studies of thermal stabilities,[567−570] thermal decompositions,[571−574] and thermal dehydrations[575] have been of interest. The formation and status of heteropoly blues in the solid state has received attention,[576−581] as have the interactions of alcohols and ketones with anhydrous heteropoly acids.[582−584] Alcohol solutions of 12-tungstoheteropoly acids were studied by ^1H NMR.[585] The configuration and mobility of $H_5O_2^+$ ions in crystalline heteropoly acids were studied by ^1H NMR,[586] as were uranomolybdic acid,[587] heteropoly molybdates having various heteroatoms,[588] and initial hydration and solvation stages of anhydrous heteropoly species.[589] A ^1H NMR study of $H_3[PW_{12}O_{40}]$ in mixed organic solvents was reported.[590] The self-diffusion of H^+ in solid heteropoly acids was elucidated.[591] A ^{31}P and XPES study of heteropoly phosphates was carried out.[592] Reorientation mobilities of the $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ complexes in crystalline hydrates of their free acids having high water content was investigated.[593] Other topics included: ^1H NMR chemical shifts of 12-molybdo and 12-tungsto heteropoly acids dissolved in ketones;[594] ^1H NMR study of Mg and K peroxytungstates, of Mg and alkali metal double peroxytungstates,[595] and of peroxotungstophosphates;[596] mechanism of the catalytic effect of solid heteropoly tungstates;[597] transformations of acetone catalyzed by 12-tungstophosporic acid;[598] polycondensation of ketones catalyzed by $H_3[PW_{12}O_{40}]$;[599] structure and mechanism of electric transport in solid thallous 12-tungstophosphate;[600] H^+ mobility of 12-tungstophosphoric acid hexasorbates;[601] solvation of $H_3[PW_{12}O_{40}]$ by DMSO;[602] structure, vibrational spectra, and electrical conductivity of the crystallosolvate $H_4[SiW_{12}O_{40}]\cdot 8DMSO$;[603] electrical conductivity of solid K, Rb, and Cs salts[604] of $[PW_{12}O_{40}]^{3-}$; ^1H and ^{31}P NMR study of crystalline hydrates and anhydrous phases of 12-tungstophosphoric acids;[605] thermal conversions of organic molecules in solvates of heteropoly acids.[606] Tungstoboric acid was investigaed by ESR[607] and niobate complexation by molybdocerates was studied.[608] A PMR study of tungstovanadophosphoric acids and of crystalline hydrates of those acids[609] was reported. PMR of $H_4[SiMo_{12}O_{40}]\cdot nH_2O$ and its hydrated sodium salt were examined.[610] Two types of reduction products were identified for $H_3[PMo_{12}O_{40}]$,[611] and a reduced 12-molybdophophate was formed in the solid phase.[612] $H_4[SiMo_{12}O_{40}]$ was also reduced in the solid phase[613] by organic oxygen-containing compounds.[614] A report was made on the thermal decomposition of solvates of $H_6[P_2W_{18}O_{62}]$ with the simplest alcohols.[615]

Although Kazanskii's forte is the application of physical methods, especially multinuclear NMR, XPES, EPR, and vibrational and electronic spectra to elucidating the molecular and electronic structures of heteropoly complexes, as well as application of relevant quantum mechanics, he participated in four investigations of the formation of new compounds: (1) the reactions between $[Ta_6O_{19}]^{8-}$ and $(NH_4)_6H_2[CeMo_{12}O_{42}]$ and $(NH_4)_6H_2[CeMo_{10}O_{36}]$ to form $(NH_4)_8[CeMo_{10}Ta_2O_{41}]\cdot 14H_2O$ and $(NH_4)_{12}[CeMo_{12}O_{49}Ta_2]\cdot 22H_2O$ and the conversion of the latter by ion exchange to $H_{12}[CeMo_{12}O_{49}Ta_2]\cdot 30H_2O$;[616] (2) the reaction of $[XMo_{12}O_{42}]^{8-}$ ($X = Th^{4+}$, U^{4+}, Ce^{4+}) with several metal ions[617] (studied by spectrophotometry, potentiometry, and ion exchange) showing that divalent metal ions form, e.g., $[CeM_2{}^{2+}Mo_{12}O_{42}]^{4-}$ and that Th^{4+} reacts to form larger complexes, e.g., $[Th(CeThMo_{12}O_{42})_3]^{8-}$; (3) preparation and properties of heteropoly blues of $[GeMo_{12}O_{40}]^{4-}$, made by ascorbic acid reduction in ether solution, leading to the 4e blue of the β isomer (while chemical and electrochemical reduction in H_2O leads to the α isomer only);[618] (4) formation of $[Al(OH)_6Mo_6O_{18}]^{3-}$ from $Al(NO_3)_3$ and $[Mo_7O_{24}]^{6-}$ or $[PMo_{11}O_{39}]^{7-}$, ^{17}O and ^{71}Ga evidence for formation of $[Ga(OH)_6Mo_6O_{18}]^{3-}$ from Ga^{3+} and $[Mo_7O_{24}]^{6-}$. $[AlO_4W_{11}O_{35}]^{9-}$, $[AlO_4W_{11}O_{35}Al]^{6-}$, and $[AlO_4W_{12}O_{36}]^{5-}$ were also reported.[619] He particpated in various studies of heteropoly blues: (1) correlations between electronic transitions and half-waves of reduction potentials;[620] (2) EPR and NMR showed that the structure of 2e blue of $[SiMo_{12}O_{40}]^{4-}$ is independent of its method of preparation; delocalization of orbitals does not occur but electron delocalization depends on thermal properties;[621] (3) ^{17}O NMR[622] for parents and 2e blues of $[PMo_{12}O_{40}]^{3-}$ and $[SiMo_{12}O_{40}]^{4-}$ shows blue electron pairs delocalized with respect to the 12 Mo's at a rate $> 10^{-8}$ s; (4) a ^1H, ^{17}O, and ^{31}P study of 2e blues of $[SiMo_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{3-}$ concluded that they are protonated. The two electrons are delocalized over the whole coordination sphere.[623] Kazanskii participated in three X-ray crystal structure determinations: $Na_8[UW_{10}O_{36}]\cdot 30H_2O$;[624] $H_4[SiMo_{12}O_{40}]\cdot 13H_2O$,[625] which shows the anions within a hydrate envelope that contains $H_5O_2^+$ and $H_7O_3^+$; and the new compound $(NH_4)_3H[ThUMo_{12}O_{42}]\cdot 15H_2O$,[626] for which the MO diagram was constructed.

The EPR spectra of solutions of $[P_2W_{17}VO_{62}]^{8-}$ (1e reduced) and its EPR spectrum at 80 K were reported and interpreted. At 80 K the added electron is on the V.[627] The proton structure of uranomolybdic acid was studied by broad line ^1H NMR at 80 K.[628]

Kazanskii participated prominently in writing five reviews: (1) “Structural principles in the chemistry of heteropoly compounds” (191 references);[629] (2) “Vibrational spectra of heteropolyanions of different structural types” (53 references);[630] (3) “Electrochemical methods in analytical chemistry of heteropoly species” (171 references);[631] (4) “Current structural and spectroscopic investigations of heteropoly compounds” (212 references);[632] (5) “Molecular, electron, and proton composition of heteropoly compounds of various types of structures” (239 refs).[633]

Kazanskii demonstrated by IR and Raman spectroscopy that $[XMo_{12}O_{42}]^{8-}$ complexes ($X = Ce^{4+}$, Th^{4+}, U^{4+}) have the same structure in solids as in solution.[634] The same was shown for various Keggin structures and various 10-tungstates.[635,636] UV spectra of 12-molybdates of Ce, Th, and U were explained as $p\pi \rightarrow d\pi$ transitions on the basis of a MO model of the anions.[637] A linear correlation was found between bond energies of the first intervalent transitions and half-wave potentials for reductions of isostructural $XM_{11}ZO_{40}{}^{4-}$ heteropoly complexes having the same charges.[638] ESR of $[PMo_xW_{12-x}O_{40}]^{n-}$ heteropoly blues showed the blue electrons delocalized over all the Mo’s.[639]

A table of ^{17}O chemical shifts and energies of first charge transfers was presented covering several isopoly and heteropoly species.[640] Solution and solid-state ^{17}O NMR spectra of $[XW_{10}O_{36}]^{n-}$ species were identical. Three types of O are present. ^{17}O NMR was used to study the heteropoly formation in solution.[641] ^{17}O NMR of isopoly and heteropoly tungsto and molybdo salts containing paramagnetic cations indicated that high-resolution ^{17}O NMR can be used to study electronic and molecular structures of polyanions in solution.[642] A ^{17}O NMR solution study of protonation and complexing of $[XMo_{12}O_{42}]^{8-}$ ($X = Ce^{4+}$, U^{4+}) showed the structure of the anion analogous to that in the crystals. Protonation occurs at bridging O’s. The complexes that form with $UO_2{}^{2+}$ or Y^{3+} are very labile. Complexing in solution involves terminal and bridging O’s of the heteropoly complex.[643] ^{17}O and ^{183}W NMR of $K_5[CoW_{12}O_{40}]\cdot 6H_2O$ and $K_5H[CoW_{12}O_{40}]\cdot 15H_2O$ were reported.[644] The ^{17}O and ^{183}W NMR chemical shifts and status of the complex $[XW_{10}O_{36}]^{n-}$ in aqueous solution were reported ($X = La^{3+} - Er^{3+}$, Ce^{4+}, Th^{4+}, U^{4+}). The character of the lanthanide-induced chemical shifts was discussed.[645] ^{31}P NMR chemical shifts in $[X(P_2W_{17}O_{61})]^{n-}$ (X = Ce, Th, U) and in $[X(P_2W_{17}O_{61})_2]^{16-}$ (X = Th, U, Ce) indicated the presence of only one isomer in solution in each case.[646] The ^{29}Si NMR chemical shifts for various heteropoly complexes were explained in terms of varying π content of Si$-$O bonds.[647] Broadline ^1H NMR spectra at 80K were reported for several acids and acid salts of 12-heteropoly species. IR spectra were taken at 80 K for some. The spectra were discussed with respect to structure and quantum chemical calculations on dioxonium ion.[648]

XPES of O’s in Keggin tungstates, molybdates, and vanadates of P^{5+}, Si^{4+}, B^{3+}, and $H_2{}^{2+}$ showed the O’s have effective orientation charges which increase with increasing basicity. Mo heteropolies have the maximum orientation charge on O’s, confiming differences in proton acceptor ability.[649] ^{31}P NMR and XPES of 2p electrons of P in a series of heteropoly phosphates are reported. The chemical shift correlates with the energies of the 2p electrons.[650] XPES were reported for $[X^{n+}W_{10}O_{36}]^{(12-n)-}$ ($X = Ce^{3+}$, Ce^{4+}, Pr^{3+}, Th^{4+}, U^{4+}) and $[U^{4+}(Z^{n+}W_{11}O_{39})]^{(8-n)-}$ ($Z^{n+} = As^{5+}$, P^{5+}, Si^{4+}, B^{3+}), and the spectra were discussed.[651] The 1s O and 3d Mo energy levels shown by XPES of H_8(or K_8)$[ZMo_{12}O_{42}]$ (Z = Ce, Th, U) are almost identical, independent of Z.[652] XPES of $[SiMo_{12-x}M_x{}^{+}O_{40}]^{n-}$ mixed valence complexes were reported.[653] ESR, NMR, and XPES of molybdophosphoric acids $H_3[PMo_{12-x}W_xO_{40}]\cdot nH_2O$ ($0 < x < 12$) and their reduced forms indicated anion charge increases by the number of entering electrons. It is said that the added electrons are localized on specific Mo’s[654] (contrast 1979 report in ref 639). The binding energies for $d_{5/2}$ Mo electrons and 1s O electrons were determined by XPES for a series of iso- and heteropoly molybdates. The effective charge on Mo and O atoms increases with decreasing number of Mo$-$O bonds.[655] An XPES study of the 6-molybdo complexes of Al^{3+}, Ga^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Rh^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} was reported.[656] High resolution of ^{31}P and ^{51}V NMR spectra of aqueous solutions of $[PW_{12-x}V_xO_{40}]^{n-}$ ($x = 1, 2$) were reported and interpreted.[657] ^{51}V NMR spectra of various isopoly and heteropoly species were reported and interpreted.[658]

The α and β isomers of $H_6[SiMo_{12}O_{40}]$ (2e blue) were studied by XPES, IR, UV$-$vis, and ESR in an effort to determine the localization of the electrons added by the reduction.[659] The XPES of $[SiZM_{11}O_{39}]^{n-}$ ($M = W^{6+}$, Mo^{6+} and Z = various metals) were reported, and the bonding energies were discussed and compared with magnetic data.[660] An XPES investigation of Cr steel passivity in $H_2SO_4$$-$molybdophosphoric acid solutions was reported.[661] ^{17}O NMR chemical shifts in polyoxotungstates was the subject of a 1979 report.[662] Kazanskii participated in determination of the crystal structure of $Na_8[UW_{10}O_{36}]\cdot 30H_2O$.[663] The vibrational spectra of $[X^{n+}W_{10}O_{36}]^{(12-n)-}$ anions were reported and discussed.[664]

The Spitsyn group, in addition to the numerous papers cited above relative to contributions of Chuvaev and Kazanskii, produced a large number of other papers about heteropoly species. As was the case for the Chuvaev and Kazanskii articles, nearly all of the other papers had several coauthors besides Spitsyn. To provide a sense of the nature of these contributions, a selection is cited below.

1966	study of luteotungstophosphoric acid and its salts by PMR[665]
1966	thermochemical study of reaction of some heteropoly and aquopoly compounds with caustic soda[666]
1967	basicity of luteotungstophosphoric acid, investigated by IR[667]

1969	thermochemical study of interaction of unsaturated tungstosilicic acid and tetrasubstituted potassium tungstosilicate with NaOH[668]
1970	thermochemical study of reaction of luteotungstophosphoric acid with NaOH[669]
1970	polynuclear complexes of rare earths with cerimolybdic acid[670]
1971	new method for isolating heteropoly acid and aquopoly acid crystals[671]
1971	unsaturated heteropoly compounds of Ce(IV)[672]
1971	molybdothoric acid and its complexing reactions[673]
1971	molybdouranic acid and its ammonium salt[674]
1972	thermochemical study of reaction of tungstoboric acid with NaOH[675]
1972	modern studies of polynuclear heteropoly complexes[676]
1973	chromium-containing polytungstates[677]
1974	synthesis and properties of hexamolybdates[678]
1974	chromium-containting polytungstates[679]
1974	molybdoneptunium heteropoly acid[680]
1975	thermal stability of some tungstoborates[681]
1975	preparation and properties of aluminotungstosilicic acid[682]
1976	formal potentials of $Pu^{4+}-Pu^{3+}$ and $Am^{4+}-Am^{3+}$ pairs in the presence of $[PW_{17}O_{61}]^{10-}$ ions[683]
1976	preparation of salts of tungtoneptunic and tungstoplutonic acids[684]
1976	stabilization of Am^{4+} and Tb^{4+} by $[SiW_{11}O_{39}]^{8-}$ and $[BW_{11}O_{39}]^{9-}$ in aqueous solutions[685]
1977	kinetics of oxidation of Am^{3+} to Am^{4+} by persulfate in the presence of heteropoly anions[686]
1977	thermochemical study of nature of H_2O in some hydrate crystals of pentasubstituted alkali salts of tungstoboric acid[687]
1977	complexes of alkaline earths[688] with $[PW_{11}O_{39}]^{7-}$ and $[P_2W_{17}O_{61}]^{10-}$
1978	preparation and properties of uranium and transuranium elements with unsaturated heteropoly tungstates[689]
1978	unsaturated heteropoly tungstates in titrimetic analysis[690]
1978	complexes of Ce^{3+} with unsaturated tungstophosphates[691]
1979	study of chromium-containging polytungstates[692]
1979	crystal structure of $CuH_6[U^{4+}Mo_{12}O_{42}]\cdot 12H_2O$[693]
1980	use of heteropoly compounds in oxidative heterogeneous catalysis[694]
1981	crystal structures of Mg and Zn molybdouranates[695]
1981	protonation constants of uranium polymolybdate and cerium polymolybdate complexes[696]
1981	pulsed radiolysis of aqueous solutions of phosphotungstic acid salts of 17th and 18th series[697]
1982	crystal structures of molybdoceric and molybdouranic acids[698]
1985	heteropoly catalysts for destructive hydrogenation[699]
1986	chemiluminescence during reduction of Ce^{4+}, Tb^{4+}, and Pr^{4+} in aqueous solutions of isopoly and heteropoly tungstates[700]
1986	luminescence of Cm^{3+} in isopoly and heteropoly tungstate solutions[701]
1986	some features of mixed tungstosilicates containing d elements[702]
1987	electronic spectra and electronic structure[703] of the vanadyl complexes of $[ZMo_{12}O_{42}]^{8-}$
1987	synthesis, crystal, and molecular structure of a new Pr^{3+} compound of composition $(NH_4)_{28}Pr_8Mo_{58}O_{200}\cdot 40H_2O$[704]
1988	thermal stability of Ni-containing potassium α-tungstosilicate[705]
1988	behavior of Ni-containing potassium α-tungstosilicate during heating in H_2[706]
1989	preparation and properties of Ni- and Co-containing tungstosilicates[707]

Eugenio Coronado

Eugenio Coronado of the University of Valencia, Spain, is basically a theoretical chemist who originally became enthusiastic about the potentialities of heteropoly compounds that contain relatively isolated clusters of paramagnetic atoms. Beginning with providing theoretical treatments of Casañ-Pastor's observation[300] that the $Co_4^{2+}O_{14}(H_2O)_2$-bridged complex, $[Co_4^{2+}O_{14}(H_2O)_2(PW_9O_{27})_2]^{10-}$ (see Figure 1e), is ferromagnetic and Coronado's subsequent observation that its Cu_4^{2+} isomorph is antiferromagnetic,[299,708] Coronado's interest in the magnetic properites of heteropoly complexes containing clusters of paramagnetic atoms increased. He reported a novel heteropoly tungstate with a triangular Ni_3^{2+} cluster having ferromagnetic interactions and an $S = 3$ ground state,[709] and he studied magnetic excitations in the Co_4 complex by inelastic neutron scattering.[710] He studied TTF salts of heteropoly complexes containing magnetic clusters.[302] This led to study of tetrathiafulvalene (TTF) salt[711] of $[Mo_8O_{26}]^{4-}$. The crystal structure and magnetic properties of the Mn_4^{2+} isomorph of the Co_4^{2+} and Cu_4^{2+} bridged complex, $K_{10}[Mn_4O_{14}(H_2O)_2(PW_9O_{27})_2]\cdot 20H_2O$, were reported,[712] as were the crystal structure and magnetic properties of the Cu-substituted Keggin complex[713] $[PW_{10}Cu_2(H_2O)_2O_{38}]^{7-}$. A general summary of some polyoxometalate magnetic materials[714] was followed by investigation[715] of $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$. Single-crystal X-ray structure and magnetic properties of the isomorphs $Na_{16}[M_4O_{14}(H_2O)_2(P_2W_{15}O_{49})_2]\cdot 52-53H_2O$ where $M = Mn^{2+}$ and Ni^{2+} were reported. The Mn's are antiferromagnetically coupled while the Ni's are ferromagnetic.[716] The synthesis and physical properties of $(BEDT\text{-}TTF)_8[CoW_{12}O_{42}]\cdot 5.5H_2O$, showing coexistence of mobile and localized electrons, was reported[717] (BEDT-TTF = bis(ethylenedithio)tetrathiafulualene). In 1995, the electronic structure of high nuclearity mixed-valence clusters was discussed.[718] The same year saw an article providing a perspective of relevant directions of research,[719] as well as a report of a novel chainlike heteropoly anion:[720] $[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]_n^{6n-}$. An article examined delocalization of electron pairs in 12-heteropoly blues with the Keggin structure[721] and one examined delocalization in Wells–Dawson blues.[722] Coexistence of magnetic and delocalized electrons in the organic–inorganic salts: $(BEDT\text{-}TTF)_8[XW_{12}O_{40}]\cdot n(\text{solvent})$, $X = H_2^{2+}$, Bi^{3+}, Si^{4+}, Cu^{2+}, Co^{2+}, Fe^{3+}, and solvent = H_2O or CH_3CN, was discussed[723] (see refs 307 and 308). Vibronic problem for Keggin 2e heteropoly blues was described.[724] The synthesis and structure of $(ET)_{8n}[PMnW_{11}O_{39}]_n\cdot 2nH_2O$, a novel chainlike heteropoly compound, were reported[725] (ET = bis(ethylenedithio)tetrathiafulvalene), followed by an article on the magnetic properties of BEDT-TTF salts of Keggin polyoxometalate anions.[726] The radical salt $(ET)_{11}$-

$[P_2W_{18}O_{62}]\cdot 3H_2O$ was reported.[727] Magnetic excitations in $[Co_4^{2+}O_{14}(H_2O)_2(PW_9O_{27})_2]^{10-}$ were observed by inelastic neutron scattering, providing evidence for anisotropic exchange interactions.[728] An article describing charge-transfer salts based on organic π-donor molecules and inorganic magnetic clusters[729] appeared in 1997 as did an article offering perspective on evolving organic–inorganic superlattices: Keggin complexes in Langmuir and Langmuir–Blodgett films.[730]

Victor W. Day and Walter G. Klemperer

Beginning in 1975 Walter G. Klemperer, currently of the University of Illinois (Urbana), published over 16 papers on polyoxometalates plus, beginning in 1979, some 10 additional ones coauthored with Victor W. Day of the University of Nebraska.

In the 1975–1979 period Klemperer published five papers on structure determinations of polyoxometalates by ^{17}O NMR, including a chemical shift scale for such anions.[731–735] In 1979 Day and Klemperer reported the synthesis and structure of $[CH_2Mo_4O_{15}]^{3-}$ and related methylenedioxymolybdates[736] and, in 1980, a polycentric, conformationally flexible anion-binding cavity in a carbomolybdate cluster.[737] In the same year Klemperer described the synthesis of $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$, M = Re or Mn,[738] and, in 1985, the syntheses[739] of $[TaW_5O_{18}S]^{3-}$ and $[NbW_5O_{18}S]^{3-}$ and intramolecular rearrangements[740] of α-$[Mo_8O_{26}]^{4-}$, $[C_6H_5AsMo_7O_{25}]^{4-}$, and $[(C_6H_5As)_2Mo_6O_{24}]^{4-}$. In 1984 and 1985 Day and Klemperer published 6 papers: (1) syntheses, structure, and isomerism[741] of $[(Me_5C_5)Rh(cis\text{-}Nb_2W_4O_{19})]^{2-}$; (2) syntheses and structures[742] of $[(C_5H_5)_3U(MW_5O_{19})_2]^{5-}$, M = Nb or Ta, and $[(C_5H_5)_3Th(MW_5O_{19})_2]^{5-}$; (3) the syntheses and structure[743] of $[(OC)_3Mn(cis\text{-}Nb_2W_4O_{19})]^{3-}$ and $[(OC)_3Re(cis\text{-}Nb_2W_4O_{19})]^{3-}$; (4) syntheses and structure[744] of $[\eta^5\text{-}C_5H_5Ti(Mo_5O_{18})]^{3-}$ and $[\eta^5\text{-}C_5H_5Ti(W_5O_{18})]^{3-}$; (5) synthesis, structure, and reactivity[745] of $[(\eta^5\text{-}C_5H_5)_2U]_2(\mu\text{-}TiW_5O_{19}\text{-}\kappa^2\text{-}O)_2]^{4-}$; and (6) an examination of early transition metal polyoxoanion chemistry as metal oxide chemistry in solution.[3e] In 1987 they reported the synthesis, characterization, and interconversion of $[Nb_2W_4O_{19}H]^{3-}$ and its anhydride and alkyl/silyl esters.[746] Klemperer described the synthesis and structural characterization[747] of the polyoxoanion supported 1,5 cyclooctadieneiridium(I) complex: $[(\eta\text{-}C_8H_{12})Ir\text{-}\kappa\text{-}O_3\text{-}C_5Me_5TiW_5O_{18}]^{2-}$, and of the polyoxoanion supported metal carbonyls:[748] $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$, $\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2]\}^{5-}$, and $[(OC)_2Ir(P_3O_9)]^{2-}$. Several hexametalate polyoxoanion-supported organometallic complexes have also been described.[749]

In 1991 Klemperer described voltammetric monitoring of redox transitions in single crystals of silicotungstic acid,[750] and, in 1993, the synthesis and characterization[751] of $[(P_3O_9)_2Ru_2(CO)_4]^{4-}$ and $[(CpTiW_5O_{18})_2Ru_2(CO)_4]^{4-}$. In 1996 he described self-assembly of silicotungstate anions on silver surfaces.[752] In 1992 Day and Klemperer[753] reported on mono- and diprotonation of $[(\eta^5\text{-}C_5H_5)TiW_5O_{18}]^{3-}$.

Richard G. Finke

Richard G. Finke is currently of Colorado State University. Many novel heteropoly complexes have been synthesized, characterized, and their applications as catalysts explored by Finke and co-workers. Finke detailed the rational synthesis, characterization and ^{183}W NMR of $P_2W_{18}M_4(H_2O)_2O_{68}{}^{10-}$ (see also ref 19a) and $P_4W_{30}M_4(H_2O)_2O_{112}{}^{16-}$ with M = Co^{2+}, Cu^{2+}, Zn^{2+} in which four metal cations are sandwiched between Keggin or Wells–Dawson moieties with three "cap" tungstens missing.[546,548,754,755] Several years later, the 2D ^{183}W NMR spectra of both sets of compounds were published with Domaille.[756]

Finke and co-workers have extensively explored trisubstituted heteropoly anions which led to the discovery of polyoxometalates as supports for organometallic complexes.[757] The synthesis and elucidation of the trisubstituted complexes, $Si_2W_{18}Nb_6O_{77}{}^{8-}$ and $SiW_9Nb_3O_{40}{}^{7-}$, and the polyoxometalate supported organometallic complex, $[(C_5Me_5)Rh\cdot SiW_9Nb_3O_{40}]^{5-}$ were reported in 1984.[758] The syntheses of these compounds were later published in *Inorganic Syntheses*.[759] In 1988 the series of complexes, $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$, $(Bu_4N)_{12}H_4P_4W_{30}Nb_6O_{123}$, $(Bu_4N)_7[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]$, and $(Bu_4N)_7$-$[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$, was first reported.[760] In these tungstosilicates and tungstophosphates, the niobium atoms replace three "cap" tungstens and the organometallic complex is attached through Nb–O–Rh or Nb–O–Ru linkages. In 1995, the X-ray crystal structure and multinuclear NMR analyses of these support-type complexes were published with Weakley.[547] Two more studies of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$[761] and the sodium salt[762] as a prototypical polyoxoanion organometallic support system were carried out.

The syntheses and characterization of related trisubstituted complexes, β-$SiW_9V_3O_{40}{}^{7-}$ and $[CpTi\cdot SiW_9V_3O_{40}]^{4-}$ with the organometallic $CpTi^{3-}$ moiety attached to the polyoxometalate support through V–O–Ti linkages, were first published in 1986.[763,764] The ^{31}P, ^{29}Si, ^{51}V, and 1 and 2D ^{183}W NMR spectra of organic solvent soluble forms of $H_xSiW_9V_3O_{40}{}^{x-7}$ and $H_xP_2W_{15}V_3O_{62}{}^{x-9}$ were reported with Domaille.[765]

In 1993, $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ was reported with ^{17}O NMR evidence for Ir–O–Nb bonding.[766] This was the first polyoxoanion-based precursor for zerovalent metal catalysts. The details of the synthesis, characterization, catalytic activity and mechanistic studies were reported at the heteropoly conference at the University of Bielefeld.[757] The fast-atom bombardment mass spectroscopy of $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$,[767] the synthesis of the tetrabutylammonium salts of the Ir^+ complex and the Rh^+ analog,[768,769] and the role of polyoxoanions such as $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ in catalysis[770,771] were also reported.

Finke has recently reported the controlled synthesis and characterization of Ir metal nanoclusters with reproducible size and catalytic activity.[772–774] The synthesis and characterization of the potassium salt of α_2-$P_2W_{17}O_{61}(M^{n+}\cdot H_2O)^{n-10}$ and the tetrabutylammonium salt of α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{n-11}$ with M = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} as oxidation resistant inorganic porphyrin analogues was reported in 1991.[775] Studies of these complexes as catalysts were carried out and compared to metalloporphyrin catalysts.[776] Another oxidation-resistant complex, $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 2KCl\cdot 60H_2O$ was described as a bimetallic inorganic porphyrin analogue.[544] The crystal structure shows that it is a Ru−O−Ru oxo-bridged dimer anion.[544]

The synthesis, characterization, and catalytic studies of a novel triperoxyniobium-containing complex, $SiW_9(NbO_2)_3O_{37}{}^{7-}$ heteropoly complex was reported by Finke and co-workers.[777] The separation of highly charged polyoxometalates via reversed-phase HPLC was carried out using ion-interaction reagents and competing ions.[778] Recently, a series of papers appeared on the heterogeneous catalytic oxidation of isobutane to isobutene by Wells−Dawson heteropoly anions.[779−781]

Dante Gatteschi

Dante Gatteschi of the University of Florence has a primary interest in magnetism, magnetic interactions, and magnetic materials. Realizing the unique potentiality of heteropoly electrolytes for this field, his deepening interest has led to several papers. For example, in 1993 and 1994, there were papers[782,783] on “Polyoxovanadates: the missing link between simple paramagnets and bulk magnets?” and in 1996, a paper[784] on giant clusters with unusual electronic and magnetic structures due to open-shell metal centers embedded far apart from each other: spin frustration and antisymmetric exchange.

Oskar Glemser and Karl H. Tytko

Prior to 1970 Oskar Glemser of the University of Göttingen had published a number of papers on isopoly complexes. In 1975 he was a coauthor of papers on the antiviral activity of $[Sb_8W_{20}O_{80}]^{16-}$ and on in vivo inhibition of Friend leukemia viruses by $[X_2W_{18}O_{62}]^{6-}$ ($X = P$ or As).[785] In 1971 he was a coauthor with his colleague Karl H. Tytko of an important paper proposing a plausible condensation mechanism for the formation of $[W_6O_{19}(OH)_3]^{5-}$ (paratungstate A) in aqueous solution.[786] Tytko also proposed plausible mechanisms for the formation of polytetramolybdate,[787] $[Mo_4O_{14}]_n{}^{6n-}$, and of heteropoly anions with octahedral heteroatoms.[788]

Britt Hedman

Britt Hedman is a structural crystallographer, formerly at the University of Umea, Sweden, and currently at the Stanford Synchrotron Radiation Laboratory. Among the structures she determined while at Umea are several isopoly anions and the following heteropoly species. In 1977, $Na_6[P_2Mo_5O_{23}]\cdot 14H_2O$[789] and the $[(HOPO_3)_2Mo_5O_{15}]^{4-}$ anion[790] were described, and in the following year a neutron diffraction study of $Na_3[PMo_9O_{31}(H_2O)_3]\cdot 12-13H_2O$[791] was reported. She was coauthor with Strandberg in reporting the structures of $Na_5H[P_2Mo_5O_{23}]\cdot 11H_2O$[792] and $[C(NH_2)_3]_4[GeMo_{12}O_{40}]$.[793] In 1980 the crystal structure and ESR spectrum of the 1e heteropoly blue $K_6[(V_2Mo_{10})VO_{40}]\cdot 13H_2O$ were determined[794] as well as the structure of $Na_3[(CH_3)_4N]_2H[(OAsO_3)_2Mo_6O_{18}]\cdot 7H_2O$.[795]

Craig L. Hill

Craig L. Hill of Emory University began publishing on polyoxometalates in the mid-1980s and soon became perhaps the most prolific researcher in the field. His work shows a strong interest in potential practical applications as well as efforts to elucidate fundamental explanations. Much of the work is devoted to catalysis and to photocatalysis in particular, but there is also a strong element of interest in biological (anti-viral) applications. The following listing of topics of publications will convey the most accurate sense of the development and scope of the contributions.

1985	catalytic photochemical dehydrogenation of organic substrates by polyoxometalates[796]
1986	sustained epoxidation of olefins catalyzed by transition metal-substituted polyoxometalates, oxidatively resistant inorganic analogues of metalloporphyrins[797]
1986	photochemistry, spectroscopy, X-ray structure of an intermolecular charge-transfer complex between an organic substrate and a polyoxometalate[798]
1986	homogeneous catalytic photochemistry; functionalization of alkanes by polyoxometalates[799]
1987	characterization of a weak intermolecular photosensitive complex between an organic substrate and a polyoxometalate; crystal and molecular structure of $\alpha\text{-}H_3PMo_{12}O_{40}\cdot 6DMA\cdot CH_3CN\cdot 0.5H_2O$ (DMA= *N*,*N*-dimethylacetamide)[800]
1987	electron donor−acceptor complexes of polyoxometalates with organic molecules; picosecond spectroscopy of $[(N\text{-methylpyrrolidinone})_2H^+]_3[PW_{12}O_{40}]$[801]
1987	polyoxometalates as homogeneous oxidatively resistant catalysts for difficult selective organic oxidations; functionalization of alkanes[802]
1987	sustained catalytical homogeneous oxo-transfer oxidation of alkanes; interaction of alkyl hydroperoxides with transition metal-substituted polyoxometalates[803]
1987	preparation of tri- and tetrasubstituted alkenes from alkanes; homogeneous catalytic photosynthesis by polyoxometalates[804]
1988	sustained thermal and photochemical homogeneous catalytic functionalization of hydrocarbons by polyoxometalates[805]
1988	homogeneous catalytic photochemical functionalization of alkanes by $\alpha\text{-}[PW_{12}O_{40}]^{3-}$; rate behavior, energetics, and general characteristics of process[806]
1988	catalytic photochemical oxidation of organic substrates by polyoxometalates; picosecond spectroscopy, photochemistry, and structural properties of charge-transfer complexes between heteropoly tungstic acids and dipolar organic compounds[807]
1988	anaerobic functionalization of remote unactivated C−H bonds by polyoxometalates[808]
1989	excited states of polyoxometalates as oxidatively resistant initiators of hydorcarbon autoxidation; selective production of hydroperoxides[809]

1990	direct selective acylation of an unactivated C−H bond in a caged hydrocarbon; approach to C−H bond functionalizations that proceed catalytically and selectively at high substrate conversion[810]
1990	anti-HIV activity, toxicity, and stability studies of representative structural families of polyoxometalates[811]
1990	photochemical dehalogenation of CCl_4 by alcohols catalyzed by polyoxotungstates[812]
1990	polyoxometalate systems for catalytic selective production of nonthermodynamic alkenes from alkanes; nature of excited-state deactivation processes and control of subsequent thermal processes in polyoxometalate photoredox chemistry[813]
1990	redox catalysis involving substrate photooxidation with catalyst regeneration by substrate reduction;[814] simultaneous oxidative C−H bond cleavage and reductive C−S bond cleavage in thioethers catalyzed by $[W_{10}O_{32}]^{4-}$
1990	preparation and use of polyoxometalates for treatment of retrovirus infections[815]
1991	stabilization of lacunary $[PMo_{11}O_{39}]^{7-}$; isolation, purification, stability characteristics, and metalation chemistry[816]
1991	roles of surface protonation on photodynamic, catalytic, and other properties of polyoxometalates, probed by photochemical functionalization of alkanes; implications for irradiated semiconductor metal oxides[817]
1991	mechanisms in thermal and photochemical alkane functionalizations catalyzed by oxidatively resistant metalporphyrin analogues and isopoly tungstates[818]
1991	comparative study of polyoxometalates and semiconductor metal oxides as catalysts; photochemical oxidative degradation of thioethers[819]
1992	catalytic oxidations with H_2O_2; use of polyoxometalates in reactions with H_2O_2[820]
1992	excited and ground-state redox properties of polyoxometalates for selective transformation of unactivated C−H centers remote from the functional group in ketones[821]
1992	syntheses, characterization, and antiimmundeficiency virus activity of water-soluble salts of polyoxotungstate anions with covalently attached organic groups[822]
1992	alkane reactions with photoactivated decatungstate in neutral and acidic solutions; MO theory[823]
1992	synthesis, structure, spectroscopic properties and hydrolytic chemistry of organophosphonoyl polyoxo-tungstates, $[C_6H_5P(O)]_2[X^{n+}W_{11}O_{39}]^{(8-n)-}$, $X = P^{5+}$ or Si^{4+} [824]
1992	instrinsic kinetic selectivities in photooxidation of organic substrates by a range of polyoxometalates varying in redox potentials[825]
1993	catalytic carbon−halogen bond cleavage chemistry by redox-active polyoxometalates[826]
1993	principles and new approaches in selective catalytic homogeneous oxidation[827]
1993	polyoxometalates in catalytic photochemical hydrocarbon functionalization and photomicrolithography; excited-state lifetimes and subsequent thermal processes[828] involving $[W_{10}O_{32}]^{4-}$
1993	photocatalytic and photoredox properties of polyoxometalate systems[829]
1993	oxo transfer to hydrocarbons from high-valent totally inorganic oxometaloporphyrin analogues,[830] $[X^{n+}W_{11}O_{39}CrVO]^{(9-n)-}$, $X^{xn} = P^{5+}$, Si^{4+}
1993	multifunctional polyoxometalates as catalysts for environmentally benign processes[831]
1993	selective ethylation and vinylation of alkanes via polyoxotungstate photocatalyzed radical addition reactions[832]
1993	hydrolytically stable organic triester capped polyoxometalates, with catalytic oxygenation activity, of formula $[RC(CH_2O)_3V_3P_2W_{15}O_{59}]^{6-}$, $R = CH_3$, NO_2, CH_2OH[833]
1993	selective homogeneous catalytic epoxidation of alkenes by H_2O_2 catalyzed by oxidation- and solvolysis-resistant polyoxometalate complexes[834]
1993	polyoxometalates in catalytic selective homogeneous oxygenation and anti-HIV chemotherapy[835]
1993	homogeneous catalytic selective oxidations based on O_2 or H_2O_2; new systems and fundamental studies[836]
1994	polyoxometalate catalysis of aerobic oxidation of H_2S to S[837]
1994	relationship of molecular size and charge density of polyoxometalates to their anti-gp120-CD4-binding activity[838]
1994	role of H_2O in polyoxometalate-catalyzed oxidations in nonaqueous media; scope, kinetics, mechanism of oxidation of thioether mustard (HD) analogues by *tert*-butylhydroperoxide catalysis by $H_5[PV_2Mo_{10}O_{40}]$[839]
1995	in vitro antimyxovirus and anti:HIV activities of polyoxometalates[840]
1995	mechanism and dynamics in $H_3[PW_{12}O_{40}]$-catalyzed selective epoxidation of terminal olefins by H_2O_2;[841] formation, reactivity, and stability of $[PO_4(WO(O_2)_2]_4{}^{3-}$
1995	introduction of functionality into unactivated C−H bonds; catalytic generation and nonconventional utilization of organic radicals[842]
1995	a “smart” catalyst that self-assembles under turnover conditions[843]
1995	early time dynamics and reactivity of polyoxometalate excited states; a short-lived LMCT excited state and a reactive long-lived charge-transfer intermediate following picosecond flash excitation of $[W_{10}O_{32}]^{4-}$ in acetonitrile[844]
1995	homogeneous catalysis by transition metal oxygen anion clusters[845]
1996	selective oxidation of thioether mustard (HD) analogues by *tert*-butlhydroperoxide catalyzed by $H_5[PV_2Mo_{10}O_{40}]$ supported on porous carbon materials[846]
1996	carbon powder- and fiber-supported polyoxometalate materials; preparation, characterization, catalytic oxidation of dialkyl sulfides as mustard (HD) analogues[847]
1996	synthesis and characterization of mixed-valence diamagnetic 2e-reduced $[W_{10}O_{32}]^{6-}$; evidence for an asymmetric d-electron distribution over the W sites[848]
1996	a bivanadyl-capped highly reduced Keggin polyanion $[PMo_6{}^{5+}Mo_6{}^{6+}(V^{4+}O)_2]^{5-}$ [849]
1996	thermal multi-electron-transfer catalysis by polyoxometalates; application to practical problem of sustained selective oxidation of H_2S to S[850]

1996	mechanism in polyoxometalate-catalyzed homogeneous hydrocarbon oxo transfer oxidation; the $[Co_4(H_2O)_2P_2W_{18}O_{68}]^{10-}$/*p*-cyano-*N*,*N*-dimethylaniline *N*-oxide selective catalytic epoxidation system[851]
1996	alkene epoxidation by *p*-cyano-*N*,*N*-dimethylanaline *N*-oxide catalyzed by d electron transition metal substituted polyoxometalates[852]
1996	biomimetic catalysis in a larger context; correlation of structure and function with genesis[853]
1996	the first combinatorially prepared and evaluated inorganic catalysts; polyoxometalates for aerobic oxidation of mustard analogue tetrahydrothiophene (THT)[854]
1996	mechanism of reaction of reduced polyoxometalates with O_2; evaluated by ^{17}O NMR[855]
1997	new environmentally benign technology for transforming wood pulp into paper; engineering polyoxometalates as catalysts for multiple processes[856]
1997	synthesis, solution and solid-state structures, and aqueous chemistry of an unstable polyperoxo polyoxometalate, $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$ [857]
1997	potent inhibition of respiratory synsytial virus by polyoxometalates of several structural classes[858]
1997	influenza virus inhibitory effects of a series of germanium- and silicon-centered polyoxometalates[859]

Geoffrey B. Jameson

Geoffrey B. Jameson presently of Massey University, New Zealand, is a structural X-ray crystallographer who has cooperated with various other workers by solving heteropoly electrolyte structures. Those cooperative efforts have already been referenced.[11,303a,324,447,467,469,506]

Walter H. Knoth, Jr., and Peter Domaille

Beginning in the late 1970s Walter H. Knoth, Jr., of the DuPont Experimental Station, took up work on heteropoly chemistry. In 1979 he described metal−metal-bonded derivatives of heteropoly complexes[860] and organic derivatives[861] of $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$, and $[SiMo_{12}O_{40}]^{4-}$. In 1981 he reported new tungstophosphates:[862] $Cs_6[P_2W_5O_{23}]$, $Cs_7[PW_{10}O_{36}]$, and $Cs_7Na_2[PW_{10}O_{37}]$, and O-alkylation[863] of $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$. In 1984, esters of phosphotungstic acid and anhydrous phosphotungstic acid were described.[864]

In 1983, Knoth began a collaboration with Peter J. Domaille, a physicist and NMR expert working at DuPont. They published[865] the preparation, properties, and ^{183}W NMR structure determination of $[PTi_2W_{10}O_{40}]^{7-}$ and $[CpFe(CO)_2Sn)_2PW_{10}O_{38}]^{5-}$ and a report[866] on halometal derivatives of $[PW_{12}O_{40}]^{3-}$ and related ^{183}W NMR studies. In 1986 they reported[867] on heteropoly complexes of the type $[M_3{}^{2+}(PW_9O_{34})_2]^{12-}$ and $[MM'M''(PW_9O_{34})_2]^{12-}$ as well as novel coordination of nitrate and nitrite.

Domaille published several heteropoly papers without Knoth. These included the first 2D ^{183}W and ^{51}V NMR determinations of isopoly and heteropoly species,[868] and the synthesis and ^{183}W NMR characterization of V-substituted polyoxometalates based on B-type tungstophosphate $[PW_9O_{34}]^{9-}$ precursors.[869] Also in 1986 the first P-centered γ 12-metalate: γ-$Cs_5[PV_2W_{10}O_{40}]\cdot xH_2O$ was reported.[870] One 1987 paper[871] covered comparisons of structure and thermal chemistry of stoichiometric and catalytic alkoxy-substituted heteropoly molybdates: ^{13}C CP-MAS NMR of a chemisorbed reaction intermediate. Domaille was a coauthor of a paper on effects of paramagnetic and diamagnetic monosubstitutions on ^{183}W and ^{31}P NMR of Keggin and Wells−Dawson heteropoly tungstates.[47] Domaille's collaborations with Finke on multinuclear and 2D NMR problems have been referenced.[756,763,765,775]

Hans-Joachim Lunk

Hans-Joachim Lunk was a Professor at the Humbolt-Univerität zu Berlin and is currently at Osram Sylvania, Inc. in Towanda, PA. Much of Lunk's early work in heteropoly chemistry involved the study of the thermal degradation of heteropoly acids by means of X-ray heating patterns, thermal analysis, IR spectroscopy, and solid-state NMR spectroscopy to study the new phases formed.[568,872−878] Many of the new Keggin heteropoly complexes synthesized and characterized by Lunk and co-workers involved Ge^{4+}, Al^{3+}, Fe^{3+}, and Cu^{2+} in tetrahedral coordination.[879−886] For example: the characterization and thermal behavior of α-$H_4[GeO_4W_{12}O_{36}]\cdot 24H_2O$,[880] the preparation of $H_5[AlO_4W_{12}O_{36}]\cdot 6H_2O$,[881] the synthesis, characterization, and ESR studies of anions containing Fe^{3+} in both tetrahedral and octahedral sites,[882] Mössbauer studies of heteropoly acids with Fe^{3+} heteroatoms,[883] and synthesis and structure studies of $Ba_2H[\alpha$-$FeO_4W_{12}O_{36}]\cdot 26H_2O$.[878,884] The crystal structure, NMR and ESR spectra of the first Keggin complex with Cu^{2+} in a tetrahedral site was reported by Lunk and co-workers.[885,886]

Lunk and co-workers have recently reported the first condensation reaction of $[A$-α-$SiO_4W_9O_{30}(OH)_3$-$Cr_3(OH_2)_3]^{4-}$ to give a dimerized Keggin anion containing low-valent heteroatoms, $(NH_4)_{11}[\{A$-α-$SiO_4W_9O_{30}(OH)_3Cr_3\}_2(OH)_3]\cdot 6H_2O\cdot 2.5NH_4Cl$, in which the Keggin moieties are linked by three Cr−OH−Cr bridges.[887] The synthesis, characterization, and crystal structure of $[\gamma$-$SiO_4W_{10}O_{32}(OH)Cr_2(OH_2)_2$-$(OOCR)_2]^{5-}$ in which $R = H$ or CH_3 has also been published.[888]

Novosibirsk Group, Raisa I. Maksimovskaya, Gennadij M. Maksimov et al.

An active group flourishes in Novosibirsk, Russia, at the Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences. Their heteropoly papers are oriented toward compounds of interest to catalysis. Since most of the papers have several coauthors, it is frequently somewhat difficult to assign primary responsibilities. Over 50 coauthors have participated in one or more heteropoly papers. Clear leaders are Raisa I. Maksimovskaya with over 70 heteropoly papers and Gennadij M. Maksimov with 20. (Dr. Maksimov also publishes on a variety of catalysis-related topics other than heteropoly complexes.) Other workers appearing as primary or coauthors on a significant number of heteropoly papers include M. A. Fedotov, K. I. Matveev, L. I. Kuznetsova, and I. V. Kozhevnikov. (See refs 1124−1202.)

The largest number of Maksimovskaya's papers (usually with M. A. Fedotov) involve multinuclear NMR (^{17}O, ^{31}P, ^{51}V, ^{183}W, ^{29}Si, ^{71}Ga) elucidating structure, thermally induced changes, and status in solution.[1124−1148] Three papers report rates of ^{17}O exchange.[1149−1151] A dozen papers are devoted to syntheses of heteropoly compounds,[1152−1161] including crystalline salts of $[Se_2Mo_2V_6O_{28}]^{6-}$, $[MoV_9O_{28}]^{5-}$, $[VMo_5O_{19}]^{3-}$,[1162] and $H_6[P_2W_{21}O_{71}]$.[1163] Seven papers describe heteropoly-catalyzed reactions.[1164−1170] Reactions of certain heteropoly species were described.[1171−1176] Some papers are based on EPR studies.[1177−1179] Four papers concern heteropoly blues.[1178, 1180−1182] Five studies of thermal decomposition and thermolysis were reported[1183−1187] and another five appeared on the status of various heteropoly species in aqueous solutions.[1188−1192] There were two papers on oxidations by heteropoly complexes.[1193, 1194]

Ten of the papers already cited were principally authored or coauthored by Gennadij M. Maksimov. These primarily centered on NMR[1135,1139,1144,1147,1151] and on syntheses[1157,1158,1160,1161] and reactions.[1171,1173] Six other papers dealt with various catalysis[1195−1200] and two[1201,1202] with multinuclear NMR (^{89}Y, ^{17}O, ^{183}W) of complexes of Y^{3+}, La^{3+}, Ce^{4+}, Th^{4+}, Lu^{3+} with $[PW_{11}O_{39}]^{7-}$. There was a vibrational spectroscopic study of the interactions of $[PW_{11}O_{39}]^{7-}$ with metal ions.[1203] Maksimov wrote a general review (17 pages) on *Advances in Polyoxometalate Synthesis and Study of Heteropoly Acids*.[1204]

The list of references, refs 1124−1203, includes 20 papers principally authored or coauthored by M. A. Fedotov (especially those on multinuclear NMR) and 19 by K. I. Matveev and 16 by L. I. Kuznetsova.

Elias Papaconstantinou

Elias Papaconstantinou of "Demokritos," the Greek atomic energy research laboratory in Athens, was, in the late 1960s and early 1970s coauthor of several papers[27,35,263] with Professor M. T. Pope, his Ph.D. mentor. He began his independent research in the mid-1970s. A number of papers[889−895] concerned use of heteropoly molybdates and tungstates for photocatalyzed oxidation of various organic compounds during radiolysis by ^{60}Co γ irradiation. This led naturally into photocatalysis by heteropoly complexes of various oxidations and to heteropoly photochemistry in general. There were papers on the photochemistry of $[P_2Mo_{18}O_{62}]^{6-}$ complex,[896] photocatalytic oxidation of organic compounds using heteropoly molybdates and tungstates,[897] photogalvanic cells using heteropoly electrolytes,[898] and photochemistry of 12-tungsto heteropoly species.[899] There was a paper on the photochemical generation of H_2 during heteropoly 12-tungstate-photocatalyzed oxidation of organic compounds,[900] and another on production of H_2 during photocatalytic multielectron photoreduction of $[P_2W_{18}O_{62}]^{6-}$ in the presence of organic compounds.[901] The oxidation of ascorbic acid in micellar and isotropic media by $[P_2Mo_{18}O_{62}]^{6-}$ was described.[902] Photochemical oxidation of organic compounds with heteropoly electrolytes was discussed with its aspects relevant to photochemical utilization of solar energy.[903] Vanadium sensitization of photochemistry of mixed molybdo- and tungstovanadates was reported.[904] Comparative reductions of $[P_2Mo_{18}O_{62}]^{6-}$ by α-tocopherol in micellar and isotropic media were studied.[905] Selective photocatalytic oxidation of alcohols by heteropoly tungstates was reported.[906] Thermal and photochemical aspects of the reduction of $[P_2Mo_{18}O_{62}]^{6-}$ by ferrous ion[907] and by iodide[908] were discussed. An overview was presented in 1989.[35a]

Thermal and photochemical catalysis by polyoxometalates with regeneration of the catalyst by oxidation with O_2 was discussed.[36e,909] The same topic was reviewed in 1994.[35b] The splitting of water by a photocatalytic process with polyoxometalates was reported.[910] Polyoxotungstate photocatalytic degradation of chlorophenols to CO_2 and HCl in aqueous solution was also reported in 1994,[911] and discussion of the mechanism of that reaction was presented.[912] Similarly, the photocatalytic degradation of phenol and *p*-cresol by polyoxotungstates was reported and its mechanism discussed.[913] A contribution to water purification using polyoxometalates (aromatic derivatives, chloroacetic acids) was discussed.[914] Recent developments in photocatalysis by polyoxometalates were reviewed in 1994.[35a]

Lage Pettersson

Lage Pettersson of Umea University, Sweden, has, since 1971, concentrated on determining the species and the equilibria present in solutions containing heteropoly complexes and their components. Combinations of methods were employed: insightful calculational methods, potentiometric measurements, large-angle X-ray scattering, spectroscopy (Raman, IR, and UV−vis), and multinuclear NMR. In 1971, formation constants were determined[915] for pentamolybdodiphosphates over the pH range 3−9. Experimental and computational methods were expounded and applied[916] to an analysis of the aqueous equilibrium system $H^+-MoO_4^{2-}-HPO_4^{2-}$. Large-scale X-ray scattering studies were reported[917] for $[P_2Mo_5O_{23}]^{6-}$ and $[Mo_7O_{24}]^{6-}$ and for 9-molybdomonophosphate complexes in aqueous solution,[918] for which solution there was also an equilibrium analysis.[919] A large-angle X-ray scattering study was made of some molybdoarsenate complexes in solution.[920] There was an equilibrium study of the system[921] $H^+-MoO_4^{2-}-HAs_4^{2-}$. Spectrophotometric and potentiometric titrations were combined to elucidate isopoly molybdates, molybdophosphates, and molybdoarsenates in solution.[922] The structure of hexamolybdodiarsenate complexes in aqueous solution was discussed,[923] and, in 1985, a ^{31}P NMR study of aqueous molybdophosphates was reported.[924] Speciation in the aqueous system $H^+-MoO_4^{2-}-HPO_4^{2-}$ was deduced from combined EMF-^{31}P NMR data.[925] Similarly, there was a combined potentiometric ^{31}P NMR study of equilibria in the molybdophenylphosphonate system in 0.6 M NaCl.[926] Monomolybdononavanadate and *cis*- and *trans*-dimolybdooctavanadate in solution were studied[927] in 1989 and aqueous molybdovanadates at high Mo:V ratio in 1991.[928] Aqueous molybdotungstates were investigated[929] and the isomers of $[PMo_{10}V_2O_{40}]^{5-}$ in aqueous solution were characterized by ^{31}P and ^{51}V NMR.[930] The aqueous vanadophosphate system[931] and the aqueous tungstovanadates[932] were elucidated.

Yukiyoshi Sasaki and Co-workers

Yukiyoshi Sasaki of the University of Tokyo, first became involved with polyoxometalates in the 1950s. As a collaborator with Lars G. Sillén (Royal Institute of Technology, Stockholm) he applied Sillén's electrochemical methods to elucidating equilibria in isopoly systems in the late 1950s and the early 1960s. Having returned to Japan, he published on heteropoly species between 1973 and 1994. The heteropoly work comprises over 33 X-ray crystal structures of fundamental importance to the field, two reviews, and some five potentiometric studies of solution equilibria systems and formation of heteropoly species.

The crystal structure studies include the following species: β-$[SiW_{12}O_{40}]^{4-}$;[933] α-$(CN_3H_6)_4[V_2W_4O_{19}]$;[934] α-$Ba_2[SiW_{12}O_{40}]$;[935] α-$[P_2W_{18}O_{62}]^{6-}$;[936] $K_7[V_5W_8O_{40}]\cdot 12H_2O$;[937] β-$K_4[SiW_{12}O_{40}]\cdot 9H_2O$;[129a] ammonium 12-molybdotetraarsenate(V)tetrahydrate;[938] $(NH_4)_4[S_2^{4+}Mo_5O_{21}]\cdot 3H_2O$;[939] α-$K_8[SiW_{11}O_{39}]\cdot 13H_2O$;[940] $[(PhAs)_2Mo_6O_{25}H_2]^{4-}$;[443] $K_5[I^{7+}Mo_6O_{24}]$;[941] $[C(NH_2)_3]_4\{[SiMo_{12}O_{4O}]\cdot H_2O$;[942] Preparation and structures of 14-vanadophosphate;[943] $[Cu_2^{2+}Si_2Mo_{18}O_{66}]^{12-}$;[944] $[H_4Mo_4As_4^{5+}O_{26}]^{4-}$;[945] polyvanadophosphate;[946] $[C(NH_2)_3]_6[As_2Mo_{18}O_{62}]\cdot 9H_2O$;[947] $Na_5[H_3Pt^{4+}W_6O_{24}]\cdot 20H_2O$;[948] $K_6Na_2[Pt^{4+}W_6O_{24}]\cdot 12H_2O$;[949] isomerism of 6-molybdoplatinate(IV); crystal structures of α-$K_{3.5}[H_{4.5}PtMo_6O_{24}]\cdot 3H_2O$ and β-$(NH_4)_4[H_4PtMo_6O_{24}]\cdot 1.5H_2O$;[950] $(NH_4)_4[Mo_5Se_2^{4+}O_{21}]\cdot 3H_2O$;[951] $K_{2.5}[H_{5.5}Pt^{4+}W_6O_{24}]\cdot 2H_2O$;[952] $Na_6H_2[V_2I_2^{7+}O16]\cdot 10H_2O$;[953] $K_5Na_2[SbW_6O_{24}]\cdot 12H_2O$;[954] synthesis and structures $[(CH_3)_4N]_6[H_3BiW_{18}O_{60}]$;[955] $[(CH_3)_4N]_4Na_2\{As_2Mo_{12}O_{42}]\cdot 6H_20$;[956] $(NH_4)_4[Mo_8((H_2O)_2Cu^{2+})_2O_{28}]\cdot 6H_2O$;[957] $K_7H_2[SbMo_6O_{25}]\cdot 7H_2O$;[958] unusual structural features of $[Mn_2^{4+}V_{22}O_{64}]^{10-}$ and $[Mn_3^{4+}V_{12}O_{40}H_3]^{5-}$;[487] $K_4[H_2P_2^{3+}Mo_5O_{21}]\cdot 2H_2O$;[959] Keggin-type 12-tungstocarbonate anion containing carbene as a heteroatom;[960] $(NH_4)_4[Cu^{2+}(OH)_6O_{18}]\cdot 4H_2O$;[961] structural characterization of crown ether complexed K^+ $(C_{12}H_{24}O_6K)_2K[Co(OH)_6Mo_6O_{18}]\cdot 12H_2O$;[962] geometrical isomerization on acidification in $[Pt^{4+}Mo_6O_{24}]$ derivatives.[963]

Sasaki wrote reviews on the "Chemistry of Heteropolyacids" [964] (1975) and the "Structural Chemistry of Polyanions and Related Compounds" [965] (1976).

Potentiometric studies were made of (1) heteropoly anion formation from methylarsenate plus molybdate,[966] (2) heteropoly anion formation from dimethylarsenate plus molybdate,[967] (3) heteropoly anion formation from telluric acid plus molybdate in 1 M NaCl,[968] (4) equilibria in H^+-molybdate-$RAsO_2H$ solutions (where $R{=}OH$, C_6H_5, CH_3),[969] and (5) equilibria in H^+-molybdate-SeO_3^{2-} in 1 M aqueous NaCl solutions.[970]

Some of Sasaki's co-workers deserve special notice. These include Akiko Kobayashi;[129a,934,935,937,941−946,948,949,958] Hikaru Ichida;[487,942,947,949,951,953,957−959,961,962,970] Uk Lee;[948−950,952,954,958,962,963] Kazuko Matsumoto,[129a,443,936,939,940,960,964] who also authored two papers independently: crystal structures of $[C(NH_2)_3]_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$[971] and of $[C(NH_2)_3]_2[CH_3AsMo_6O_{21}(H_2O)_6]\cdot 6H_2O$ and $[C(NH_2)_3]_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$.[972]

At least four other scientists surnamed Sasaki and with initial "Y" have published relative to heteropoly complexes. These are Yo Sasaki, Yoichi Sasaki, Yoh Sasaki, and Yasuyoki Sasaki. The first of these coauthored a paper with Toshihiro Yamase on the effect of the $W^{6+}{-}OH$ group on electrochromism of polyoxotungstate film.[973] Yoichi Sasaki was a coauthor with Shinji Idari and Tasuku Ito of three papers involving bridged Mo^{5+} and W^{5+} polyanions.[974] Yoh Sasaki of Kinki University was a coauthor with Toshihiro Yamase on the crystallographic characterization of $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$ and energy transfer in its crystal lattices.[975] He had also collaborated in the 1980s on some papers about isopoly species,[976−978] one on electrochromic films derived from cathodic deposition of polyoxometalates,[979] and one on structural retention of isopoly decatungstates upon photoreduction. In 1991 he reviewed the crystal structures of polytungstate salts used as electrochromic materials and, in 1993, the primary and secondary structures of various polyoxometalates.[980] Yasuyoki Sasaski coauthored a paper describing the preparation of aromatic carboxylic acids using heteropoly acids.[981]

Yoichi Shimura

Yoichi Shimura of Osaka University published six papers on heteropoly compounds plus a review. In 1954 he confirmed by UV−vis spectroscopy[982] that the heteroatoms in the 6-molybdo complexes of Cr^{3+}, Fe^{3+}, and Co^{3+} and in the $Co_2^{3+}Mo_{10}$ complex are octahedrally coordinated[983] as are the Ni^{4+} and Mn^{4+} in $[(Mn\ \text{or}\ Ni)Mo_9O_{32}]^{6-}$.[22] In 1957 he concluded, on the basis of such spectra, that the Co^{2+} and Co^{3+} atoms are tetrahedrally coordinated in the tungstocobaltate complexes and the Mn^{4+} is octahedral in the MnW_5 complex.[107d] A review with 40 references discussed polyacids of transition elements.[984] In 1973, $[Co_4I_3O_{18}(OH_2)_6]^{3-}$ (described in ref 4) was derivatized by substituting six NH_3's or three bidentate ethylenediamine, glycinate, or L-alaninate ligands for the six H_2O's. The complexes with bidentate ligands were optically active.[985] Complexes having an organic group and a heteropoly group were discussed in 1980[986] (see ref 117), and crown or cryptand heteropoly complexes in 1981[987] (see refs 390−392). In 1986 tristelluratocobaltate(III) and trisethylenediaminetristelluratotetracobaltate(III) were reported.[988]

Rolf Strandberg

Rolf Strandberg of Umea University, Sweden, is a structural X-ray crystallographer who has determined the structures of a number of heteropoly compounds in the crystalline state: $Na_6[P_2Mo_5O_{23}]\cdot 13H_2O$;[989] $Na_3H_6[Mo_9PO_{34}]\cdot xH_2O$;[990] $H_3[PMo_{12}O_{40}]\cdot 29{-}31H_2O$;[991] $Na_4[GeMo_{12}O_{40}]\cdot 8H_2O$;[992] $Na_5H[P_2Mo_5O_{23}]\cdot 11H_2O$;[792] $[C(NH_2)_3]_4[GeMo_{12}O_{40}]$;[793] $[C(NH_2)_3]_4[(C_6H_5PO_3)_2Mo_5O_{15}]$;[993] and $[C(NH_2)_3]_4H_2[P_2Mo_5O_{23}]\cdot H_2O$.[994]

Toshihiro Yamase

Beginning in the mid-1970s Toshihiro Yamase of the Tokyo Institute of Technology published extensively on several aspects of *isopoly* molybdate and tungstate chemistry including preparations, structures, catalytic applications, and medical applications.[323,973,975−979,995−1016] Beginning in 1987, his publications began to include heteropoly species although attention to isopoly complexes continued.[1017−1025] Papers on heteropoly species include the following topics.

1987 preparation of alkali metal salts of heteropoly acids as pharmaceuticals and luminescent agents[1026]
1987 solid state photochemistry of polyoxometalates regarded as fragments of metal oxide lattices[1027]
1987 preparation of alkai salts of heteropoly acids as pharmaceuticals and chemical catalysts[1028]
1988 medical chemistry of polyoxometalates. Potent antitumor activity of polyoxomolybdates on animal transplantable tumors and human xenograft[1029]
1989 antiviral salts of heteropoly acids[1030]
1989 heteropoly tungstate salts as antirheumatic agents[1031]
1989 photoredox property of decatungstodititanophosphate anion[1032]
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1990 electrochemical study of 1:1 polyoxometalate-flavin mononucleotide complex in aqueous solution[1034]
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1990 crystallographic characterization[975] of $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$
1990 esters of heteropoly acids as antitumor agents[1037]
1990 virucides containing heteropoly salts for treatment of AIDS[1038]
1990 anticancer agents containing heteropolytungstates[1039]
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1990 biological activities of polyoxometalates[1041]
1991 structure of photoluminescent[1042] $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot aq$
1991 X-ray structural and photoluminescence spectroscopic investigation of the polymer $Eu_2(H_2O)_{12}[Mo_8O_{27}]\bullet 6H_2O$ and intramolecular energy transfer in the crystal lattice[1043]
1991 antiviral activity of polyoxomolybdoeuropate PM-104 against HIV type 1[1044]
1991 photoluminescence of $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot aq$[1045]
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1993 photoluminescence and crystal structure of $K_3Na_4H_2[TbW_{10}O_{36}]\cdot 20H_2O$[1056]
1993 charge transfer photoluminescence of polyoxotungstates and molybdates[1057]
1993 electroluminescence cell based on polyoxometalates. Pulsed electric field-induced luminescence of decatungstoeuropate dispersion layers[1058]
1993 structure of $K_3Na_4H_2[GdW_{10}O_{36}]\cdot 21H_2O$[1059]
1993 structure of $K_3Na_4H_2[SmW_{10}O_{36}]\cdot nH_2O$[1060]
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1993 heteropoly salts as antiviral agents[1062]
1993 structure of $NaSr_4[EuW_{10}O_{36}]\cdot 34.5H_2O$[1063]
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1993 electrochromism of polyoxometalates[1066]
1993 polyoxometalates for molecular devices: antitumor activity and luminescence[1067]
1994 effect of lanthanide contraction on the structures of the decatungstolanthanoate anions in $K_3Na_4H_2[LnW_{10}O_{36}]\cdot nH_2O$ crystals; Ln = Pr, Nd, Sm, Gd, Tb, Dy[1068]
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1994 structure of $Na_8H[GdW_{10}O_{36}]\cdot nH_2O$[1070]
1994 structure of $Na_6H_3[SmW_{10}O_{36}]\cdot 28H_2O$[1071]
1995 crystal Structure and Photoluminescence of $K_2Eu_3H_3[Ge_2Ti_6W_{18}O_{77}]\cdot 37H_2O$[1072]
1995 structure−activity relationship and strain specificity of polyoxometalates in HIV activity[1073]
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1996 MRSA inhibitors containing Keggin heteropolytungstates[1075]
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1996 in vitro antimyxovirus activity and mechanism of anti-influenza virus activity of the polyoxometalates PM-504 and PM-523[1077]
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1997 study of polyoxometaloeuropates[1079]
1997 synergistic anti-influenza virus A (H_1N_1) activities of PM-523 (polyoxomolybdate) and ribavirin in vitro and in vivo[1080]

Jon A. Zubieta

Jon A. Zubieta of Syracuse University and coworkers have extensively studied the chemistry of polyoxometalates involving organic ligands and organic solvent solubilities. Several reports of syntheses, characterizations, and X-ray crystal structures of polyoxomolybdates that can be described as having bi-,[1081−1088] tri-,[1089−1092] tetra-,[1093−1100] hexa-,[1101−1105] and octanuclear[1106−1111] cores with organic ligands have been made. Zubieta has written two comprehensive reviews which detail much of his work (as well as that of others in this field).[3i,1112]

Several polyoxoalkoxyvanadates[1113−1117] have also been studied and although some have core structures similar to the molybdates, the chemistry does not parallel that of the Mo clusters.[1113] An interesting polyoxovanadate complex $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$, that is described as a chiral inorganic double helix, was synthesized hydrothermally.[1118] Many other novel polyoxovanadates[1119] and molybdates[1120−1123] like: $(NH_4)_5Na_4\{Na[Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)]_2\}$,[1121] $Na_4[Mo_6As_6O_{20}(OH)_2\cdot 9H_2O$,[1122] and $[H_4As^{III}{}_2As^{V}Mo^{V}{}_8Mo^{VI}{}_4O_{40}]^{1-}$,[1123] have been prepared by hydrothermal methods.

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