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Polyoxometalates

Noble Metals in Polyoxometalates

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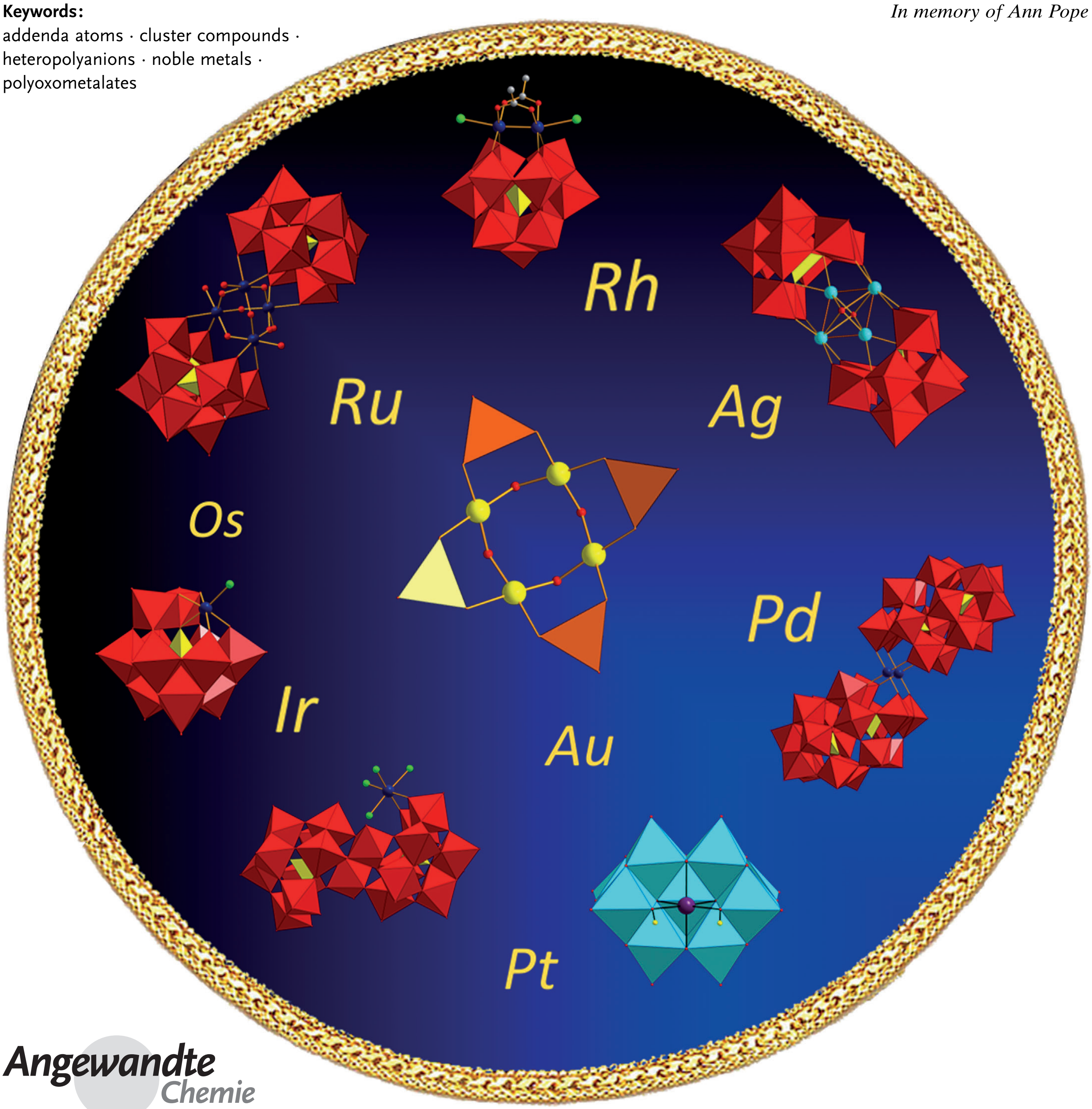
Keywords:
addenda atoms · cluster compounds · heteropolyanions · noble metals · polyoxometalates

In memory of Ann Pope



Polyoxometalates containing noble metal ions, such as ruthenium, osmium, rhodium, palladium, platinum, silver and gold, are a structurally diverse class of compounds. They include both classical heteropolyanions (vanadates, molybdates, tungstates) in which noble metals are present as heteroatoms, as well as the recently discovered class of polyoxometalates with noble metal “addenda” atoms. The focus of this Review is on complexes that should, in principle, exist as discrete molecular species in solution, and which are therefore of interest for their reactivity, their future synthetic utility and potential applications, for example, in catalysis or nanoscience.

From the Contents

1. Introduction

Polyoxometalates (POMs, predominantly molybdates and tungstates) can incorporate most metallic and non-metallic elements of the Periodic Table as heteroatoms. It is to be expected that the hard sigma-donor properties of the oxygen atoms of the POM matrices that surround the heteroatom(s) would favor the incorporation of oxophilic hard-metal cations. Nevertheless, as was recognized several years ago, the availability of vacant d-orbitals of appropriate symmetry on the metal atoms adjacent to the heteroatom allows the POM matrix to function as a π-acceptor ligand to a greater or lesser extent depending on local symmetry and the redox potentials of the “addenda” atoms Mo or W.

The eight elements in the second and third transition series of Groups 8–11 (ruthenium through gold) lie close to the ill-defined borderline between class ***a*** (hard acid) and class ***b*** (soft acid) coordination behavior, a factor that is undoubtedly relevant to the well-established catalytic activity of these elements. In the past, POMs incorporating these elements have received relatively little attention, but more recent investigations, presumably stimulated by potential catalytic applications, have begun to reveal an unexpected new structural chemistry.

This Review covers discrete POM ions containing the above-mentioned eight elements. In Section 2 POMs containing the noble metals as heteroatoms are presented. These POMs may be termed conventional heteropolyanions (vanadates, molybdates, tungstates); Section 3 covers a recently discovered new class of POMs in which noble metals (to date palladium, platinum, and gold) act as the addenda atoms. Our focus is on complexes that could, in principle, exist as discrete (and therefore potentially reactive) species in solution, although this property may not always have been demonstrated in the relevant publication. We have chosen to exclude consideration of two rapidly expanding areas of POM chemistry: a) organometallic derivatives of polytungstates, -molybdates, and -vanadates,[++] and b) two- and three-dimensional linked polyoxometalate anions of interest to the solid-state and nanochemistry community.

Within these restrictions, the numbers of publications that are potentially relevant to this Review are shown in Figure 1. It must be noted however that unambiguous identification and characterization of specific POMs has always been challenging, especially for the early investigators. But even more recently it is evident that there have been some misinterpretations or incorrect assignments claims.

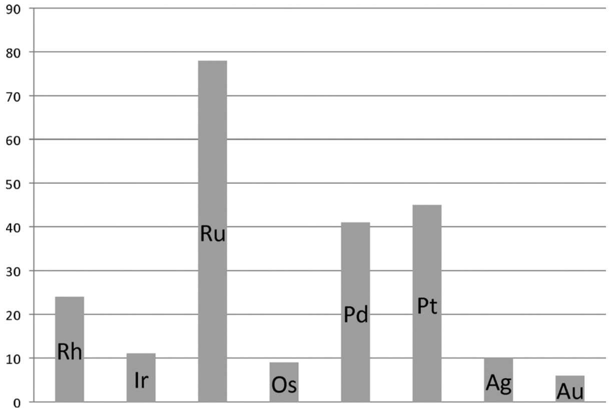


Figure 1. Research activity (publication numbers) involving the complex classes discussed in the text.

2. Polyoxovanadates, -molybdates, and -tungstates

Rather than attempting to catalogue the ever-increasing numbers of structures that populate the literature, we base our discussion in terms of a set of four structure types that are based upon the local environment(s) of the heteroatom(s).

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[++] An excellent introduction to this chemistry is provided by the comprehensive Review of P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77–111; see also A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.* **2010**, *110*, 6009–6048, and for the noble-metal derivatives, P. Putaj, F. Lefebvre, *Coord. Chem. Rev.* **2011**, *255*, 1642–1685.

2.1. E-Structures

These incorporate "**E**mbedded" heteroatoms. Examples are the familiar Keggin and Anderson-Evans anions,[1] for example, $[Co^{II}W_{12}O_{40}]^{6-}$ and $[Cr(OH)_6Mo_6O_{18}]^{3-}$ (Figure 2). The heteroatoms in these structures have no free coordination sites and the reactivity of such complexes is limited to electron- or proton-transfer processes. To date only four noble metals have been identified in such structures:

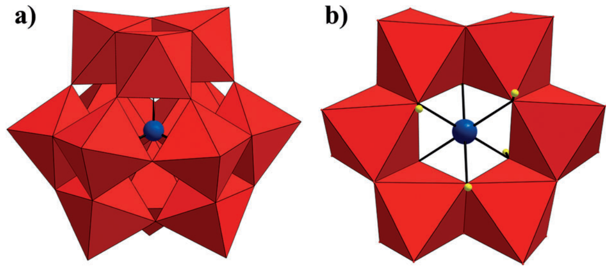


Figure 2. Combined ball-and-stick/polyhedral representation of a) Keggin $[MW_{12}O_{40}]^{n-}$ and b) Anderson-Evans $[M(OH)_6Mo_6O_{18}]^{n-}$ polyoxoanions. $\{WO_6\}$ or $\{MoO_6\}$ red, M blue, H yellow.

2.1.1. Rhodium

Ammonium and potassium salts of the Anderson–Evans anion $[Rh(OH)_6Mo_6O_{18}]^{3-}$ (Figure 2b) were first described (as "$3(NH_4)_2O{\cdot}Rh_2O_3{\cdot}12MoO_3{\cdot}20H_2O$") almost a century ago and were recognized as analogues of the earlier-discovered Al^{III}, Fe^{III}, Cr^{III}, and Co^{III} derivatives.[2] This conclusion has subsequently been confirmed by crystal structure analyses of the ammonium and gallium salts.[3,4]

Several other reported heteropolymolybdo- and tungstorhodates with empirical formulas "$[RhM_6O_{21}]^{3-}$" (which would correspond to an anhydrous version of the Anderson anion), and "$[RhM_{10}O_{35}]^{7-}$" (M = Mo, W) and "$[RhMo_8O_{28}]^{5-}$" are based upon incomplete and unreliable experimental evidence. Similar doubts can be expressed for the reported Keggin-like species "$[RhM_{12}O_{40}]^{5-}$" and "$[(RhO_4)W_{11}O_{35}Ni(H_2O)]^{7-}$".[5–7]

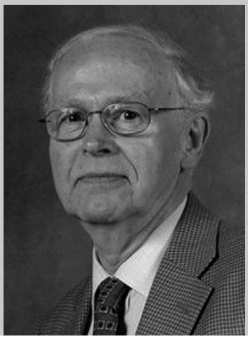
2.1.2. Palladium

The recently reported crystal structure of $K_{0.75}Na_{3.75}[Pd^{IV}Mo_6O_{24}H_{3.5}]{\cdot}17H_2O$ shows a "dimer" of Anderson structures linked by a Pd^{IV}-O···H···O-Pd^{IV} hydrogen bond, with the oxidation state of Pd based on bond valence sums. X-ray photoelectron spectroscopy showed the presence of both Pd^{II} and Pd^{IV}, the signal arising from Pd^{IV} diminishing in intensity during the process of irradiation.[8] The diamagnetic crystals were isolated after 1–3 months in 24–40% yield from an aqueous solution of sodium molybdate and $K_2[Pd^{II}Cl_4]$. In the absence of any added oxidant, aerial oxidation, however unlikely, was presumed, and independent confirmation of this substance is desirable.

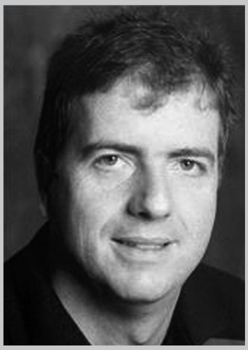
The vanadopalladate(II) anion shown in Figure 3a, $[Pd^{II}V_6O_{18}]^{4-}$, prepared in acetonitrile solution, has a boat conformation of the hexametavanadate ring stabilized by the attachment of the Pd^{II} center. The rigid structure in solution (no evidence of boat–chair interconversion) was confirmed by variable temperature ^{51}V NMR, ^{17}O NMR spectroscopy and was further characterized by ESI mass spectrometry.[9]

Reaction of the heterometallic cuboidal clusters $[Mo_3S_4Pd^0(H_2O)_9Cl]^{3+}$ and the tri-vacant $[AsW_9O_{33}]^{9-}$ anion in aqueous media results in the four-lobed assembly $[(H_2AsW_9O_{33})_4\{Mo_3S_4Pd^0(H_2O)_5\}_2]^{20-}$ which encloses a double-cuboidal moiety $\{Mo_3S_4Pd{-}PdS_4Mo_3\}^{8+}$ (Figure 4).[10] Each Pd atom is linked to the opposite $\{Mo_3S_4\}$ unit through a Pd–Pd bond (2.77 Å) and a Pd–S bond. Alternatively, the structure of this polyanion can be viewed as a previously reported supramolecular cage $[\{(H_2O)_5Mo_3S_4(H_2As_2W_9O_{33})(H_4AsW_9O_{33})\}_2]^{14-}$[11] incorporating a {Pd–Pd} core. Based upon ^{183}W NMR and UV/Vis

Natalya V. Izarova was born in Novosibirsk, Russia. She graduated in Chemistry (2003) from Novosibirsk State University, and completed her Ph.D. (2006) with Prof. Maxim N. Sokolov and Prof. Vladimir P. Fedin at Nikolaev Institute of Inorganic Chemistry (NIIC). During her Ph.D. she spent a year in the group of Prof. Dieter Fenske (University of Karlsruhe, Germany). After postdoctoral studies at NIIC she joined the group of Prof. Ulrich Kortz at Jacobs University (2008). Her interests include inorganic synthesis, the chemistry of polyoxometalates and polynuclear aqua/hydroxo complexes of metal ions, and crystallography.



Michael Thor Pope was born in Exeter, England and educated at Oxford University (D.Phil. with R. J. P. Williams). Following postdoctoral research at Boston University (L. C. W. Baker) he spent three years at Laporte Industries Ltd. in England. He joined the faculty of Georgetown University (1962), where he has remained for his entire academic career. His research activities have focused on all aspects of the chemistry, structures, and applications of polyoxoanion complexes of the early transition metals.



Ulrich Kortz studied Chemistry and Chemical Engineering in Giessen and Darmstadt (1982–1989), before he moved to Georgetown University in Washington, DC for his Ph.D. under the supervision of Michael T. Pope (1995). After postdoctoral studies with Dante Gatteschi (Florence, Italy) and André Tézé and Gilbert Hervé (Versailles, France) he started his independent academic career at the American University of Beirut in Lebanon. In 2002 he joined the newly established International University Bremen (now Jacobs University) as an Associate Professor, and in 2007 became a Full Professor. His research interests include synthetic inorganic and organometallic chemistry, structural inorganic chemistry, polyoxometalates, catalysis, magnetism, and electrochemistry.

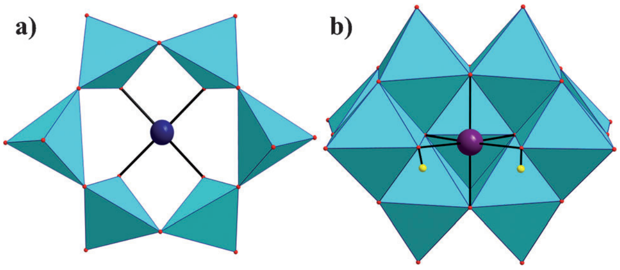


Figure 3. Combined ball-and-stick/polyhedral representation of a) $[Pd^{II}V_6O_{18}]^{4-}$ and b) $[H_2Pt^{IV}V_9O_{28}]^{5-}$. $\{VO_4\}$ and $\{VO_6\}$ turquoise, Pd blue, Pt violet, O red, H yellow.

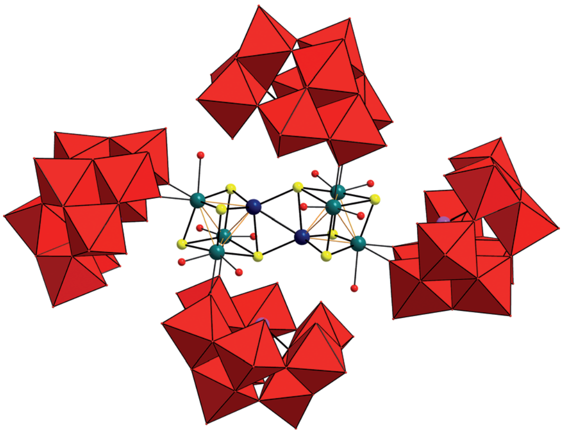


Figure 4. Combined ball-and-stick/polyhedral representation of $[(H_2AsW_9O_{33})_4\{Mo_3S_4Pd(H_2O)_5\}_2]^{20-}$. $\{WO_6\}$ red, Pd blue, Mo green, As pink, S yellow, O red.

spectroscopy studies the molecular structure of $[(H_2AsW_9O_{33})_4\{Mo_3S_4Pd(H_2O)_5\}_2]^{20-}$ is retained in solution. Addition of exogenous ligands L (e.g. I^- or pyridine) causes dissociation into the monomers with Pd–L coordination.[10]

2.1.3. *Platinum*

In a series of twenty papers between 1983 and 2010 Lee and colleagues have reported crystal structures of various salts of hexamolybdo- and hexatungstoplatinate(IV) anions with different degrees of protonation, hydration, and hydrogen-bonded networks.[12,13] These compounds were prepared by treating $[Pt^{IV}(OH)_6]^{2-}$ with molybdate or tungstate under different conditions of acidity and countercation. In every case except two, the polyanions have the anticipated planar Anderson structure. The exceptions, $(NH_4)_4[H_4Pt^{IV}Mo_6O_{24}]\cdot 1.5\,H_2O$[12a,c,f] and $K_4[H_4Pt^{IV}Mo_6O_{24}]\cdot 2\,H_2O$,[12e] isolated at pH ≈ 5.4, contains the "bent" (C_{2v}) heptamolybdate structure first described by Lindqvist.[14] There is however no evidence that the Lindqvist structure for the molybdoplatinate(IV) is retained in solution under any pH value.[12e] In some crystal structures, the polyanions with D_{3d} symmetry form hydrogen-bonded dimers $[(Pt^{IV}M_6O_{24})_2H_n]^{(16-n)-}$.[12b,f,j,l,13d,g] Recently Day, Klemperer et al. were able to crystallize also the trimeric and tetrameric homologues $[(Pt^{IV}Mo_6O_{24})_3H_n]^{(24-n)-}$ and $[(Pt^{IV}Mo_6O_{24})_4H_{23}]^{9-}$.[15] Thermolysis of the hexamolybdoplatinate(IV) salts supported on MgO, SiO_2, or Al_2O_3 generates catalysts for alkane dehydrogenation, ethene hydrogenation or ethane hydrogenolysis, respectively.[16]

Using the same source of platinum(IV), $Na_2[Pt(OH)_6]$, Lee, Kortz et al. have synthesized the decavanadate-derived salt $Na_5[H_2Pt^{IV}V_9O_{28}]\cdot 21\,H_2O$ (Figure 3 b). The two protons were located on oxygen atoms that bridge Pt and V and participate in inter-anion hydrogen bonds that generate dimeric assemblies in the solid state.[17a] Similar dimers have been observed with salts of decavanadate itself.[18] Solutions of the vanadoplatinate(IV) anion yielded the anticipated four-line ^{51}V NMR spectrum, and a well-resolved ^{195}Pt NMR signal was observed at $\delta = 3832$ ppm, distinct from that of $[Pt(OH)_6]^{2-}$ at $\delta = 3294$ ppm.[17a] The ^{51}V and ^{195}Pt NMR chemical shifts for $[H_2Pt^{IV}V_9O_{28}]^{5-}$ were successfully modeled by DFT methods.[19] The crystal structure of the guanidinium salt $(CH_6N_3)_5[H_2Pt^{IV}V_9O_{28}]$ has also been reported recently.[17b]

2.1.4. *Silver*

Some examples of silver-centered E-structures may also be considered as cryptates, because they have been prepared by encapsulation of Ag^+ ions into preformed POM assemblies. Thus Sokolov, Cadot et al. have shown that addition of Ag^+ to an aqueous solution of the supramolecular assembly $[\{(H_2O)_5Mo_3S_4(H_2As_2W_9O_{33})(H_4AsW_9O_{33})\}_2]^{14-}$ generates $[\{Ag(H_2O)_5Mo_3S_4(H_2As_2W_9O_{33})(H_2AsW_9O_{33})\}_2]^{16-}$, in which the two Ag^+ ions are each coordinated to oxygen atoms of the $\{AsW_9O_{33}\}$ units and the S atoms of two $\{Mo_3S_4\}$ clusters located in different monomeric units of the parent supramolecular assembly.[11] The incorporation proceeds in two successive steps as based on potentiometric titration studies, and the ^{183}W NMR spectrum is consistent with rapid hopping of both enclosed Ag^+ ions between two equivalent sites.

The 20 W and 2 Si atom containing anion $[(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{8-}$, first reported by Mizuno et al.,[20] has been shown to function as a size-selective cryptand that can incorporate Ag^+ and other metal ions.[21] The structure of the silver-incorporated anion in the tetraethylammonium salt reveals a crystallographically disordered Ag^+ ion at the center (Figure 5 a).

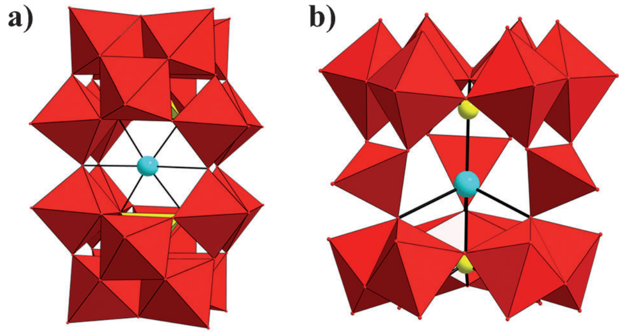


Figure 5. Combined ball-and-stick/polyhedral representation of a) $[Ag\{(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4\}]^{7-}$ and b) $[AgAs_2Mo_{15}O_{54}]^{11-}$; $\{WO_6\}$, $\{MoO_6\}$, $\{MoO_4\}$ red, Ag turquoise, As yellow.

Xue et al. have reported the cage-like polyoxomolybdate ion $[AgAs_2Mo_{15}O_{54}]^{11-}$. It consists of $[AsMo_6O_{27}]^{15-}$ and $[AsMo_6O_{24}]^{9-}$ subunits linked by three MoO_4 tetrahedra and a central Ag^+ ion. The Ag^+ ion occupies a trigonal-pyramidal coordination site defined by lone pairs of two As^{III} atoms (As-Ag-As bond angle of 180°) and three μ_3-oxo groups of the MoO_4 tetrahedra (Figure 5 b). ESI-MS and UV/Vis studies showed slow decomposition of $[AgAs_2Mo_{15}O_{54}]^{11-}$ in aqueous solution via a $\{AgAs_2Mo_3O_{18}\}^{11-}$ species.[22]

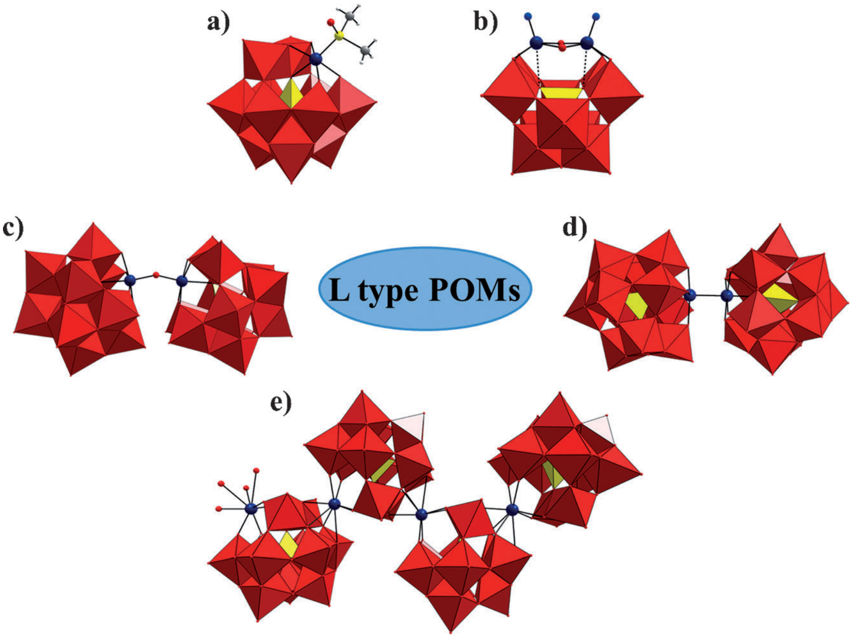


Figure 6. Examples of L-structure polyanions derived from mono-lacunary α-$[XW_{11}O_{39}]^{n-}$ and di-lacunary γ-$[XW_{10}O_{36}]^{8-}$ Keggin type units: a) $[SiW_{11}O_{39}Ru(dmso)]^{5-}$; b) γ-$[SiW_{10}O_{38}(RuN)_2]^{6-}$; c) $[\{SiW_{11}O_{39}Ru^{III/IV}\}_2O]^{11-}$; d) $[(PW_{11}O_{39}Rh^{II})_2]^{10-}$; e) $\{[PW_{11}O_{39}Ag]^{6-}\}_n$.

2.2. L-Structures

"**L**acunary anion-derived" anions are those in which secondary (addenda-like) heteroatom(s) have a single external ligand. Examples are α-$[PW_{11}O_{39}Co(OH_2)]^{5-}$ and γ-$[SiW_{10}O_{38}(RuN)_2]^{6-}$ (Figure 6). Such species are prepared by treating discrete lacunary anions (in which one or more addenda atoms, usually Mo or W, are "missing" from a parent E-structure) with an appropriate complex of the heteroatom. Such species have also been isolated from other reaction mixtures, that is, without prior formation of a presumed lacunary anion. The majority of L-structure complexes contain six-coordinate secondary heteroatoms each of which therefore retains a potentially replaceable ligand.[*]

By far the largest number of reports that describe noble metal POMs involve L-structure anions. However, in many cases a completely unambiguous characterization of the species is lacking, especially with respect to the identity of the terminal ligand and the separation of mixtures of isostructural byproducts.

2.2.1. Ruthenium

An early successful incorporation of ruthenium into POMs involved treating α-$[SiW_{11}O_{39}]^{8-}$ with hydrated ruthenium(III) chloride, "$RuCl_3{\cdot}n\,H_2O$", to yield a substance formulated as $K_5[SiW_{11}O_{39}Ru^{III}(H_2O)]{\cdot}15\,H_2O$ which was shown to be catalytically active in liquid-phase oxidations of alkenes.[23] Later, cyclic voltammetric examination of the product suggested that it may have been a mixture of undefined products[24,25] as the commercially available hydrated $RuCl_3$ is a mixture of chloro- and oxo- species of ruthenium in different oxidation states (II to IV). Subsequent reports from other researchers have described the use of "$RuCl_3{\cdot}n\,H_2O$" (sometimes "activated" by treatment with HCl) to prepare L-structure Keggin and Wells–Dawson type POMs. However, independent verification of the oxidation state of Ru and its terminal ligand is not always evident; although not fully characterized, the substances were shown to be catalytically active.[26–28] The use of the more substitution-labile Ru^{II} species, such as $[Ru(H_2O)_6]^{2+}$[24] and $[Ru(dmso)_4Cl_2]$,[29] as well as $[Ru^{III}(acac)_3]$ under hydrothermal conditions,[30] with appropriate lacunary anions leads cleanly to well-characterized products with terminal aqua or sulfoxide ligands. Bonchio et al. suggested using microwave irradiation to activate $[Ru(dmso)_4Cl_2]$ for reaction with the POM precursor.[31a] The method was recently extended by Izzet et al. to prepare the Ru^{III} aqua derivative starting from $[Ru(dmf)_6]^{3+}$ and either $[PW_{11}O_{39}]^{7-}$ or $[P_2W_{19}O_{69}(H_2O)]^{14-}$.[31b] The sulfoxide ligand in $[XW_{11}O_{39}Ru(dmso)]^{4-}$ is S-bonded to ruthenium, as confirmed by ^{31}P NMR[24] and EPR spectroscopy[32] (for X = P), as well as single-crystal X-ray diffraction (for X = Si; Figure 6 a)[33] and by DFT calculations.[34] A detailed electrochemical investigation[24] of $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$, and subsequently for the Si-centered analogue,[30b] showed that Ru oxidation states II, III, IV, and V (the IV and V states with terminal hydroxo and oxo ligands, respectively) can be reversibly accessed. Recently, the electronic properties of $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ and its oxidized derivatives have been studied theoretically.[35] For POMs $[PW_{11}O_{39}Ru^{III}(L)]^{4-}$, containing ligands (L), such as pyridine, and η^2-alkenes, and prepared by direct substitution of the aqua-ruthenium derivative, only the $Ru^{II/III}$ couple could be detected, whereas both $Ru^{II/III}$ and $Ru^{III/IV}$ couples have been recently detected for $[SiW_{11}O_{39}Ru(L)]^{5-}$ (where L is pyridine or a derivative).[24,31a,33,36] Several arguments, based on measurements including comparative ^{183}W NMR chemical shifts, redox potentials, and electronic spectra, demonstrate

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[*] We note that for L-structure complexes involving large secondary heteroatoms (lanthanides and actinides) the number of free coordination sites increases up to four. Such species are not relevant to the present Review.

that in such L-structures the POM “ligand”, by virtue of its reducibility, functions as a π-acid as well as a “hard” σ-donor.[24] The polyanion $[PW_{11}O_{39}Ru^{II}(dmso)]^{5-}$ displays remarkable catalytic activity in the oxidation of cyclooctene and adamantane by $NaIO_4$ and $KHSO_5$, respectively.[31a] Under microwave assistance $Li_5[PW_{11}O_{39}Ru^{II}(dmso)]$ catalyzes the selective oxo-transfer from O_2 to dmso in water leading to the quantitative formation of the sulfone.[37a] A complex with a non-planar Mo^V porphyrin, $[\{Mo(DPP)(O)\}_2(H_2SiW_{11}O_{39}Ru(dmso))]^{3-}$ (DPP^{2-} = dodecaphenyl porphyrin), acts as an efficient catalyst for the oxidation of benzyl alcohols with C_6H_5I in $CDCl_3$ at room temperature.[37b] Recently, $[PW_{11}O_{39}Ru^{II}(dmso)]^{5-}$[38] and $[XW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ (X = Si, Ge)[39] have been shown to catalyze water splitting with the oxidant Ce^{IV}. For the latter compounds, analysis of the reaction mechanism has shown that the compounds undergo two-electron oxidation of the ruthenium center to give a $Ru^V{=}O$ complex. The electrophilic terminal oxo group undergoes attack by solvent water resulting in O–O coupling.[39]

If the concentrations are increased in the hydrothermal reaction of $[SiW_{11}O_{39}]^{8-}$ and $[Ru^{III}(acac)_3]$, or if basic aqueous solutions of $[SiW_{11}O_{39}Ru^{II}(H_2O)]^{6-}$ are heated, the oxo-bridged product $[\{SiW_{11}O_{39}Ru^{III/IV}\}_2O]^{11-}$ is formed.[30b] The $[\{SiW_{11}O_{39}Ru^{III/IV}\}_2O]^{11-}$ can be reversibly oxidized to the Ru^{IV}-O-Ru^{IV} species, and reduced to the Ru^{III}-O-Ru^{III} and Ru^{III}-O-Ru^{II} species.[30b,40] The Ru^{IV}-O-Ru^{IV} form was characterized by single-crystal X-ray diffraction (Figure 6c) as the hydrated Rb salt $Rb_{10}[\{SiW_{11}O_{39}Ru^{IV}\}_2O]\cdot 9.5\,H_2O$. The six-line ^{183}W NMR spectrum indicates rapid rotation about the non-linear Ru-O-Ru axis in solution.[40]

Prolonged (5 days) hydrothermal reaction of $[SiW_{11}O_{39}]^{8-}$ with $[Ru^{III}(acac)_3]$ yields $[SiW_{11}O_{39}Ru^{II}CO]^{6-}$ which could be isolated as the cesium salt, and characterized by ^{183}W and ^{13}C NMR spectroscopy and electrochemistry. The electrochemical studies showed that the $Ru^{II}(CO)$ POM can be reversibly oxidized to the unexpectedly stable $Ru^{III}(CO)$ derivative.[41] The photoreduction of CO_2 to CO in a toluene solution containing Et_3N and the tetrahexylammonium salt of $[SiW_{11}O_{39}Ru(H_2O)]^{6-}$ that had previously been dehydrated by purging with Ar, has been interpreted in terms of a weakly bonded $[SiW_{11}O_{39}Ru(CO_2)]^{6-}$ complex. Supportive evidence includes EPR, ^{13}C NMR spectroscopy, and DFT calculations.[42] Also based on DFT calculations $[PW_{11}O_{39}Ru^{II}(H_2O)]^{5-}$ has been proposed as a potential reagent for the activation of N_2O through formation of $[PW_{11}O_{39}Ru^{II}(N_2O)]^{5-}$ containing a strong Ru–NNO bond.[43] Nitrido derivatives, such as $[PW_{11}O_{39}Ru^{VI}N]^{4-}$, prepared in non-aqueous solution, have been shown to undergo N atom transfer processes, for example yielding $[Ph_3PNPPh_3]^+$ from triphenylphosphine.[44] The comparative reactivity of several observed and hypothetical $[XW_{11}O_{39}M^{VI}N]^{n-}$ species (M = Cr, Mo, W, Tc, Re, Ru, Os) has been the subject of DFT calculations.[45]

Other L-structure POMs have been derived from the divacant lacunary anion γ-$[SiW_{10}O_{36}]^{8-}$ and its Ge analogue (Figure 6b). With ruthenium, incorporation of $\{(H_2O)Ru^{III}(\mu_2\text{-}OH)_2Ru^{III}(H_2O)\}^{4+}$[46] and $\{NRu^{VI}(\mu_2\text{-}O)_2Ru^{VI}N\}^{2+}$[47] moieties has been achieved, although only the nitrido structure has been confirmed crystallographically. Nevertheless, DFT calculations support the probability of an analogous structure for the aqua derivative.[48] Additional calculations have compared the electronic structures and reactivities of hypothetical Al^{III}-, P^V-, and S^{VI}-centered anions as well as the corresponding molybdates.[49] Chemical reduction of the nitrido complex γ-$[SiW_{10}O_{38}(RuN)_2]^{6-}$ with four equivalents of $[PW^VW^{VI}{}_{11}O_{40}]^{4-}$ yielded almost quantitative release of NH_3 and the presumed formation of γ-$[SiW_{10}O_{38}(Ru^{IV}O)_2]^{8-}$.[47]

2.2.2. *Osmium*

L-structure complexes containing Os are so far restricted to nitrido-osmium(VI) species. A very early report describing $[PW_{11}O_{39}OsN]^{4-}$[50] has been confirmed by the more extensive investigations of Maatta, Proust et al.[51] in which this anion, together with both the α_1 and α_2 isomers of $[P_2W_{17}O_{61}OsN]^{7-}$, have been thoroughly characterized by multinuclear NMR spectroscopy and other spectroscopic techniques. POM nitrido species in general have attracted the attention of theoreticians. A DFT study of the hypothetical Os^{VIII} species $[PW_{11}O_{39}OsN]^{2-}$ has compared the behavior of that anion with the corresponding Re^{VII}, Re^{VI}, and Re^V complexes.[52] A more recent DFT analysis of $[PW_{11}O_{39}M^{VI}N]^{4-}$ (M = Ru, Os, Tc, Re, Mo, W) has concluded that the Mn^{VI} and Fe^{VI} analogues might be stabilized by the lacunary polytungstate,[45b] and another report discusses the possible variation in nitrogen-transfer reactivity caused by changing M (Ru, Os, Re) or the central tetrahedral atom (Al, Si, P, As).[45c]

2.2.3. *Rhodium*

Reaction of rhodium(III) with lacunary heteropolytungstates was first reported in 1979,[53] but the products, formulated as “$[Rh(PW_{11}O_{39})_2]^{11-}$” and “$[Rh(P_2W_{17}O_{61})_2]^{17-}$” which would imply eight coordinate Rh^{III}, are implausible. These results could not be reproduced in later work by Zonnevijlle and Tourné in which salts of complexes, such as $[SiW_{11}O_{39}Rh(H_2O)]^{5-}$ with six different lacunary polytungstates were described.[54] Unfortunately this work did not exploit the development and use of techniques such as ^{183}W NMR spectroscopy and relied predominantly upon elemental analyses, electronic spectroscopy, and titrimetry. It was concluded that the aqua ligand on rhodium could be deprotonated to produce the hydroxo and oxo derivatives which were isolated and analyzed. Confirmation of this behavior would be of considerable interest in view of the subsequent reports by Hill et al. on terminal oxo complexes of isoelectronic tetravalent palladium and platinum, which we discuss in Section 2.3.6. However there is some doubt about the identity of the terminal ligand in those cases in which rhodium was introduced as $RhCl_3$ or $[RhCl_6]^{3-}$ rather than $Rh(NO_3)_3$. Nevertheless the Zonnevijlle anion “$[SiW_{11}O_{39}Rh(H_2O)]^{5-}$” when transferred into benzene with *n*-hexylammonium bromide, was found to be catalytically active in the oxidation of alkanes by *tert*-butyl hydroperoxide.[26c] Absorption of carbon monoxide by a material described as “$K_5[SiW_{11}RhO_{39}]/Al_2O_3$” (possibly containing the aqua derivative, but otherwise uncharacterized) has been investigated by diffuse reflection infrared spectroscopy at temperatures up to 900 K.[55]

High-yield syntheses of $[PW_{11}O_{39}Rh^{III}X]^{5-}$ (X = Cl, Br) have been achieved by hydrothermal reactions of the lacunary polytungstate with $RhCl_3$ in the presence of excess halide anion.[56] Salts of these complexes were characterized by elemental analysis, ^{31}P and ^{183}W NMR spectroscopy. Controlled potential electrolytic reduction of the chloro derivative generated the dimeric anion $[(PW_{11}O_{39}Rh^{II})_2]^{10-}$ confirmed by analytical ultracentrifugation and X-ray structure analysis of the potassium salt (Figure 6 d). Solutions of the dimer provide convenient routes to other $[PW_{11}O_{39}Rh^{III}X]^{n-}$ (X = I, CN, H_2O, acetate, pyridine, dmso) derivatives, each of which can be distinguished by its ^{31}P NMR chemical shift. Although not as active on this transformation as the analogous Rh^{II}-porphyrin dimers, an acetone solution of $[(PW_{11}O_{39}Rh^{II})_2]^{10-}$ and benzyl bromide yielded $[PW_{11}O_{39}Rh^{III}Br]^{5-}$ and dibenzyl under prolonged (5 h) photolysis at ambient temperature.[56] No benzylrhodium species were detected as products in the photolysis, but rhodium–carbon bond formation occurred in hydrothermal reactions of aqueous solutions of lacunary heteropolytungstates with $RhCl_3$ in 0.5 M acetate buffer. The products $[XW_{11}O_{39}Rh^{III}CH_2COOH]^{n-}$ (X = P, Si) were obtained in high yield (over 90 %) and fully characterized by multinuclear NMR spectroscopy and structural analysis of the silicon-centered anion.[57a] The amide $[PW_{11}O_{39}RhCH_2CONHC_6H_5]^{5-}$ was prepared in 60 % yield and isolated as the cesium salt.[57a] ESI-MS studies have shown that another convenient route to various derivatives with a Rh–C bond is heating $[PW_{11}O_{38}RhCl]^{5-}$ with different organic substrates (e.g. phenylacetate, malonate, Me_3SnCl) in acetonitrile.[57b]

2.2.4. Iridium

Liu et al. have reported the synthesis of tetra-*n*-butylammonium salts of anions formulated as $[XW_{11}O_{39}Ir^{IV}(H_2O)]^{n-}$ (X = B, Si, Ge, P),[58] $[PMo_{11}O_{39}Ir^{IV}(H_2O)]^{3-}$,[59] and α_2-$[P_2W_{17}O_{61}Ir^{IV}(H_2O)]^{6-}$[28a] by reaction of $[IrCl_6]^{2-}$ with the appropriate lacunary polyoxoanion. No confirmatory crystal structures are available and the reported ^{31}P and ^{183}W NMR spectra of these paramagnetic species are ambiguous or of insufficient quality for reliable structural characterization. Nevertheless, whatever the true composition of these iridium-containing materials, subsequent work has shown that they display electrocatalytic activity for nitrite reduction[60] and catalytic activity for epoxidation of allylic alcohols by H_2O_2 in biphasic systems.[28b] Recently, Sokolov et al. have shown that $(Bu_4N)_4[PW_{11}O_{39}Ir^{III}(H_2O)]$ can be prepared in almost quantitative yield from the lacunary anion and $K_2[IrF_6]$ under hydrothermal conditions.[61] The product was thoroughly characterized by crystal-structure determination, ^{31}P and ^{183}W NMR spectroscopy, ESI-MS, and cyclic voltammetry.

2.2.5. Palladium

The interaction between monolacunary Keggin- and Dawson- type polyoxotungstates α-$[XW_{11}O_{39}]^{n-}$ (X = B^{III}, Si^{IV}, Ge^{IV}, and P^{V}) and α_2-$[P_2W_{17}O_{61}]^{10-}$ and $[Pd(H_2O)_4]^{2+}$ or $PdCl_2$ has been studied by several groups under aqueous and non-aqueous conditions with a variety of spectroscopic (e.g. IR, UV/Vis, ^{17}O, ^{31}P, ^{183}W NMR) and microanalytical techniques.[28,58,59,62–70] Unfortunately no X-ray structural investigations of any products obtained were carried out and confident assignment of L-structures to these compounds cannot be confirmed. Most studies have been carried out with the phosphorus-centered lacunary species, the products often being formulated as $[PM_{11}O_{39}Pd(H_2O)]^{5-}$ (M = W, Mo) and $[P_2W_{17}O_{61}$-$Pd(H_2O)]^{8-}$ which would imply uncommon and presumably paramagnetic octahedral or square-pyramidal Pd^{II} centers. Recent studies suggest a different explanation of these results in terms of the S-structure species that are described in Section 2.3.3. Reports of the activity of the not-fully-characterized products in homogeneous or biphasic solution, or supported on alumina, include catalytic oxidation of allylic alcohols,[28b] hydrogenation of arenes,[67] benzene oxidation,[63,69] reduction of nitrogen oxides by methane,[64] and electrocatalytic reduction of nitrite and H_2O_2.[65,66] Metal nanoparticles prepared by reduction of "$K_5[PPdW_{11}O_{39}]$" with H_2 have been shown to be efficient catalysts for Suzuki-, Heck-, and Stille-type C–C and C–N coupling reactions of bromo- and chloroarenes.[70]

2.2.6. Platinum

POMs incorporating Pt have so far received limited attention, especially compared with those of Pd. The reaction of $[PtCl_4]^{2-}$ with $[PW_{11}O_{39}]^{7-}$ in aqueous solution has been investigated by electronic, infrared, and NMR (^{31}P, ^{195}Pt) spectroscopy.[63] At pH 4 the resulting solution showed two ^{31}P NMR signals at $\delta = -10.9$ and -13.2 ppm, with the signal at $\delta = -10.9$ corresponding to the residual lacunary anion and accounting for 80 % of the integrated spectral intensity. The ^{195}Pt NMR spectrum of the same solution had a signal at $\delta = 3347$ ppm, in contrast to that of $[PtCl_4]^{2-}$ at $\delta = 2909$ ppm. It was assumed that the product was $[PW_{11}O_{39}Pt]^{5-}$, but no analytical evidence for this was presented.[63]

The reaction of $[PtCl_6]^{2-}$ with the lacunary anion α_2-$[P_2W_{17}O_{61}]^{10-}$ was reported to yield $[P_2W_{17}O_{61}Pt^{IV}(OH_2)]^{6-}$, isolated as the tetra-*n*-butylammonium salt.[71] The NMR spectra of the product showed only one ^{31}P and seven ^{183}W signals (instead of the expected two and nine lines). The missing lines were attributed to relaxation effects caused by a "paramagnetic" Pt^{IV} center, which seems implausible.[71] The structure of the guanidinium salt of $[SiW_{10}Pt^{IV}{}_2O_{40}]^{8-}$ has been reported,[72] but the existence of this compound has been challenged.[73,74]

2.2.7. Silver

The introduction of silver in POM chemistry has to date involved only silver(I) which has an ionic radius significantly larger than those of the other (polyvalent) noble metal cations employed. The larger size of Ag^{I} leads to higher coordination numbers, and it is therefore not surprising that the majority of published reports in which silver is incorporated into POM structures describe 2D and 3D polymeric assemblies, and not the discrete molecular species that are the focus of this Review. For example, in a putative L-structure complex $[PW_{11}O_{39}Ag]^{6-}$ (Figure 6e) the silver cation is displaced outside the hole (Ag–O, ca. 2.4 Å) and is bonded to four bridging oxygen atoms (Ag–O, 2.56–3.00 Å) of an adjacent complex.[75] The result is a chain polymer with an eight-coordinate silver center in a distorted square-antiprismatic environment similar to that observed in corresponding 1:1 lanthanide–POM complexes.

The only apparently discrete L-structure POMs containing silver are those based upon $[As^{III}_4W_{40}O_{140}]^{28-}$, a cyclic anion comprising four $\{AsW_9O_{33}\}$ units linked by four WO_6 octahedra. Solution studies reveal that the anion $\{As_4W_{40}\}$ can bind up to four Ag^+ ions, but only two di- or trivalent transition-metal ions. Furthermore, the $\{As_4W_{40}M_2\}$ complexes can bind an additional two silver cations.[76] A crystal-structure determination of the ammonium salt of the dicobalt(II) derivative reveals the four "equivalent" holes (lacunae) shown in Figure 7, two (diametrically opposed) occupied by Co^{2+} ions and the other two by ammonium ions. It was argued that the attachment of the Co^{2+} ions causes the anion to fold (using the WO_6 "hinges") into a boat-like conformation to generate standard Co–O distances of about 2.0 Å. Such "allosteric" folding opens up the remaining two lacunae to a size large enough to accommodate the ammonium cations (NH_4–O, 2.8 Å) which can be further substituted by Ag^+ ions.[77] Structure determinations of the $\{As_4W_{40}Ag_4\}$ and $\{As_4W_{40}M_2Ag_2)$ derivatives would be of value to elucidate the precise coordination geometry of the Ag centers.

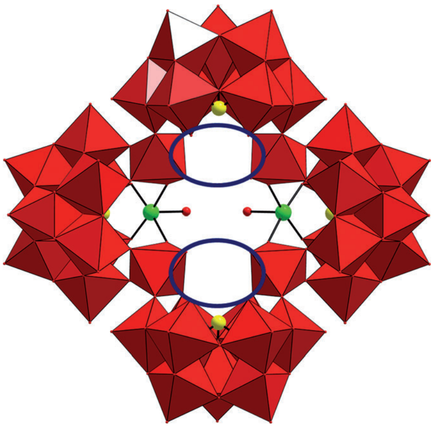

Figure 7. Combined ball-and-stick/polyhedral representation of $[\{Co(H_2O)\}_2As^{III}_4W_{40}O_{140}]^{24-}$; the presumed positions for possible Ag^+ coordination are indicated by the blue ellipses. $\{WO_6\}$ red, As yellow, Co green, O red.

2.3. S-structures

So-called "**S**andwich"-type structures are based most commonly (but not exclusively) on tri-vacant derivatives XW_9 of the Keggin ion, and enclose three (or four) sandwiched heterometal ions. Four such structure types are illustrated in Figure 8. The sandwiched blue atoms shown in the Figure represent the sites of potential heteroatoms M, but they may also represent one or more W^{VI} centers. Indeed the "parent" versions of structures (a), (b), and (d) in Figure 8 where all the M centers are tungsten atoms are known. Lacunary versions of structures (a) and (b) in Figure 8 also exist containing only one or two sandwiched tungsten atoms. Depending upon the identity and coordination requirements of the atoms M which may have zero, one, two, or three terminal ligands (commonly aqua or hydroxo for M = 3d metal ions and oxo for $M = W^{VI}$).

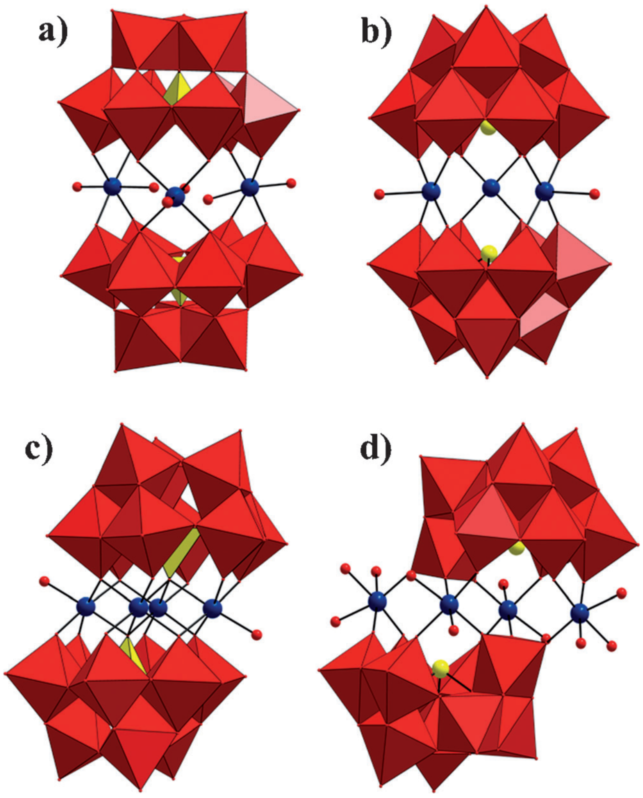

Figure 8. Combined ball-and-stick/polyhedral representation of a) $[M_3(A\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$, b) $[M_3(B\text{-}\alpha\text{-}XW_9O_{33})_2]^{n-}$, c) $[M_4(B\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$, d) $[M_4(B\text{-}\beta\text{-}XW_9O_{33})_2]^{n-}$. $\{WO_6\}$ red, $\{XO_4\}$ yellow, M blue, X yellow. Red spheres indicate the locations of terminal ligands which may not always be present. Some of the M sites may also represent W^{VI} centers or be missing (see text for details).

2.3.1. Ruthenium

Several S-structure POMs based on two *B*-type $[XW_9O_{34}]^{n-}$ tri-vacant fragments of the Keggin structure (see Figure 8c) have been reported to incorporate two or more ruthenium atoms. The first of these are the species formulated as $[WZnRu^{III}_2(OH)(H_2O)(XW_9O_{34})_2]^{11-}$ (X = Zn, Co^{II}) prepared by reaction of $[Ru(dmso)_4Cl_2]$ with an aqueous solution of $[WZn_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ at 90 °C.[78,79] These complexes, as tricaprylammonium salts, especially the cobalt-free species, were found to catalyze the hydroxylation of adamantane at the tertiary position using dioxygen at autogenous pressure.[79–81] The process was mentioned to function in a dioxygenase-like fashion incorporating both oxygen atoms of O_2 into two substrate molecules,[80] but this claim has been disputed in favor of a classical autoxidation mechanism.[82] The same POM has also been shown to catalyze various epoxidation and oxidation reactions in different media, as well as under biphasic conditions.[78,83] However, recent investigations of the complexes themselves by other research groups have revealed difficulties with the reproduction of some syntheses and activities, and have questioned the precise identity and distribution of the "sandwiched" atoms.[29b,84,85] Complexes formulated as $[Ru^{III}_4(P_2W_{15}O_{56})_2]^{12-}$ and $[Ru^{IV}_4(P_2W_{15}O_{56})_2]^{9-}$ which might be expected to have S-structures analogous to the above $\{M_4(XW_9)_2\}$ complexes have been reported, but with no convincing structural evidence.[86]

Virtually simultaneous, independent reports from three research groups describe S-structure anions based on a tetraruthenium adamantane-like core stabilized by two $\{\gamma\text{-}SiW_{10}O_{36}\}$ POM species, $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$[87,88] (Figure 9), and $[Ru^{IV}_4(\mu\text{-}O)_2(\mu\text{-}OH)_4Cl_4(\gamma\text{-}SiW_{10}O_{36})_2]^{12-}$.[89] Electrochemical studies show that the $Ru_4^{(IV,IV,IV,IV)}$ species undergoes stepwise, reversible redox and protonation/deprotonation processes to $Ru_4^{(V,V,V,V)}$ and $Ru_4^{(III,III,II,II)}$ states.[46b,88,90] The aqua derivative has been subjected to intense examination because it proved to be an active and efficient catalyst for water oxidation to dioxygen proceeding via the $Ru_4^{(V,V,V,V)}$ intermediate. Under acidic conditions with Ce^{IV} as oxidant the turnover frequency (TOF) was 450 h^{-1} with a yield of 90% with respect to the amount of oxidant.[88,90] At pH 7 using electrochemically regenerated $[Ru(bpy)_3]^{3+}$ (bpy = bipyridine) the dioxygen yield varied with the amount of catalyst present, with a maximum yield of about 75%.[87] There is considerable current research activity aimed at optimizing strategies of incorporating the Ru_4-POM into efficient devices for water oxidation and other applications.[92–95] Combining $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ with a tetranuclear Ru^{II} dendrimeric photosensitizer and $S_2O_8^{2-}$ as a sacrificial oxidant the POM showed photocatalytic activity in the visible-light region producing O_2 with a quantum yield of 30%.[93] Water splitting with an overpotential as low as 0.35 V and TOFs approaching the solution behavior was achieved by immobilization of the Ru_4-POM catalyst on the surface of a semiconductor anode based on multiwalled carbon nanotubes functionalized by polyamidoamine dendron moieties.[95a] A number of theoretical studies aimed at shedding light on the electronic properties and structural evolution of the tetraruthenium catalytic domain have also been reported.[46b,88,96,97] In addition, catalase-like activity of $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ in the decomposition of H_2O_2 to H_2O and O_2[98] and electrocatalytic activity in nitrite reduction and oxidation of different substrates has been reported.[99] The analogous anion based on the less-stable $\gamma\text{-}[PW_{10}O_{36}]^{7-}$ has been prepared and its catalytic activity examined.[100a] Very recently it was shown that two adamantane-like tetraruthenium(IV) cores $\{Ru_4O_6(H_2O)_9\}^{4+}$ can also be stabilized in the polyanions $[\{Ru^{IV}_4O_6(H_2O)_9\}_2Sb_2W_{20}O_{68}(OH)_2]^{4-}$ and $[\{Ru^{IV}_4O_6(H_2O)_9\}_2\{Fe(H_2O)_2\}_2\{\beta\text{-}TeW_9O_{33}\}_2H]^{-}$ with a topology shown in Figure 8d. One of the Ru^{IV} centers in each tetraruthenium motif is bound in an external position to the polyanion and the other three Ru^{IV} ions coordinate three terminal aqua ligands each in a highly accessible fashion, providing potential for future catalytic applications.[100b]

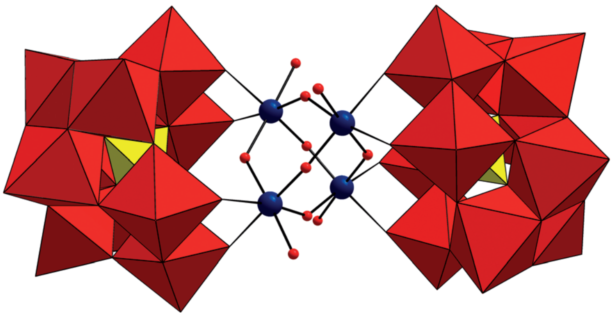

Figure 9. Combined ball-and-stick/polyhedral representation of $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$. $\{WO_6\}$ red, $\{SiO_4\}$ yellow, Ru blue, O red.

Complexes incorporating linear $Ru^{IV}\text{-}O\text{-}Ru^{IV}$ moieties sandwiched between mono-vacant lacunary anions have been characterized: $[(ClRu^{IV}ORu^{IV}Cl)(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$[25] and $[(HORu^{IV}ORu^{IV}OH)(PW_{11}O_{39})_2]^{10-}$.[101] The latter anion was shown to undergo reversible redox processes to $Ru^{III,III}$ and $Ru^{IV,V}$ derivatives, but no other activities were reported. A complex formulated as "$[(H_2ORu^{IV}ORu^{IV}OH_2)(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$" was proposed to have an analogous structure,[102] but this is unlikely given the dimensions of the polytungstate ligands, and is not supported by the experimental evidence provided.

2.3.2. *Rhodium*

Tourné et al. reported the S-structure complexes $[WM_3(H_2O)_2(MW_9O_{34})_2]^{12-}$ ($M = Zn$, Co^{II}), in which two of the sandwiched M cations could be replaced by a variety of divalent transition-metal cations including Pd^{II} and Pt^{II}.[103] Trivalent Rh and Ru derivatives were subsequently reported by Neumann et al.; the dirhodium(III) species showed high overall activity for the catalytic epoxidation of alkenes with H_2O_2.[83a,104a] Recently, Sokolov's group reported the polyanion $[\{Rh_4(\mu_3\text{-}O)_2(H_2O)_2\}(H_2W_9O_{33})_2]^{12-}$ containing a tetrarhodium(III) oxo core $\{Rh_4(\mu_3\text{-}O)_2(H_2O)_2\}$ sandwiched between two trilacunary $\{H_2W_9O_{33}\}^{10-}$ units. The polyanion is stable in aqueous solution as confirmed by ^{183}W NMR spectroscopy and shows activity in electrocatalytic water oxidation.[104b]

2.3.3. *Palladium*

Until very recently, with the exception of the structure of $[Pd^{II}_2(W_5O_{18})_2]^{8-}$ (Figure 10) reported by Angus-Dunne et al. in 1994,[105] all reported S-structure POMs containing palladium were based upon the frameworks illustrated in Figure 8a or b, but with presumed or verified square-planar coordination of the sandwiched Pd^{II} centers. In 1986 Knoth and co-workers reported the synthesis and characterization of several $[M_3(PW_9O_{34})_2]^{12-}$ complexes where M is divalent Mn,

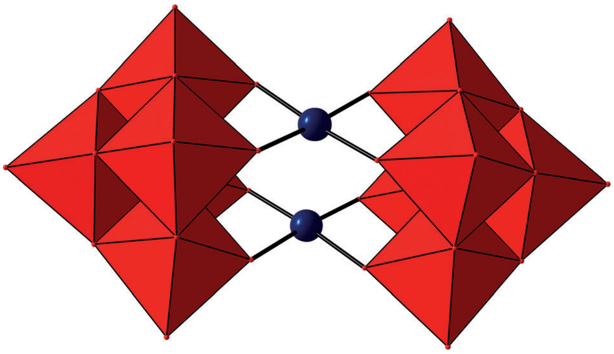

Figure 10. Combined ball-and-stick/polyhedral representation of $[Pd^{II}_2(W_5O_{18})_2]^{8-}$. $\{WO_6\}$ red, Pd blue.

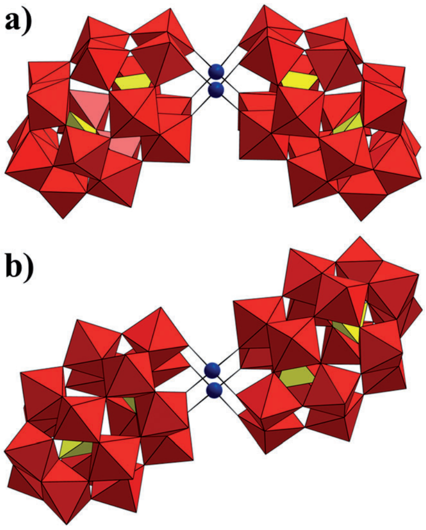

Figure 11. Combined ball-and-stick/polyhedral representation of a) *syn*- and b) *anti*-isomers of $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$. $\{WO_6\}$ red, $\{PO_4\}$ yellow, Pd blue.

Fe, Cu, Zn, and Pd, or mixtures of these. Based upon X-ray structural analysis of the Cu^{II} complex, an analogous structure was assumed for the other derivatives.[106] More recently, Detusheva et al. and later Villanneau et al. have confirmed this assumption by ^{31}P and ^{183}W NMR studies.[107,108] Villanneau et al. also reported structures of $[\{Pd_2WO(H_2O)\}(PW_9O_{34})_2]^{10-}$ and $[\{Pd(WO(H_2O))_2(PW_9O_{34})_2]^{8-}$ prepared from the corresponding lacunary $\{P_2W_{19}\}$ and $\{P_2W_{20}\}$ anions, respectively.[108] The existence of bimetallic analogues with sandwiched $\{Pd^{II}{}_2Cu^{II}\}$, $\{Pd^{II}{}_2Fe^{III}\}$, and $\{Pd^{II}Fe^{III}{}_2\}$ has been supported by NMR spectroscopy studies.[107] Other structurally characterized, related complexes are $[\{Pd_2WO(H_2O)\}(SiW_9O_{34})_2]^{12-}$,[109] $[NaPdWO(H_2O)(\alpha\text{-}AsW_9O_{33})_2]^{11-}$,[110] $[Pd_3(X^{III}W_9O_{33})_2]^{12-}$ (X = As, Sb),[110] and $[Pd_3(Te^{IV}W_9O_{33})_2]^{10-}$.[111] In addition, Detusheva et al. have reported a series of di-substituted tungstoarsenates(III) with the general formula $[M^zPd^{II}As_2W_{19}O_{67}(H_2O)_2]^{(12-z)-}$ (M = Pd^{II}, Fe^{III}, Co^{II}, Cu^{II}, Ti^{IV}, V^V) prepared by interaction of $\{As^{III}{}_2W_{19}\}$ with Pd^{II} and M^{Z+} ions in the ratio 1:1:1, but a more thorough characterization of these complexes is needed.[112] A claim that $[Pd_4(PW_9O_{34})_2]^{10-}$ (Figure 8c) is produced from the reaction of $PdCl_2$ with thermolyzed $Na_8[HPW_9O_{34}]$ (to convert it into the *B*-form) has not been confirmed and seems implausible.[113]

The application, as oxidation catalysts, of various S-structure palladium-containing POMs, has been reported, however the precise coordination environment of the Pd atoms in some of these species are not yet fully characterized.[69,78,83]

Reaction of Pd^{II} with the monovacant lacunary polytungstates $\alpha\text{-}[PW_{11}O_{39}]^{7-}$ and $\alpha_2\text{-}[P_2W_{17}O_{61}]^{10-}$ has recently been shown to lead to the S-structures $[Pd_2(PW_{11}O_{39})_2]^{10-}$ and $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_n)_2]^{(16-2n)-}$,[114] rather than incorporation of Pd^{II} into the vacancy of the POM which would result in L-structure complexes, as had been previously supposed (see Section 2.2.5).[28,58,59,62–70] Two monolacunary Keggin or Wells-Dawson units in these polyanions are linked by two square-planar coordinated Pd^{II} centers, in a fashion analogous to that observed in $[Pd_2(W_5O_{18})_2]^{8-}$.[105] The $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_n)_2]^{(16-2n)-}$ polyanion can exist as *anti* and *syn* isomers with respect to the relative orientation of the POM ligands (Figure 11). ^{31}P and ^{183}W NMR spectroscopy studies showed all three POMs to be stable in aqueous and organic media with no apparent facile *syn–anti* isomerization.

2.3.4. Platinum

Platinum-containing S-structure polyanions are represented by the not yet fully characterized, $[ZnWPt^{II}{}_2(ZnW_9O_{34})_2]^{12-}$[103] complexes mentioned above. The catalytic activity of such species in the oxidation of different organic substrates has been reported.[78,83]

2.3.5. Silver

Three S-structure complexes contain silver ions. The polyanion $[Ag_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{4-}$, isolated as a tetra-*n*-butylammonium salt, was reported by Gouzerh et al.[115] The structure is related to that of $[Pd_2(W_5O_{18})_2]^{6-}$, but with some significant differences. Whereas in the polytungstate the Pd–Pd vector is perpendicular to the PdO_4 planes, the Ag–Ag vector is tipped by 40.5 degrees from the corresponding O_4 planes. Furthermore, the Ag atoms are displaced by 0.23 Å from these planes, leading to a short Ag–Ag separation of 2.87 Å, indicative of an argentophilic interaction. A larger silver cluster, $\{Ag_4(dmso)_2\}^{4+}$ (Ag–Ag separations 2.96–3.07 Å), stabilized by two $\{\gamma\text{-}SiW_{10}O_{36}\}$ units (Figure 12) has recently been reported by Mizuno et al.[116] This polyanion was isolated as a tetrabutylammonium salt from an acetone solution and was shown to be an active catalyst for the hydrolytic oxidation of various structurally diverse silanes to the corresponding silanols.

The reported structure of a three-lobed assembly formulated as $[Bi^{III}{}_2Ag_3Na(W_3O_{10})(\alpha\text{-}Bi^{III}W_9O_{33})_3]^{19-}$, isolated as a hydrated sodium salt from prolonged boiling of a solution of $Na_9[BiW_9O_{33}]$ and $AgNO_3$ in an acetate buffer, reveals three $\{BiW_9O_{33}\}$ units surrounding a central $\{W_3O_{10}\}$ group. Three Ag^I, two Bi^{III} and one sodium countercation act as bridging cations between the three $\{BiW_9O_{33}\}$ groups. The stability and effective structure of the POM in solution was not addressed.[117]

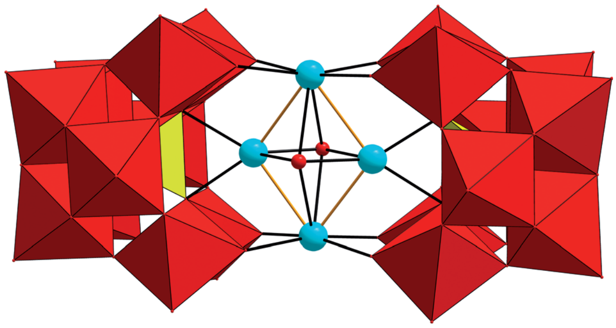

Figure 12. Combined ball-and-stick/polyhedral representation of $[Ag_4(dmso)_2(\gamma\text{-}H_2SiW_{10}O_{36})_2]^{8-}$. $\{WO_6\}$ red, $\{SiO_4\}$ yellow, Ag turquoise, oxygen atoms of dmso molecules red. S and C atoms of dmso are omitted for clarity.

2.3.6. Terminal Pd^{IV}, Pt^{IV}, and Au^{III} Oxo Complexes

We conclude our discussion of S-structures containing noble metal heteroatoms with the terminal oxo palladium, oxo platinum, and oxo gold species reported by Hill et al. Four complexes were described:

$[\{OPd^{IV}(OH)\}\{WO(OH_2)\}(PW_9O_{34})_2]^{13-}$ $\{PdP_2W_{19}\}$[118a,b]
$[\{OPt^{IV}(OH_2)\}(PW_9O_{34})_2]^{16-}$ $\{PtP_2W_{18}\}$[118c]
$[\{OAu^{III}(OH_2)\}(PW_9O_{34})_2]^{17-}$ $\{AuP_2W_{18}\}$[118d]
$[\{OAu^{III}(OH_2)\}\{WO(OH_2)\}_2(PW_9O_{34})_2]^{9-}$ $\{AuP_2W_{20}\}$[118d]

They appeared to have S-structures, based upon X-ray- and neutron-diffraction data, corresponding to that illustrated in Figure 8a. The noble metal atom was thought to occupy a quasi-octahedral coordination site (nominally local C_{4v} symmetry) with a terminal oxo ligand *trans* to hydroxo or aqua ligands. The remaining two "sandwiched" atom positions are either vacant or occupied by oxotungsten(VI). Since a six-coordinate d^6 or d^8 metal center with a terminal oxo group is unprecedented and unexpected because of the occupation of the metal's $d_{xz,yz}$ orbitals that would otherwise accept π-density from the terminal ligand, the original publications drew considerable initial interest, comments and skepticism.[74, 121] In spite of this attention there has been no subsequent confirmation of these complexes by other laboratories[74] and there have been reasons to believe that the original experimental data had been misinterpreted. For example, the Pd and Pt complexes were synthesized from divalent precursors with atmospheric oxygen, considered to be the (unlikely) oxidant, yet no direct experimental confirmation of the tetravalent state in the products was made and thus the presence of Pd^{II} and Pt^{II} as observed in analogous S-structure complexes[106–112] could not be ruled out. In contrast, several techniques (the most compelling being XANES) confirmed Au^{III} in $\{AuP_2W_{18}\}$ and $\{AuP_2W_{20}\}$, and this raised another question. Since the syntheses of these complexes introduced $AuCl_3$ as the source of gold, it poses the conundrum of understanding the source of the terminal oxo ligand (nominally O^{2-}) in the products because no reducing agent was identified. Further, recent relativistic DFT calculations predict the ^{17}O NMR chemical shifts and linewidths to differ greatly from the experimental ones attributed to the terminal gold oxo ligand.[19b] The authors have recently retracted the original papers,[119] and now report[120a] that the "Pt^{IV} and Au^{III} complexes" are just salts of the long-known 19-tungsto-2-phosphate $[\{WO(OH_2)\}\{PW_9O_{34}\}_2]^{14-}$,[120b] with crystallographically undetectable, colored Pt and Au impurities, and that the "Pd^{IV} complex" is a disordered version of the Pd^{II} derivative.[108]

2.4. F-Structures

We use this term to describe POM structures with "Sur**F**ace-attached" secondary heteroatoms. Although the majority of structures of this type involve attachment of organometallic groups and are not pertinent to this Review, there are a few inorganic examples. Among these inorganic examples we have chosen to discuss only those reports in which the secondary heteroatom(s) are attached to the POM's surface oxygen atoms by two or three bonds, as these species can be demonstrated, or at least plausibly assumed, to have some solution stability. There is as yet no convincing evidence that any of the very large reported number of crystal structures showing secondary heteroatoms ("counterions") that are attached to the POM by a single bond, survive in solution.

2.4.1. Ruthenium

In addition to the two Ru_4-containing S-structure complexes[100b] described in Section 2.3.1, which also exhibit an F-structure feature, a variety of F-structure complexes that incorporate *fac*-$\{Ru^{II}(dmso)_3\}$ or *cis*-$\{Ru^{III}(dmso)_2(H_2O)\}$ groups to known or novel POM frameworks has been described in recent years. These include:

$[Ru(dmso)_3Mo_7O_{24}]^{4-}$ [122]
$[HW_9O_{33}\{Ru(dmso)_3\}_2]^{7-}$ [123]
$[Ru(dmso)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Si, Ge)[124]
$[PW_{11}O_{39}\{Ru(dmso)_3(H_2O)\}]^{5-}$ [125]
$[\{PW_{11}O_{39}Ru(dmso)_3\}_2\{(WO_2(H_2O))_2O\}]^{8-}$ [126]
$[HXW_7O_{28}Ru(dmso)_3]^{6-}$ (X = P, As)[127]
$[\{[Ru(dmso)_3]_3PV^{V}_{11}V^{IV}Ru^{III}O_{37}(OH)_3\}_2]^{8-}$ [128]
$[Sb_2W_{20}O_{68}(dmso)_2\{Ru^{III}(dmso)_2(H_2O)\}_2]^{4-}$ [129]
$[HVW_7O_{28}Ru(dmso)_3]^{6-}$ [130]

A curious, open polyvanadate structure, $[\{[Ru(dmso)_3]_3PV^{V}_{11}V^{IV}Ru^{III}O_{37}(OH)_3\}_2]^{8-}$, formed adventitiously in low yield from a mixture of $[Ru(dmso)_4Cl_2]$, $NaVO_3$, and NaH_2PO_4, also contains an $Ru^{III}O_6$ octahedron that is strongly antiferromagnetically coupled to the adjacent V^{IV} center.[128]

2.4.2. Osmium

Osmium analogues of the F-structure ruthenium POMs $[Ru^{II}(dmso)_3Mo_7O_{24}]^{4-}$ show similar catalytic activities for the aerial oxidation of alcohols to ketones/aldehydes.[122] A similar mode of attachment of Os is observed in structures, such as $[PW_{11}O_{39}\{Os(dmso)_3(H_2O)\}]^{5-}$ [125] and

$[HAsW_7O_{28}Os(dmso)_3]^{6-}$,[131] which are structural analogues of the reported ruthenium species.

2.4.3. *Rhodium*

Reaction of dirhodium(II) tetracarboxylates with $[PW_{11}O_{39}]^{7-}$ under hydrothermal conditions generates the complexes $[PW_{11}O_{39}Rh_2(RCOO)_2L_2]^{n-}$ ($R = CH_3$, $L = dmso$, $n = 5$; $R = CH_3$, CH_2Cl, CH_2OH, C_3H_7, *o*-/*p*-C_6H_4OH, $L = Cl$, $n = 7$) shown in Figure 13.[132,133] Complexes of this type offer new methods of derivatization of polyoxoanions to give products that are also more resistant to hydrolysis at neutral pH value for bio-labeling purposes.[133] Although the rhodium acetate precursor is an efficient catalyst for cyclopropanation, the POM derivative appears to be less active in this reaction. More recent investigations have employed such derivatives, including those apparently based on the corresponding molybdophosphate, to modify solid-state electrodes for electrocatalytic oxidations.[134]

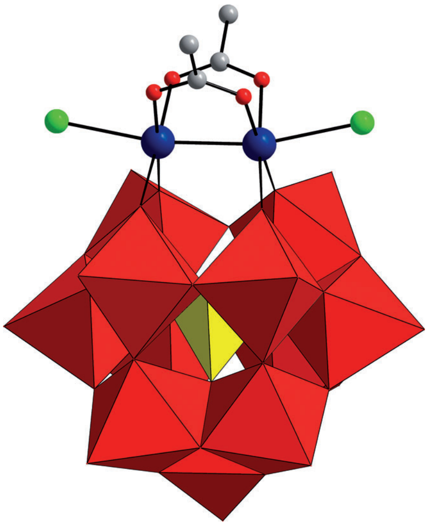

Figure 13. Combined ball-and-stick/polyhedral representation of $[PW_{11}O_{39}\{Rh_2(CH_3COO)_2Cl_2]^{7-}$. $\{WO_6\}$ red, $\{PO_4\}$ yellow, Rh blue, O red, Cl green, C gray.

2.4.4. *Iridium*

An F-structure iridium(III)-containing polytungstate has been reported by Hill et al.[135] Reaction of an aqueous solution of $IrCl_3$ with a solution of a mixture of potassium salts of α_2-$[P_2W_{17}O_{61}]^{10-}$ and WO_4^{2-} yields $[(IrCl_4)KP_2W_{20}O_{72}]^{14-}$, the structure of which is shown in Figure 14. The polyanion undergoes slow dissociation in solution, presumably to $[KP_2W_{20}O_{72}]^{13-}$ and $[IrCl_4(H_2O)_2]^-$, although the anticipated two-line ^{31}P NMR spectrum can be observed initially, as can an Ir^{III}/Ir^{IV} redox couple at +0.785 V. The complex was shown to catalyze the reduction of $[Ru(bpy)_3]^{3+}$ to $[Ru(bpy)_3]^{2+}$ with the concomitant oxidation of solvent water.

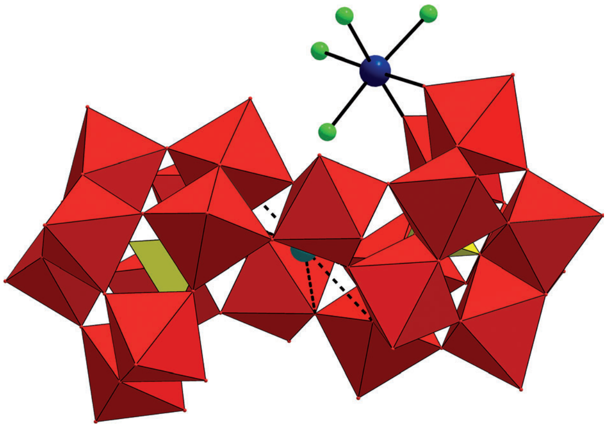

Figure 14. Combined ball-and-stick/polyhedral representation of $[(IrCl_4)KP_2W_{20}O_{72}]^{14-}$. $\{WO_6\}$ red, $\{PO_4\}$ yellow, Ir blue, Cl green, K blue-green.

2.4.5. *Platinum*

An F-structure has been proposed, based on ^1H and ^{183}W NMR spectra, for α-$[PW_{11}O_{39}\{Pt(NH_3)_2\}_2]^{3-}$ prepared by reaction of $[PW_{11}O_{39}]^{7-}$ with *cis*-$[Pt(NH_3)_2Cl_2]$ in aqueous solution.[136a] This suggestion was confirmed very recently by single-crystal XRD on $Cs_3[PW_{11}O_{39}\{cis\text{-}Pt(NH_3)_3\}]\cdot 8\,H_2O$, which demonstrated that the *cis*-$\{Pt^{II}(NH_3)_3\}$ groups are attached to the lacunary polyanion in a fashion similar to that in the S-structure polyanion $[Pd_2(PW_{11}O_{39})_2]^{10-}$ described above. The platinum-containing tungstophosphate is an active catalyst for water reduction.[136b]

2.5. *Unknown or Unconfirmed Structures*

2.5.1. *Ruthenium*

A number of reported ruthenium-containing POMs have received no structural confirmation. In some cases even a reliable formula is in doubt.

1. Reaction of both α- and β-isomers of supposed *B*-type $[SiW_9O_{34}]^{10-}$ with excess of "$RuCl_3{\cdot}n\,H_2O$" yield potassium salts of anions formulated as α- and β-$[SiW_9O_{37}\{Ru_4(H_2O)_3Cl_3\}]^{7-}$.[137a] No X-ray suitable crystals were obtained, and a structure analogous to that found for $[PW_9O_{34}(OH)_3Ni^{II}_4(H_2O)_6]^{4-}$[138] with a cubane Ni_4 cluster atop the *B*-form of the PW_9 anion was proposed.[137a] This is unlikely, as *B*-type $\{XW_9O_{34}\}$ anions, which incorporate a terminal X=O group, are known only for $X = P^V$.[139] The syntheses employed for the species with X=Si are known to yield *A*-type precursors with C_{3v} (α) and C_s (β) symmetry. In an attempt to reproduce $[B\text{-}\alpha\text{-}SiW_9O_{37}\{Ru_4(H_2O)_3Cl_3\}]^{7-}$ Patzke and co-workers isolated a polyanion formulated as $[A\text{-}\alpha\text{-}SiW_9O_{34}\{Ru^{IV}_2Ru^{III}O_3(H_2O)Cl_2\}]^{7-}$. No single-crystal XRD structure was obtained, but based on ESI-MS, IR and Raman spectroscopy, elemental analysis, and DFT calculations a $\{(Ru^{IV}Cl)_2(Ru^{III}(H_2O))O_3\}$ moiety is embedded in a trilacunary $\{A\text{-}\alpha\text{-}SiW_9O_{34}\}$ Keggin unit. The polyanion was shown to act as

a catalyst for visible-light induced photocatalytic water oxidation.[137b]

2. Incompletely characterized products of the reaction of $K[Ru^{IV}(OH)Cl_5]$ with $[PW_{11}O_{39}]^{7-}$, and subsequent electrolytic conversion into presumed Ru^{II}, Ru^{III}, and Ru^{V} derivatives have been reported. The Ru^{IV} species formed in the initial reaction with $[PW_{11}O_{39}]^{7-}$ was shown to be catalytically active in the oxidation of primary alcohols with $KClO_3$.[140]
3. A crystalline product of empirical formula $Na_4(NH_4)[RuMo_7O_{25}]\cdot 8\,H_2O$, subsequently identified as "Ru_2Mo_{14}", without convincing reasoning, has been shown to exhibit catalytic activity for alcohol oxidation with peroxides and dioxygen.[141]

2.5.2. Platinum

The earliest reports of POMs that contain platinum appeared in the late nineteenth century. Gibbs described several molybdates and tungstates with formulas such as $4\,M_2O\cdot PtO_2\cdot 10\,WO_3\cdot n\,H_2O$ (M = Na, K, NH_4) and $3\,(NH_4)_2O\cdot 2\,PtO_2\cdot 8\,MoO_3$,[142] but these are probably mixtures. Rosenheim was unable to reproduce the tungstates and instead reported a material, $5\,Na_2O\cdot 2\,PtO_2\cdot 7\,WO_3\cdot 35\,H_2O$, which he believed to be a double salt containing sodium paratungstate.[143]

3. Polyoxopalladates, -platinates, -aurates

Recently an entirely new class of polyoxoanions, in which the noble metal atoms Pd, Pt and Au act as "addenda" atoms rather than as heteroatoms, has been discovered and the number of such complexes is currently growing rapidly.

3.1. Palladium

During the past four years Kortz et al. have developed a strategy for the synthesis of water-soluble polyoxoanions constructed of square-planar coordinated d^8 metal centers (Pd^{II}, Au^{III}) by condensation of tetra-aqua/hydroxo-complexes of these metals in the presence of a heterogroup. The heterogroup terminates the condensation process allowing isolation of discrete species.

Following this approach three heteropolypalladates(II) with the general formula $[Pd^{II}_{13}O_8(LXO_3)_8]^{n-}$ ($X = As^V$, L = O, Ph; $X = Se^{IV}$, L = lone pair) were obtained by reaction of Pd^{II} salts with either As_2O_5, $PhAsO_3H_2$, or SeO_2 in aqueous solution (pH 4.8–7.5). The polyanions take the form of a distorted cube and comprise a central Pd^{II} ion surrounded by a shell of twelve Pd^{II} ions linked by eight "inner" oxo ligands and eight "outer" tetrahedral heterogroups LXO_3 (Figure 15 a).[144,145] Interestingly, the nature of the external heterogroup influences the symmetry of the $\{Pd^{II}_{12}O_8(LXO_3)_8\}$ shell and leads to unusual coordination numbers of 6 and 8 for the central Pd^{II} center in the Se^{IV} and $As^{V}Ph$ derivatives, respectively.[145]

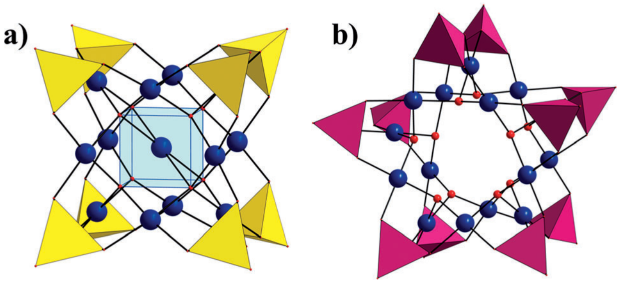

Figure 15. Combined ball-and-stick/polyhedral representation of a) $[Pd^{II}_{13}O_8(AsO_4)_2(AsO_3(OH))_6]^{8-}$ and b) $[Pd^{II}_{15}O_{10}(PO_4)_{10}]^{20-}$. $\{AsO_4\}$ yellow, $\{PO_4\}$ pink, Pd blue, O red.

The central Pd^{II} cation guest in the $\{Pd_{12}\}$ nanocuboid host can be replaced by a large range of lanthanide (Ln) and transition-metal (M) ions (Table 1), by performing the synthesis in neutral or slightly acidic solution in the presence of the respective lanthanide/transition-metal salt.[146–149] The central guest cations in all the $[MPd_{12}O_8(LXO_3)_8]^{n-}$ polyanions are octa-coordinate with perfect or slightly distorted (in the case of Cu^{II}/PO_4^{3-} and some M^{z+}/SeO_3^{2-} derivatives) cubic symmetry. However, EPR studies on $Na_9[Mn^{II}Pd^{II}_{12}P^{V}_8O_{35}(OH)_5]\cdot 32\,H_2O$ showed that the central $\{MnO_8\}$ cube, which appears to be symmetrical based on X-ray diffraction studies, is actually strongly distorted on the faster EPR time scale.[147] The Ln−O bond lengths within the inner $\{LnO_8\}$ cube follow the expected trend, decreasing from Ln = Pr to Lu, indicating the flexible nature of the $\{Pd_{12}O_8(PhAsO_3)_8\}$ shell which can adapt to the size of the encapsulated cation guest.[146] The solution stability of the diamagnetic $[MPd_{12}O_8(LXO_3)_8]^{n-}$ polyanions has been confirmed by ^{31}P or ^{77}Se NMR spectroscopy on the Se-, PhP-, and P-capped, Zn^{II}- and Lu^{III}-centered derivatives.[147,149] Mass spectrometry measurements on some of the Se^{IV}- and $PhAs^{V}$-capped POMs showed that in solution they exist as aggregates with Na countercations and protons.[148,149]

Table 1: Transition-metal- and lanthanide-centered polyoxopalladates $[MPd_{12}O_8(LXO_3)_8]^{n-}$.

LX	M	*n*	Ref.
$PhAs^{V}$	Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, Yb^{III}, Lu^{III}, Sc^{III}, Y^{III}, Fe^{III}	5	[146]
$PhAs^{V}$	Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	6	[149]
PhP^{V}	Cu^{II}, Zn^{II}	6	[149]
Se^{IV}	Fe^{III}, Lu^{III}	5	[149]
Se^{IV}	Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	6	[148,149]
OP^{V}	Fe^{III}	13	[147]
OP^{V}	Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}	14	[147]

Reaction of Pd^{II}, PO_4^{3-}, and Cu^{II} under slightly more basic conditions (pH 6.9–7.5) leads to the largest polyoxopalladate to date. The anion $[Cu^{II}_2Pd^{II}_{22}P_{12}O_{60}(OH)_8]^{20-}$ comprises two identical $\{Cu^{II}Pd^{II}_{11}P_6O_{30}(OH)_2\}$ fragments connected by four hydroxo bridges. Each $\{Cu^{II}Pd^{II}_{11}P_6O_{32}\}$ building block can be "derived" from the cubic $\{CuPd_{12}P_8\}$ structure by loss of a $\{PdP_2O_8\}$ edge. Magnetic studies of $Na_{20}[Cu^{II}_2Pd^{II}_{22}P_{12}O_{60}(OH)_8]\cdot 58\,H_2O$ showed an unexpectedly large magnetic exchange interaction ($J = -4.0(1)$ K), considering the internuclear separation of 7.4 Å between the two Cu^{II} ions.[150]

The pentagonal, star-shaped polyoxopalladate $[Pd_{15}O_{10}(PO_4)_{10}]^{20-}$[151] ($\{Pd_{15}P_{10}\}$, Figure 15 b) has been isolated from the reaction of Pd^{II} with PO_4^{3-} in the absence of any transition-metal ion (the $\{Pd_{13}O_8(PO_4)_8\}$ anion still unknown). The selenium(IV) analogue has also been prepared by reaction of $Pd(CH_3COO)_2$ and Na_2SeO_3 in CH_3CN/H_2O (5:1) followed by recrystallization of its sodium salt from water[152] or by direct self-assembly of $Pd(CH_3COO)_2$ with SeO_2 in sodium acetate buffer.[145,149]

Cronin et al. have been able to show the incorporation of two Pd^{II} ions in the inner cavity of the $\{Pd_{15}P_{10}\}$ assembly with a binding constant of approximately 1.2×10^3 to yield $[Pd^{II}_2\subset\{H_7Pd^{II}_{15}O_{10}(PO_4)_{10}\}]^{9-}$.[153] The solution stability of the star-shaped polyanion has been confirmed by ^{31}P NMR spectroscopy[151,153] and mass spectrometry.[149,152,153]

Although a conventional vanadopalladate is known (Figure 3 a),[9] reaction of $Pd(OAc)_2$ with ortho- or metavanadate in 2 M KOAc, yields the mixed-metal, bowl-shaped polyoxoanion $[Pd^{II}_7V^{V}_6O_{24}(OH)_2]^{6-}$ comprising seven square-planar $Pd^{II}O_4$, four tetrahedral $V^{V}O_4$, and two square-pyramidal $V^{V}O_5$ addenda units.[154] Temperature-dependent ^{51}V NMR spectra are consistent with the integrity of the polyanion structure in aqueous solution. DFT calculations of ^{51}V NMR chemical shifts suggest the presence of cationic ion pairs $[K_{7-x}Na_xHPd_7V_6O_{25}(OH)]^+$ ($x=0$–2) involving a relatively dense, positively charged shell of countercations surrounding the negatively charged polyanion bowl. The formation and exact composition of such assemblies were confirmed by ESI-MS measurements.[154] $Na_8[Pd_{13}As_8O_{34}(OH)_6]\cdot H_2O$ and $Na_{12}[Pd_{0.4}Na_{0.6}Pd_{15}P_{10}O_{50}H_{6.6}]\cdot 36\,H_2O$ show catalytic activity in the oxidation of alcohols by dioxygen in aqueous solution[144,151], whereas $Na_9[Fe^{III}Pd^{II}_{12}P_8O_{36}(OH)_4]\cdot 16\,H_2O$ and $Na_{10}[Cu^{II}Pd^{II}_{12}P_8O_{36}(OH)_4]\cdot 31\,H_2O$ have been shown to be precatalysts for olefin hydrogenation.[147]

3.2. Platinum

No platinum analogues of polyoxopalladates(II) have been reported to date. However, in 2004 Pley and Wickleder discovered the first POM built exclusively of d^7 noble-metal centers, prepared by a sealed-tube reaction of $Pt(NO_3)_2$ with concentrated H_2SO_4 at 350 °C, and isolated as the ammonium salt $(NH_4)_4[Pt^{III}_{12}O_8(SO_4)_{12}]$. The Pt atoms lie on the corners of an icosahedron formed by six $\{Pt_2\}^{6+}$ (Pt–Pt 2.53 Å) moieties with Pt···Pt separations of 3.45 Å between adjacent $\{Pt_2\}$ groups. Each Pt^{III} center is coordinated by five oxygen atoms (two from the oxo-groups and three from SO_4^{2-} groups).[155] The structure of a mixed cesium/potassium salt of the same polyanion has since been reported.[156] It is of some topological interest to note that the icosahedral arrangement of the Pt centers matches that of the metal centers in the conventional heteropolymolydates $[X^{IV}Mo_{12}O_{42}]^{8-}$ (X = Ce, Th, U, Np) with short and long (oxygen-bridged) Mo···Mo separations of 3.18 and 3.84 Å, respectively.[157]

3.3. Gold

Alkaline hydrolysis of $H[AuCl_4]$ followed by condensation of the resulting $[Au(OH)_4]^-$ ions in the presence of AsO_4^{3-} (under a reduction of the pH value to 5.0–7.8) resulted in the polyoxoaurate(III) $[Au^{III}_4As^{V}_4O_{20}]^{8-}$.[158a] The polyoxoaurate exhibits a tetrameric structure with four square-planar coordinate Au^{III} ions linked by four oxo and arsenate bridging ligands (Figure 16). In the solid state, two heteropoly-4-aurates(III) are linked by a belt of five Na countercations resulting in the cuboidal polyanion assembly $[(H_2O)_4(NO_3)_2Na_5Au_8As_8O_{40}]^{13-}$, reminiscent of the structure of the $[MPd^{II}_{12}O_8(LXO_3)_8]^{n-}$ species described above. Very recently the Se^{IV} analogue $[Au^{III}_4O_4(Se^{IV}O_3)_4]^{4-}$ has also been prepared.[158b] Solution ^{77}Se NMR spectroscopy and ESI-MS studies confirmed the polyanion structure in aqueous solution, but the species decomposes slowly (30% within two days) by releasing selenite.

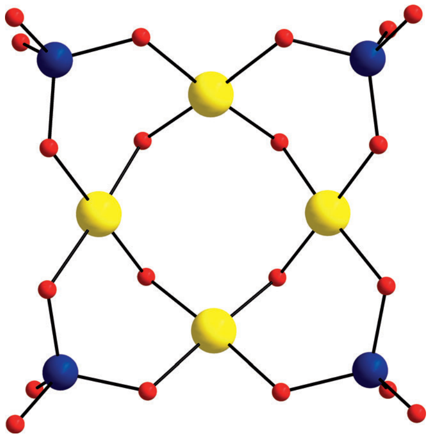

Figure 16. Ball-and-stick representation of $[Au^{III}_4O_4(AsO_4)_4]^{8-}$. Au yellow, As blue, O red.

4. Conclusion

The area of POMs containing late transition elements, the so called noble metals (ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold), has experienced significant, but variable (see Figure 1), progress within the last two decades. This development is not only due to academic interest in such compounds and the development of POM chemistry in general, but also to the widely recognized catalytic properties of noble-metal complexes.

We can distinguish three general roles of noble-metal atoms in POMs: 1) as individual isolated centers, as in $[PW_{11}O_{39}Ru^{II}(OH_2)]^{5-}$ and other L-structure anions, 2) as oligomeric clusters, as in $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, or 3) as the predominant addenda atoms with external heteroatoms, as in $[Pd^{II}_{13}As_8O_{34}(OH)_6]^{8-}$. Historically, most attention has been directed towards the first of these types of POMs with the recognition that they can be viewed as inorganic and oxidation-resistant analogues of metalloporphyrins, which can offer opportunities for catalytic applications, especially in oxidation by electron- or atom transfer. However, it must be recognized that completely unambiguous identification and structural characterization of specific POMs has always been challenging, and even with the range of sophisticated techniques available to the contemporary chemist it is still possible to draw misleading conclusions as to the nature of the active (pre)catalyst.

Undoubtedly, there are opportunities to develop this chemistry with less-studied noble metals, such as Os or Ir, and by modifying (tuning) the π-acceptor properties of the POM matrix by partial reduction, or replacement of W with Mo or V, but also the relatively recent recognition of compounds of types (2) and (3) offer other exciting possibilities. They open the question whether there might be other oxometal type (3) clusters in addition to obvious platinum or gold analogues, and to the possibility of intermediates between (2) and (3) with larger assemblies of noble-metal heteroatoms. A possible route to such larger assemblies involves large cyclic polytungstate templates, such as $[P_8W_{48}O_{184}]^{40-}$, which has been shown to incorporate as many as $20\,Cu^{II}$ and $16\,Fe^{III}$ cations.[159] We also believe that mixed-noble-metal polyanions of type (3) can be formed. In addition this class of POMs could perhaps be expanded by using multinuclear, cationic coordination complexes as central templates, around which a noble metal-oxo shell could be constructed, potentially leading to even larger assemblies than those known to date.

In summary, there are good reasons to believe that the current state of "noble metals in polyoxometalates" (as described herein) will continue to evolve, leading to expected and unexpected derivatives with fascinating structures and properties.

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