Polyoxometalate-based complexes as ligands for the study of actinide chemistry

Journal:	*Dalton Transactions*
Manuscript ID	DT-PER-08-2020-002755.R1
Article Type:	Perspective
Date Submitted by the Author:	10-Sep-2020
Complete List of Authors:	Auvray, Thomas; University of Rochester, Chemistry Matson, Ellen; University of Rochester, Chemistry

PERSPECTIVE

Polyoxometalate-based complexes as ligands for the study of actinide chemistry

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Thomas Auvray*[a] and Ellen M. Matson*[a]

The complexation of actinide cations by polyoxometalates (POMs) has been extensively studied over the past 50 years. In this perspective article, we present the rich structural diversity of actinide-POM complexes and their contribution to the extension of our knowledges of actinide chemistry, especially regarding aspect of their redox chemistry, as well as application for the capture and separation of these cations in the context of nuclear fuel remediation. These heterometallic assemblies have also proven highly valuable as model for heterogeneous systems based on actinides supported by metal oxide surfaces. In particular, activation of the An-O bond of actinyl fragments upon complexation with lacunary POMs has been reported, creating opportunities for future developments regarding the reactivity of these heterometallic assemblies.

Introduction

Fundamental investigations into the chemical and electronic interactions between actinides, their ligand frameworks, and the surrounding chemical environment, is a rich area of research with implications in catalysis, chemical separations, and waste remediation strategies.[1,2] Understanding these interactions is vital to establishing effective processes for chemical separation of actinide elements,[3] as well as implementing methods for the long-term storage of radioactive waste.[4] Furthermore, the development of well-defined, chemical uses for the long-lived radionuclides of the nuclear fuel cycle, including both the products of front-end enrichment processes (e.g. ^{238}U), and the back-end spent fuels (e.g. ^{239}Pu), provides incentives for reprocessing these waste streams.[5]

An important step in the advancements of our understanding of the chemistry of actinides has been the identification of ligands specifically designed to accommodate the broad range of oxidation states, high coordination numbers, and variable coordination geometry of actinides cations. First, the challenging separation of the different actinides from other cations requires the use of highly selective ligands which are now used to chelate actinides in environmental and biological contexts, with defined specification for the development of potential new chelating agents.[2,6,7] The extensive investigation of organoactinides, starting with $[U(\mu^5\text{-}C_5H_5)_3Cl]$ reported in the 1950's,[8] have provided invaluable insight into the covalency of actinide-ligand bond.[9,10] These compounds have also being shown to be capable catalysts for numerous been transformations.[11-14] In this context, ligands have also been shown to be involved in the reactivity, by stabilizing key intermediates,[15] and accommodate change in oxidation state during the chemical or photochemical processes.[16,17]

A class of compounds that have proven interesting as ligands for actinide cations are polyoxometalates (POMs).[18] These anionic oxo-clusters, based predominantly on tungsten(VI), molybdenum(VI) and vanadium(V), have been studied for almost two centuries.[19,20] The general structure of POMs can be described by $\{MO_6\}$ octahedra connected through bridging oxo (O^{2-}) ligands via shared vertices, edges or faces (Figure 1) forming a scaffold stable at high temperatures.[21,22] These clusters have been shown to form coordination complexes with transition metals,[25,26] lanthanides[27] and actinides.[28] The latter exhibit mainly electrostatic interactions with their ligands, a situation where the high negative charge of polyoxoanions is beneficial for the formation of robust compounds.

---

[a] University of Rochester, Department of Chemistry, Rochester NY 14627 USA

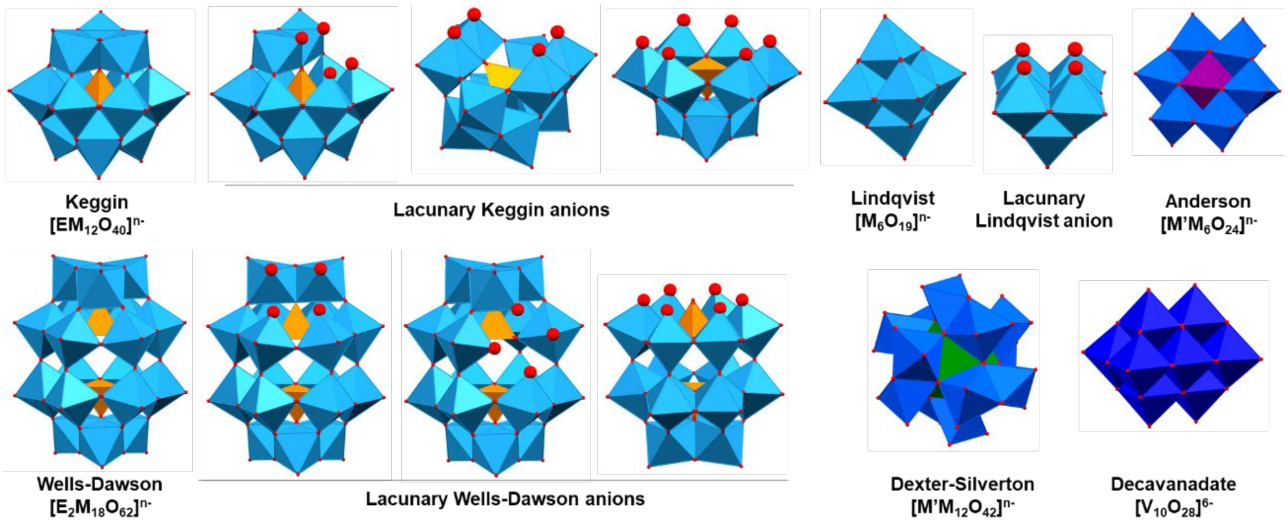


Figure 1. Polyhedral representation of selected examples of plenary and lacunary polyoxometalates. The vacant site(s) in lacunary structures are highlighted by spherical oxygen atoms.

It is important to note that polyoxometalate-based actinide complexes are members of the large family of actinide oxoclusters. While several classes of compounds will be discussed in this perspective, we chose not to discuss the rapidly extending chemistry of uranyl (per)oxide capsules, and related species, that emerged in 2005. We refer interested readers to the recent review from Nyman and Burns.[29] Additionally, we will not consider structures in which the actinide cation is trapped within the cluster, that is the Dexter-Silverton type clusters[30] (Figure 1) and the cryptant-like structures such as the Preyssler anion $[ZP_5W_{30}O_{110}]^{n-}$ (Z = encapsulated actinide ion).[31] While the latter have been extensively studied, the harsh synthetic conditions required to replace the native Na^+ encapsulated within the cluster by other cations such as actinides limits the scope of their potential applications.[32,33] More information on these can be found in the recent review by Loiseau *et al.* dealing with the incorporation of actinide ions into polyoxometalate frameworks.[34]

In the following pages, an overview of work describing the potential of polyoxometalate-based complexes as a platforms for the study of actinide chemistry will be presented. We will first discuss the strength of binding of actinide cations by both plenary and lacunary POMs. Next, extensive electrochemical investigations conducted on mononuclear An-POM complexes will be summarized, highlighting the stabilization of low-valent actinides in aqueous media and its application in several steps of the nuclear fuel cycle. Next, we describe the potential use of polyoxometalate-supported organoactinide complexes as model for both homogenous and heterogenized organoactinides catalysts. Investigations of the An-O bond activation in actinyl subunits following coordination of these thermodynamically robust fragments to the polyoxoanions are then presented. Finally, the opportunities brought to light by this overview of the state of the art of polyoxometalate-based actinides complexes are discussed, in an effort to kindle the future development of these molecular assemblies.

Nature of Interactions Between POMs and An^{n+}

Coordination Chemistry of Actinide Ions to Plenary POMs

Establishing the thermodynamic parameters of the interactions of actinide ions with metal oxides is of critical importance, as their interactions with MO_x particles in clay is regarded as an important parameter for understanding their mobility in the environment.[35,36] Motivated by the structural similarities between POMs and metal oxides, Choppin and coworkers have studied the interactions of these clusters in aqueous solution with various cations, including actinides.[37-40]

Early work focused on the interactions between plenary POMs such as the Keggin and Wells-Dawson anions, and cations present in repository sites (e.g. Ca^{2+}, Eu^{3+}, Th^{4+} and $\{UO_2\}^{2+}$). The authors established the following trend in binding strength: $Th^{4+} > Eu^{3+} > \{UO_2\}^{2+} \geq Ca^{2+}$, indicating that interactions between these cations and plenary metal oxide clusters are predominantly electrostatic in nature (i.e. cations possessing higher charge possess a stronger binding constant to the surface of the metal oxide cluster).

In the absence of crystallographic data, Choppin and coworkers proposed potential coordination sites for actinide cations on the plenary polyoxoanions based on work of Klemperer *et al.* (these results describe the protonation sites of the decavanadate anion).[41,42] These seminal studies revealed that in polyoxovanadate clusters the most basic oxygen atoms, i.e. the most likely coordination sites, are those that bridge between constituting cations. Thus, coordination of actinide ions to these basic bridging oxygen atoms in plenary Keggin, Wells-Dawson and decavanadate anions was proposed (Figure 2). Notably, these suggested coordination sites support the observation that $\{UO_2\}^{2+}$ binds less efficiently than Eu^{3+}, but similarly to Ca^{2+}, despite the higher effective charge of the uranium centre in $\{UO_2\}^{2+}$ (+3.2); the steric hindrance of the trans located oxo ligands inhibits the coordination of the uranyl moiety to the surface of polyoxoanions (Figure 2, bottom).

Table 1. Selected stability constants in aqueous media for actinide or lanthanide POM-based complexes.

	$[P_2W_{18}O_{62}]^{6-}$	$[P_2W_{17}O_{61}]^{10-}$ $\log\beta_2$	HOPO* $\log\beta_1$
Th^{4+}	$\log\beta_1$ 11.3 [a] $\log\beta_2$ 17.8 [a]	30.2 [b]	40.1 [c]
U^{4+}	--	33.3 [b]	40 [c]
Np^{4+}	--	35.0 [b]	40 [c]
Pu^{4+}	--	> 36.3 [b]	> 41.5 [c]
Am^{3+}	--	21.9 [b]	--
Am^{4+}	--	41.7 [b]	--
Ce^{3+}	--	17.3 [b]	17.4 [c]
Ce^{4+}	--	37.4 [b]	41.5 [c]
$\{UO_2\}^2$	$\log\beta_1$ 2.21 [a]	$\log\beta_1$ 3.9 [d]	--

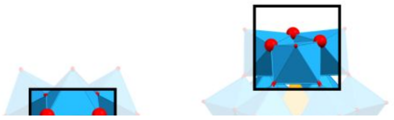
* HOPO stands for 3,4,3-LI(1,2,-HOPO); $\log\beta_1$ for An + L = [AnL], $\log\beta_2$ for An + 2L = $[AnL_2]$; a) ref. 37, b) ref. 56, c) ref. 57, d) ref. 47

Coordination Chemistry of Actinide Ions to Lacunary POMs

A common strategy for the generation of metal-functionalized POM derivatives involves the formation of metastable lacunary species prepared by controlled hydrolysis of the plenary polyoxoanion (Figure 1).[43-45] These vacancy-containing Keggin and Wells-Dawson polyoxoanions are easily prepared by addition of base to an aqueous solution of the parent species, resulting in the loss of one or more {M=O} fragment(s) (M= Mo, W). In the case of monolacunary polyoxoanions, numerous studies have shown that the vacant site can be filled by other cations, with reported examples including most transition metals, as well as multiple elements of the *p*-block.[46] Coordination of these cations to the vacant site is favored by the preorganization of the oxygen atoms and the comparable ionic radii of these cations to that of tungsten. More importantly, lacunary clusters bind more strongly with cations due to the increased basicity of the exposed oxygen atoms (pKa = 4 for the protonated monolacunary cluster *vs.* 1 for the protonated plenary species, in water).[40] The increased basicity of the lacunary variants is credited to the higher negative charge following the loss of a positively charged $\{M=O\}^{4+}$ fragment.

Despite an increased basicity in the case of lacunary POMs, the complexes formed following coordination of high-valent actinide cations to these vacancy-containing polyoxoanions have only slightly higher stability constants than those reported for the actinide-bound plenary species (Table 1).[47] In both cases, the interaction with the polyoxoanion are limited by the high steric demand of the actinyl fragment, $\{AnO_2\}^{n+}$, which restrains ligands within the equatorial plane of the pentagonal-bipyramidal coordination environment. It was proposed that the actinide cation is thus only interacting with two of the oxygen atoms of the vacant site within the lacunary assembly.[47] This was confirmed in 2011 by Sokolova *et al.* who reported the structure of $[K(UO_2)(H_2O)(SiW_{11}O_{39})_2]^{13+}$, the sole structural example of actinyl fragment bound to a monovacant POM.[48]

In contrast to the sterically demanding actinyl cations, tri- and tetravalent actinides form highly stable complexes with monolacunary polyoxoanions, with a 2:1 composition based on solution studies (Figure 3). In this case, the increased basicity of the ligand results in higher binding constants, as expected due to electrostatic nature of the An-O bond in these assemblies.



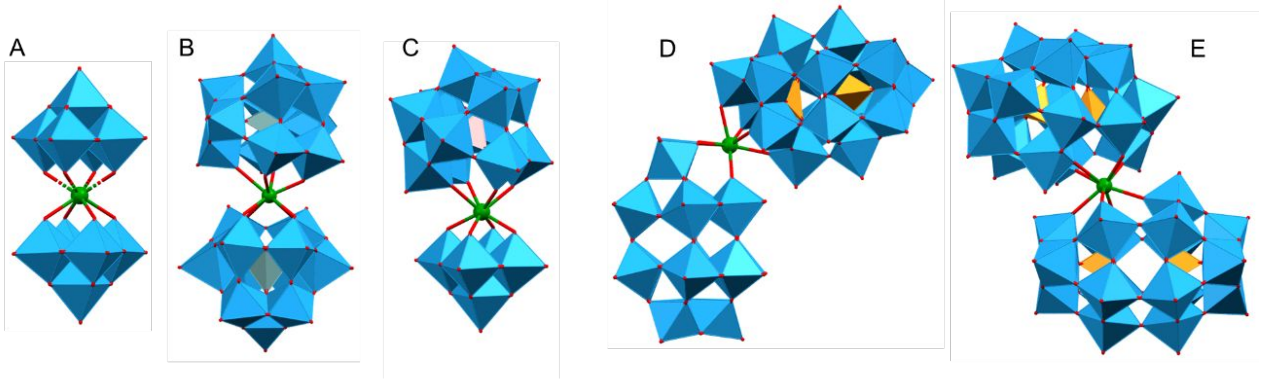


Figure 3. Structures of selected examples of actinide complexes based on monolacunry polyoxoanions. A) Lindqvist $[M_5O_{18}]^{n}$; B) Keggin, $[EM_{11}O_{39}]^{n-}$; C) Keggin and Lindqvist, D) Wells-Dawson a2-$[E_2M_{17}O_{61}]^{n-}$ and E) Wells-Dawson a1-$[E_2M_{17}O_{61}]^{n-}$. Actinide cations are designated as a green sphere.

The increased strength of these interactions can be seen in Table 1, with Th^{4+} having binding constants to the monolacunary, Wells-Dawson polyoxotungstate, $[P_2W_{17}O_{61}]^{10-}$, almost twice that of those reported for the corresponding plenary anion, $[P_2W_{18}O_{62}]^{6-}$. Similarly, an important increase in stability is observed for tetravalent cations in comparison to their to trivalent congeners (e.g. $\log\beta_2$ Am(III) = 21.9 *vs.* $\log\beta_2$ Am(IV) = 41,7). This observation is in agreement with the proposed electrostatic nature of the actinide-POM interactions.

The formation of 2:1 species is explained by the larger ionic radii of lanthanides and actinides compared to tungsten (W(VI) = 0.6 Å, Ce(IV) = 0.97 Å, U(IV) = 1.0 Å)[49], preventing these large cations to replace tungsten in the vacant site as observed in the case of transition metals. It was first documented by Weakley *et al.* studying the complexation of lanthanides by monovacant POMs.[50,51] This led to the identification of the Weakley-Peacock structures, in which two monovacant polyoxoanions (Keggin $[EW_{11}O_{39}]^{n-}$, Wells-Dawson $[E_2W_{17}O_{61}]^{n-}$ or Lindqvist $[W_5O_{18}]^{n-}$ anions; with E = Si, P, As,…) are coordinating to the lanthanide cation in a sandwich-like configuration (Figure 3). Later, isostructural complexes were identified by Tourné *et al*. for the actinide series, with the first structurally characterized actinide-containing Weakley-Peacock complex, $Cs_{12}[U(GeW_{11}O_{39})_2]$.[52,53] While broadly speaking, the isolation of homoleptic complexes, i.e. actinide cations with two identical polyoxoanions bound as ligands, are prevalent, several example of mixed-anion systems (i.e. heteroleptic complexes), have been reported as well (Figure 3).[54,55] In all cases, the actinide ions of this class of compounds possess a square antiprismatic coordination environment.

The occupancy of *5f*-orbitals with electron density in low-valent actinides translates to opportunities for covalent interactions between monovacant polyoxometalate ligands and reduced actinide centres. In support of the existence of covalency between actinide centres and their POM ligands, Yusov and coworkers reported that late actinides, such as Am or Cm, possess a slightly higher stability constant than lanthanide cations with the monolacunary Wells-Dawson $[P_2W_{17}O_{61}]^{10-}$ cluster ($\log\beta_2$ Am^{3+} = 21.85, $\log\beta_2$ Tb^{3+} = 18.72; Table 1).[56] Since these cations have the same charge and similar ionic radii (Am^{3+} = 1.09 Å, Tb^{3+} = 1.04)[49], the difference in binding affinity cannot be attributed to solely electrostatic effects. Thus, the authors conclude that the Am-O bonds formed upon complexation of the reduced actinide centre to the POM-derived ligand, must have some covalent interactions with the metal oxide assembly, though the bond remains predominantly electrostatic in nature.[56]

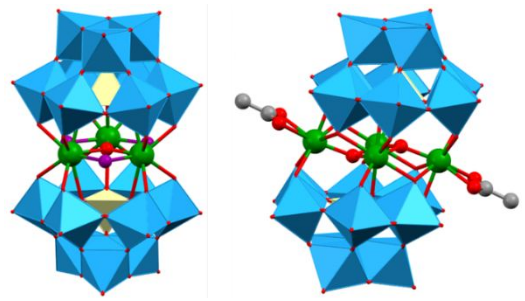


Figure 4. Polyhedral representation of tetravalent actinide complexes prepared using trilacunary Keggin anions (green: Th (left) U (right); purple sphere: μ^2-OH; red sphere: O; grey sphere: C; blue octahedron: W; yellow tetrahedron: Si).[54]

The binding constants determined for monolacunary polyoxoanions and low-valent actinide ions are comparable to those obtained with 3,4,3-LI(1,2-HOPO), an octadentate hydroxypyridinone ligand intensively studied as a promising agent for biological chelation and separation of radionuclides.[6,57] The similarity in binding strength, while determined in different pH conditions, attests to the efficient chelation of actinide cations by lacunary POMs.

Duval *et al.* have recently extended the coordination of tetravalent cations to trilacunary Keggin anions (Figure 4), investigating the complexes formed by Ce(IV), Th(IV), U(IV) and Hf(IV) with $[SiW_9O_{34}]^{10-}$.[58] The Th(IV) complex, $[Th_3(\mu^3\text{-}O)(\mu^2\text{-}OH)_3(SiW_9O_{34})_2]^{13-}$ (Figure 4, left), possesses a trinuclear core capped by two trilacunary polyoxoanions. It is similar to the Hf(IV) complex, except for the additional $\{\mu^3\text{-}O\}$ connecting the three thorium centres. Interestingly, Ce(IV) and U(IV) form similar species, namely $[M_4(\mu^3\text{-}O)_2(SiW_9O_{34})_2(CH_3COO)_2]^{10-}$ (M= Ce, U), with a tetrameric unit capped by two acetate ligands (Figure 4, right). These polyactinide complexes are of interest for the exploration of potential cooperativity between the actinide centres and POM ligands, namely via delocalized electron density between the *5f*-element and metal oxide assembly.

Electrochemical Investigations of Mononuclear AnPOM Complexes

Because the mobility of actinide cations in the environment is directly related to their oxidation state, it is crucial to understand how interactions with minerals affect the redox properties of the *5f*-elements.[16,35,36] In this context, the mononuclear actinide-POM complexes described in the previous section constitute attractive models to investigate the impact of the interactions between soluble molecular oxides and actinide cations on their redox properties. Actinide-functionalized Wells-Dawson anions, in particular, have been extensively investigated.[53,59,60]

There are two possible isomers for these monovacant polyoxoanions, referred to as α_1 and α_2, corresponding to removal of a metal centre either from one of the central belts (Figure 2E), or alternatively from one of the caps (Figure 2D), the latter being more stable. Three reduction events are observed for $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, each involving two electrons.[53,61] Of note is the fact that upon reduction, the solution of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ will develop a blue colour due to the broad intervalence charge transfer bands ($W^V(d) \rightarrow W^{VI}(d)$) characteristic of some reduced polyoxoanions, known as heteropolyblues.[62]

The redox behavior of the complexes of general formula $[An^z(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{z-20}$ has been explored in aqueous media.[59,60,63] In this work, comparison of the potential for the An(IV)/(III) couple in the aquo and Wells-Dawson complexes shows that coordination of actinide cations to α_2-$[P_2W_{17}O_{61}]^{10-}$ shifts these potentials by ≈ -1 V (Table 2). As a result, low-valent oxidation states of the actinide centre are stabilized in these

Table 2. Selected redox potentials of actinide cations with H_2O or $[P_2W_{17}O_{61}]^{10-}$ as ligands. Data compiled by Soderholm *et al.*[60] All potentials were determined in aqueous conditions and are reported in V *vs.* Ag/AgCl. Potentials in parentheses are estimated, as no experimental value is available.

	$[An^z(H_2O)_n]^z$ $E(An^{IV}/An^{III})$	$[An^z(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{z-20}$ $E(An^{IV}/An^{III})$
U	-0.77	(-1.73)
Np	-0.04	-0.84
Pu	+0.81	-0.12
Am	(+2.4)	+1.21
Cm	(+2.8)	(+1.9)
Bk	+1.47	+0.44
Cf	(+3.1)	(+2.0)

complexes; for example, early actinides (Th, U, Np, Pu) are stabilized in their tetravalent state while Am and subsequent actinide elements are isolated in their trivalent form. Of note is the case of americium and berkelium whose oxidation to the tetravalent state become accessible in water following coordination to the metal oxide cluster (e.g. 1.21 and 0.44 as opposed to 2.4 (estimated) and 1.47 V *vs.* Ag/AgCl for the respective aquo species).

More recently, Soderholm *et al.* re-examined the electrochemistry of these actinide-functionalized Wells-Dawson assemblies, with a focus on the potential hybridization between localized 5*f* states of the actinide and W-O band states of the polyoxoanions (Table 3).[59] To this end, the authors compared the redox profile of the free ligand $[P_2W_{17}O_{61}]^{10-}$ with those of several actinide complexes. The potentials were determined in aqueous solution (pH 3.5 using a 2:1 v/v mix of 0.5 M CH_3COOLi / 1M $HClO_4$) by cyclic voltammetry. Looking at the electrochemical data collected for the various $[An^z(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{z-20}$ complexes, it appears that the coordination of the actinide cation affects the POM-based reduction processes, with shifts up to ± 0.2 V, and in some cases, the appearance of additional redox processes.

Based on the linear correlation between An-O bond lengths and the potential of the first reduction, Soderholm *et al.* proposed these variations to be related to dipolar interactions.[59] For example. in the thorium complex, $[Th(IV)(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$, a fourth reduction is observed between -0.26 and -0.70 V *vs.* Ag/AgCl (by comparison, the monovacant POM precursor only possesses three reduction events). Since Th(IV) has no electroactivity in the potential window of the study, the fourth wave is attributed to the reduction of an additional W(VI) centre in the polyoxoanion. Thus, coordination of the actinide centre to the monolacunary Wells-Dawson ion results in increased reductive stability of the tungsten oxide scaffold.

Unlike thorium, uranium is known to have rich electrochemistry in water.[64] An oxidation process is indeed observed in the case of $[U(IV)(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$, at 0.55 V *vs.* Ag/AgCl, attributed to the U(V)/(IV) couple. However, attempt to use bulk electrolysis to prepare the U(V) species resulted in degradation of the sample, as indicated by the observation of the signatures for $\{UO_2\}^{2+}$ (formed by disproportionation of U(V) species) and free $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ in the cyclic voltammogram. Similar observations had been reported by Pope *et al.* studying the complex based on monovacant Keggin phosphotungstate, $[U(IV)(PW_{11}O_{39})_2]^{10-}$, with a similar oxidation potential for the U(V)/(IV) couple.[65]

On the other hand, the plutonium and neptunium complexes were expected to present an additional reduction corresponding to the An(IV)/(III) redox couple overlapping with the redox processes of the polyoxoanions. These reductions were observed at -0.84 and -0.12 V *vs.* Ag/AgCl, for the Np(IV) and Pu(IV) complexes, respectively. Because the intervalence charge transfer bands of the reduced polyoxoanions masked the spectral signature of the reduced actinides, the authors studied the electronic structure of the actinide centre by An L3-edge XANES. Integration of the data allowed for determination of the formal redox potential for the Np(IV). More importantly, the number of electrons injected were extracted from Nernst plots and indicated that less than one electron was involved in the reduction of Pu(IV) to Pu(III), which coincidently takes place at a similar potential to the first W(VI) centred reduction, suggesting the existence of some (albeit limited) delocalization into the Pu-W states involving the two tungsten centres adjacent to the vacant cap of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$.

Electrochemical investigations of POM-based complexes of low-valent actinides have proven highly valuable for the study of their electronic structure. Furthermore, these reports have revealed the existence of some degree of electronic delocalization between 5*f* orbitals and POM-based orbitals, specifically in the case of Pu(IV). These studies have also demonstrated the potential of monolacunary polyoxoanions to stabilize early actinides (e.g. U, Np and Pu) in their tetravalent state, unusual in oxygenated aqueous solutions.[64] The possibility to oxidize Am(III) to Am(IV) in water in the presence

Table 3. Redox potentials of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and related actinide complexes determined in aqueous solution (pH 3.5 using a 2:1 v/v mixture of 0.5 M CH_3COOLi / 1 M $HClO_4$). Potentials are reported in V *vs.* Ag/AgCl (nr : non reversible, * determined using XANES spectroelectrochemistry)[55]

	Oxidation	Reduction				
$[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$	--	-0.28	-0.51	-0.71 (nr)	--	--
$[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$	--	-0.26	-0.42	-0.59	-0.70 (nr)	--
$[U(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$	+0.55	-0.45	-0.60	-0.82	--	--
$[Np(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$	--	-0.15	-0.33	-0.49	-0.65 (nr)	-0.84 *
$[Pu(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$	--	-0.12	-0.26	-0.36	-0.61 (nr)	--
$[Am(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$	+1.21	-0.44	-0.56	-0.67 (nr)	-0.85 (nr)	

of monolacunary POMs was applied for the separation of Am from Cm in the SESAME process.[66] Similarly, the strong binding of berkelium by $[P_2W_{17}O_{61}]^{10-}$, coupled to the stabilization of its tetravalent state, was applied in its isolation as Bk(IV).[67] In a more analytical approach, stabilization of U(IV) by complexation with monovacant Wells-Dawson anions has been used in off-line analysis of U(IV) in the U/Pu separation step of the PUREX process.[68]

Modelling An^{n+} Chemistry on MO_x Surfaces

The development of chemical environments capable of supporting multielectron redox reactions across actinide ions has been identified as a principle challenge for controlling the homo- and heterogeneous reactivity of these elements. However, examples of *catalysis* with homogeneous actinide-based systems are limited, presumably due to the inability of these molecular species to “turn-over” under relevant reaction conditions. Although the activation of energy-poor substrates by low-valent actinides is supported by the large thermodynamic driving force of accessing higher oxidation states in these elements, subsequent re-entry into the catalytic cycle is too energetically demanding for the molecular examples reported to date. In contrast, few examples of multielectron, catalytic small molecule activation processes by heterogenous actinide-derived materials have been reported.[69] Since the 1920s, uranium oxides have been cited in heterogeneous catalysis as active surfaces for multielectron transformations, such as the oxidation of hydrocarbons[70,71], the oxidative degradation of chlorinated organic substrates[71-73] and the activation of NO_x[74,75]. Since that time, researchers have noted that *doping* common metal-oxide systems with small amounts of actinides can result in improved chemical activity, as in the example of the hydrocracking of shale oil (UO_3/Al_2O_3, $UO_3/CoMoO_4$),[76] the ammoxidation of propylene to acrylonitrile (USb_xO_y),[77,78] and the production of chlorine (U_3O_8/ZrO_2)[79]. Furthermore, some recent studies touting surface analysis and theoretical investigations of actinide-doped metal-oxide materials have concluded that atomically disperse UO_x moieties are the catalytically-active sites in these systems.[79]

The ability of single actinide atoms to engage in multielectron catalysis, when supported on a metal-oxide surface, suggests that the chemical environment imparted to 5*f*-elements by their solid-state supports yields conditions that favour catalytic turn-over. Given the established electronic consequences of heterometal (e.g. transition metals, lanthanides) doping on metal-oxide supports,[80-82] the observations of distinct reactivity with atomically-disperse actinide ions on similar materials has prompted investigation into the extent of electronic communication between these elements and metal-oxide surfaces.

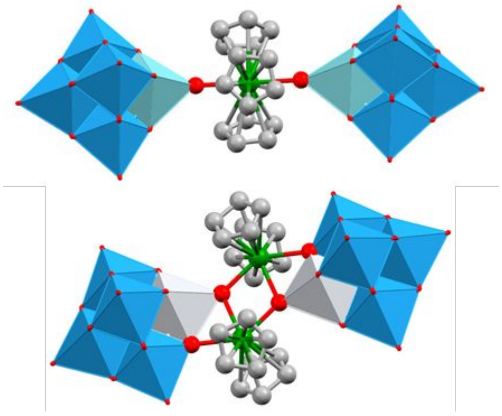


Figure 5. Structure of the complexes based on uranium cyclopentadienyl moieties supported by substituted Lindqvist anions reported by Klemperer *et al.*[86-87] Hydrogen atoms, counter-cations and co-crystallized solvents have been omitted for clarify (green: U; red: O; grey sphere: C; grey octahedron: Ti; cyan octahedron: Nd; blue octahedron: W).

However, the characterization of the local chemical environment of *5f*-elements supported by metal oxides remains challenging and require the development of model systems such as actinide-polyoxometalate assemblies. The studies presented hereafter illustrate their attractivity as model platforms for 1) the characterization of heterogenized organoactinide species, and 2) the reactivity of actinyl unit supported on metal oxide surfaces.

POM-supported Organoactinide Complexes

A common approach for the development of industrially relevant catalytic systems is the preparation of metal oxide-supported organometallic systems, as it combines the easier processability of the active species with the well-understood reactivity of homogeneous species.[83,84] Surprisingly, despite the rich scope of chemical transformations driven by organoactinide complexes,[11-13] the investigations by Marks *et al.* of the change in reactivity of thorium and uranyl cyclopentadienyl complexes on alumina and/or silica constitute the only example of organoactinide complexes supported by metal oxide.[85,86] Their study stressed the importance of characterizing the isolated active sites to establish structure-properties relationships and to inform the development of more efficient heterogenized catalytic systems. Polyoxometalate-supported organometallic complexes have been extensively investigated as models of the metal-oxide environment for various organometallic moieties, in particular cyclopentadienyl and carbonyl transition metal complexes.[26,87-89] The combination of their well-defined structure that mimics that of metal oxide surface and their tunable solubility, via the nature of the counter cations, makes polyoxoanions attractive for this application.

Regarding polyoxometalate-supported organoactinide complexes, the only examples in the literature were investigated by Klemperer and coworkers.[90,91] They first prepared 2:1 complexes based on Nb(V) or Ta(V) mono-substituted Lindqvist polyoxotungstates, $[MW_5O_{19}]^{3-}$, binding to a $\{Cp_3An\}^+$ unit (An = U^{4+}, Th^{4+}) via the terminal oxo connected to Nb or Ta (Figure 5, top). In these compounds, the actinide cation adopts a sterically encumbered trigonal bipyramidal coordination environment. The structurally resolved binding differs from related transition metal species like $[Cp^*Rh(Nb_2W_4O_{19})]^{2-}$ which exhibits a complex mixture of permutational isomers involving bonding to the terminals oxo attached to either Nb or W atoms.

However, ^{1}H NMR analysis on the diamagnetic Th(IV) species showed that the Th-O bond are labile in solution, based on the observation of the formation of an acetonitrile adduct, $[Cp_3Th(MW_5O_{19})(NCMe)]^{2-}$, along with one equivalent of free polyoxoanion within a few hours. Besides, a nitromethane solution containing a 1:1 ratio of $[Cp_3Th(NbW_5O_{19})_2]^{5-}$ and $[Cp_3Th(TaW_5O_{19})_2]^{5-}$ evolves to a statistical mixture of 3 species in a 1:1:2 ratio, the third species being the heteroleptic complex $[Cp_3Th(NbW_5O_{19})(TaW_5O_{19})]^{5-}$.

Rationalizing these observations by the steric hindrance around the actinide and the low basicity of the terminal oxo in $[MW_5O_{19}]^{3-}$ (M = Nb, Ta), Klemperer *et al*. turned to another polyoxoanion: $[ClTiW_5O_{18}]^{3-}$. The use of Ti(IV) instead of Nb(V) leads to an increase of the negative charge of the cluster, making its oxygen atoms more basic (*vide supra*).[90] However, instead of the anticipated complex, $[Cp_3U(ClTiW_5O_{18})]^{2-}$, with the polyanion behaving as a tridentate ligand, they obtained a binuclear complex, $[\{Cp_2U(TiW_5O_{19})\}_2]^{4-}$, where each U^{4+} cation lost a Cp ligand while the chlorides were replaced by μ^3-O^{2-} ligands bridging between the Ti centre and both $\{UCp_2\}$ unit (Figure 5, bottom). The coordination sphere of the U(IV) centre is completed by one of the cluster's bridging oxo ligand, resulting in each polyoxoanion acting as bidentate ligand to one $\{UCp_2\}$ unit and monodentate to the other.

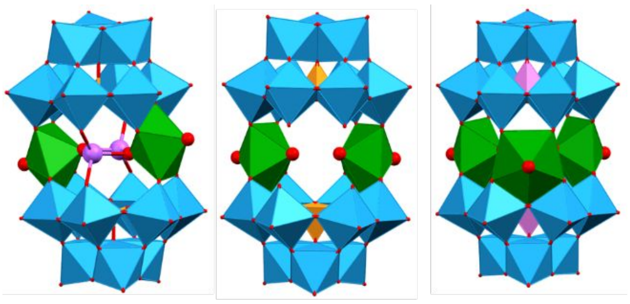
Interestingly, the bonding pattern in $[\{Cp_2U(TiW_5O_{19})\}_2]^{4-}$ is an analog to that observed for organoactinides on alumina.[85] However, in the case of the POM-bound organoactinide species, due to the increased basicity of the oxygen atoms, this binuclear compound appears to be more stable: it is not readily attack by weak nucleophiles such as acetonitrile, ethanol or even water. The enhanced stability is also attributed to the protection offered by the steric bulk of the POM which restricts access to the uranium cation. The extent of that stabilization is however limited, as the compound rapidly decomposes in the presence of stronger nucleophiles such as hydroxide anion or diethylamine. The proposed degradation mechanism involves structural rearrangement, as these reagents could not reach the uranium centre otherwise.[90] Unfortunately, no further reactivity studies were conducted, as comparison to the performance of the system reported by Marks *et al.* would have provided important insight in the potential application of polyoxometalate-supported organoactinide assemblies.

An-O Bond Activation upon Coordination to POMs

Uranium, neptunium and plutonium are commonly found as actinyl cations $\{AnO_2\}^{n+}$ in the environment.[35] These species are thermodynamically stable owing to strongly covalent An-O bonds and were long thought to be resistant to any chemical functionalization in the laboratory until the report of Arnold *et al.* of the reductive silylation of uranyl.[92] Interestingly, these high valent species are commonly reduced to tetravalent species in the environment via microbial processes or in the presence of Fe^{2+} containing minerals.[35] As a result, investigation of the activation of these inert oxo groups is of great academic interest, especially since its initial lack of reactivity contrasts with its transition metal analogues.[93] As a result, the (reductive) functionalization of these An-O bonds, especially in the case of uranyl, is an active field of research within the overall development of actinide chemistry.[93-95] In these studies, structural and spectroscopic measurements are extensively used to access information regarding the bonding within the actinyl ion.

Previously discussed examples of POM-based actinyl complexes were characterized by the weak interaction between actinyl and the plenary or monolacunary polyoxoanion, making the possibility for An-O bond activation unlikely. In contrast, several well-defined polyactinyl complexes based on trivacant Keggin anion have been reported.[96] Pope and coworkers initially summarized the formation of these uranyl complexes while May and coworkers extended this family of compounds by preparing the neptunyl and plutonyl analogs.[97-99] Interestingly, these complexes exhibit a cation-directed structure change, resulting in the different structures presented in Figure 6 depending on the counter cations present in the synthetic media. In all cases, the actinide cations have the typical pentagonal-bipyramidal geometry of actinyl, with two oxo ligands in axial positions and five oxygen atoms from the two trilacunary Keggin anions in the equatorial plane. The lacunary anions are coordinating via terminal oxygens from edge-sharing pairs of {WO6} octahedra in the lacuna as well as bridging oxygens located between two corner-sharing octahedra.

The cation-directed structural changes have been observed in the case of the preparation of uranyl complexes.[96] When excess sodium was present in the reaction of $[PW_9O_{34}]^{9-}$ with uranyl acetate, the final product was $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ with two Na^+ cations interacting with both the polyoxoanions and the oxo ligands of the uranyl units (Figure 6, left). However, when ammonium or potassium were present during synthesis, or added to the sodium-containing product, a different structure was obtained (Figure 6, middle) $[M_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (M= K^+ or NH_4^+), in which the two uranyl are partly-delocalized in three equivalent coordination sites, making it impossible to locate the ammonium or potassium cations. Later, Khoshnavazi and coworkers showed that similar compounds could also be prepared via self-assembly, using WO_4^{2-} and $HAsO_4^{2-}$ instead of the preformed $[AsW_9O_{34}]^{9-}$, in the



$[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$
$[Na_x(NpO_2)_2(PW_9O_{34})_2]^{z-}$

$[M_2(UO_2)_2(PW_9O_{34})_2]^{12-}$
(M= K^+ or NH_4^+)

$[(UO_2)_3(AsW_9O_{34})_2]^{12-}$
$[(PuO_2)_3(GeW_9O_{34})_2]^{14-}$

Figure 6. Polyhedral representation of bi- and tri-nuclear actinide complexes prepared using trilacunary Keggin anions[92-99] (green: actinide; pink sphere: Na; red sphere: axial O of actinyl fragment; blue octahedron: W, pink tetrahedron: P; orange tetrahedron: Si).

presence of uranyl acetate, resulting in $[M_2(UO_2)_2(AsW_9O_{34})_2]^{12-}$ (M= Na^+, K^+ or NH_4^+).[100] In contrast, using uranyl nitrate, the authors obtained a trinuclear complex $[(UO_2)_3(AsW_9O_{34})_2]^{12-}$ (Figure 6, right).[101] Other trilacunary Keggin anions were used with variation of the central heteroatom such as Si,[102] Ge[98], Sb or Te.[103] In some cases, the preformed trivacant polyoxoanions appeared to undergo partial hydrolysis during the reaction leading to more complex structures. The rich structural diversity of these actinide oxo-clusters incorporated in polyoxometalates has recently been reviewed.[34]

Regarding the neptunyl and plutonyl complexes, they have analogous structures to that reported for the uranyl-derived species. The plutonyl compound is a tri-actinide complex, $[K_3(PuO_2)_3(GeW_9O_{34})_2]^{11-}$, while both $\{NpO_2\}^{2+}$ and $\{NpO_2\}^+$ have been reported as the di-sodium product, $[Na_2(NpO_2)_2(EW_9O_{34})_2]^{14-}$ (E = Ge(IV) for Np(VI), P(V) for Np(V)).[97,98] Interestingly, May and coworkers attempted to convert $[Na_2(NpO_2)_2(PW_9O_{34})_2]^{12-}$ into $[(NH_4)_2(NpO_2)_2(PW_9O_{34})_2]^{12-}$, as described for the uranyl analogue, but they could not fully displace both sodium cations, resulting in formation of $[Na(NpO_2)_2(PW_9O_{34})_2]^{13-}$.[104] The more efficient binding of the sodium cation by the axial oxo ligands of the $\{NpO_2\}^+$ units compared to those of the $\{UO_2\}^{2+}$ units illustrates the poor donor capacity of the latter.

The presence of interactions between alkali cations and oxo ligands of the actinyl fragment could indicate the activation of the An-O_{axial} bonds in these POM-based actinyl species. However, structural investigations showed that in all cases, the An-O_{axial} bonds of the actinyl fragments are not statistically different than in their aquo or acetate variants. In contrast, strong spectroscopic evidences for weakening of these bonds were observed. Indeed, in the uranyl complexes, the Raman shift for the symmetric stretching vibration of $\{UO_2\}^{2+}$, ν(OUO), is observed around 800 cm^{-1} compared to 870 cm^{-1} in the aquo species.[103,105] Furthermore, the weakening of the U-O bond is stronger for polyoxoanions with larger anionic charge, indicating that the strong donation from the POM ligand is involved in the activation of the actinyl subunit.[103] The weakening of the An-O_{axial} bond can also be observed in both absorption and emission spectra of these complexes. Indeed, activation of the An-O bond causes a change in the energy maxima of the O→An charge transfer. In the case of uranyl, both the energy and the vibrational fine structure of the absorption feature occurring around 430 nm can be used to probe the strength of the U-O bond.[103,105]

In the case of the neptunyl cation, the symmetric stretching vibration of $\{NpO_2\}^{2+}$ appears in the same range than the W-O vibrations of the trilacunary Keggin polyoxoanion, making its observation impossible by vibrational spectroscopies.[97] In contrast, the lower quantity of material available when working with nuclides with stronger radioactive decay, such as Np and Pu, makes absorption and emission spectroscopies highly attractive method of characterization, as they require low concentration of material in solution. Furthermore, the study of the neptunyl and plutonyl systems can take advantage of additional spectral features due to their partially filled *5f* orbitals, allowing for *f-f* transition. These transitions are shifted in the case of the POM-based complexes, reflecting on both the presence of actinyl-actinyl interaction and the strong donation from the polyoxoanion. In the case of neptunium, both $\{NpO_2\}^+$ and $\{NpO_2\}^{2+}$ species have been studied, with $5f^2$ and $5f^1$ configuration, respectively. The former present a sharp *f-f* transition at 980 nm when coordinated with water which undergoes a bathochromic shift of 20 to 40 nm upon coordination with the polyoxoanions.[97,106] In the absorption spectra of Np(VI) species, the additional band with fine vibrational structure around 600 nm is attributed to the O→Np(VI) ligand to metal charge transfer (LMCT), while the sharp *f-f* transition is blue-shifted from 1223 nm in the aquo complex to 1137 nm, with a decreased intensity.[104] The aquo-plutonyl complex presents a sharp *f-f* transition at 830 nm in its absorption spectra which shifts to lower energy, around 856 nm, for $[Na_3(PuO_2)_3(GeW_9O_{34})_2]^{11-}$.[99]

More importantly, Np(VI) complexes are known to be emissive in the near infrared region, with emission maxima at 1490 and 1580 nm for the *f-f* transitions. Upon coordination to $[PW_9O_{34}]^{9-}$, both intensity and lifetime of the neptunyl units' emission are enhanced, while the relative intensities of both transitions are modified. These changes in the photophysical properties are attributed to: 1) displacement of water ligands which act as quenchers for the emission of the actinide centre, 2) change in the local symmetry at the metal centre, and 3) the possibility of the POM to act as an antenna via excitation of the O→W LMCT, which has been demonstrated for lanthanides previously.[98,104,107]

While there are strong spectroscopic evidences for the activation of An-O bonds upon complexation with trilacunary polyoxotungstates, the reactivity of these actinyl complexes remains unexplored. The only mention of some form of reactivity is found in the initial report of Pope *et al.* who observed that the uranyl complexes $[M_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (M= Na^+, K^+ or NH_4^+) were unstable in the presence of carboxylate, especially in the presence of light.[96] Interestingly, Pope *et al.* observed the apparition in solution of a Weakley-Peacock type complex, $[U(IV)(PW_{11}O_{39})_2]^{10-}$, after photodecomposition of the uranyl complex, indicating that the trilacunary polyoxoanions reorganize into the monolacunary species to bind with the U(IV) cations. Further investigation of the photochemistry of actinyl-POM complexes appear desirable. The photochemical reactivity of uranyl is well established and has recently been used to mediate various organic transformations.[93,108] However, the use of uranyl cations as robust photocatalysts is limited by the insolubility of the U(IV) species formed after disproportionation of the singly reduced $\{UO_2\}^+$ units.[17]

Conclusion

After more than 50 years of exploration, a large variety of An-POM complexes have been reported. The rich structural variety of this class of compounds has not translated, however, to a wide range of applications for these molecular species. Indeed, despite several successful studies related to nuclear waste treatment, the impact of this class of compounds remains tenuous compared to that of the transition metals and lanthanides supported by polyoxoanions. This can be explained, in part, by the fact that many studies of POM-supported actinide complexes are limited to structural descriptions, thus restricting the access to information regarding their electronic structures or their reactivity beyond stability in synthetic media.

Indeed, POM-based actinide complexes have been shown to be suitable platforms for investigation of actinide cations in both high and low valent states in aqueous solution, which is critical for the study of the overall speciation of actinide cations within the nuclear fuel cycle. The study of the electronic properties of these compounds is crucial to establish the extent of the possible electronic delocalization between *5f* and *6d* orbitals of the actinides, *3*, *4* or *5d* orbitals of the transition metals and *2p* orbitals of the oxo in the polyoxoanion-derived ligands. Determining the extent of this electronic delocalization is desirable to gain additional insight into the properties of functional actinide-containing metal oxides.[14,109] Additionally, complexation of actinyl by trilacunary Keggin polyoxoanions leads to the activation of the An-O bonds in the actinyl subunits, laying the framework for potentially studies into the thermal and photochemical reactivity of these assemblies.

Another promising avenue for the development of the chemistry of An-POM complexes would be the transition to organosoluble species. This is a surprisingly underexplored opportunity considering the well-established protocols for cations exchange in POM chemistry.[110,111] Pope, May and coworker have however provided proof of concept in their studies of POM-supported actinyl species.[96,97] Additionally, the two examples of polyoxometalate-supported organoactinide complexes discussed above show that POMs can be used as sterically hindered ligands to complete the coordination sphere of organoactinide species, offering opportunity for the development of actinide complexes with both organic and inorganic ligands to tune their reactivity. Interestingly, the field of uranyl (per)oxoclusters is currently taking a similar path. Recent studies demonstrate that the use of organic solvents modulates the reactivity of both U(IV) and U(VI) precursors, allowing further investigation of the mechanism of formation of this class of compounds.[112-116]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Heavy Element Program, under award DE-SC0020436.

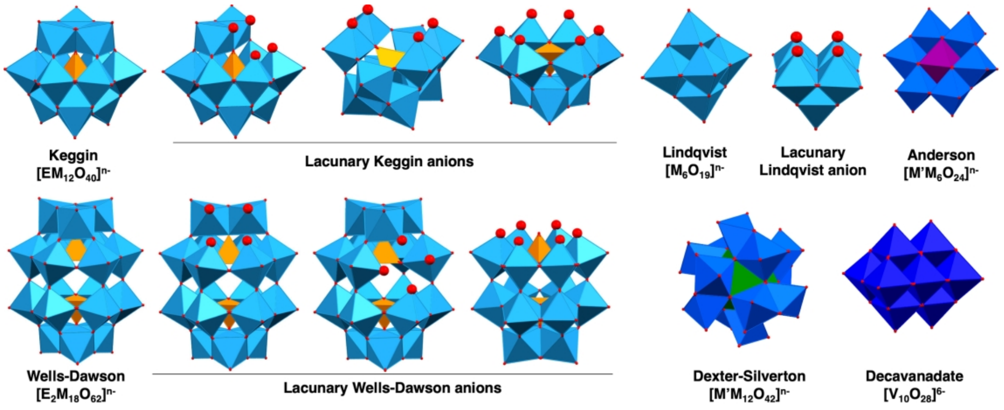
Notes and references

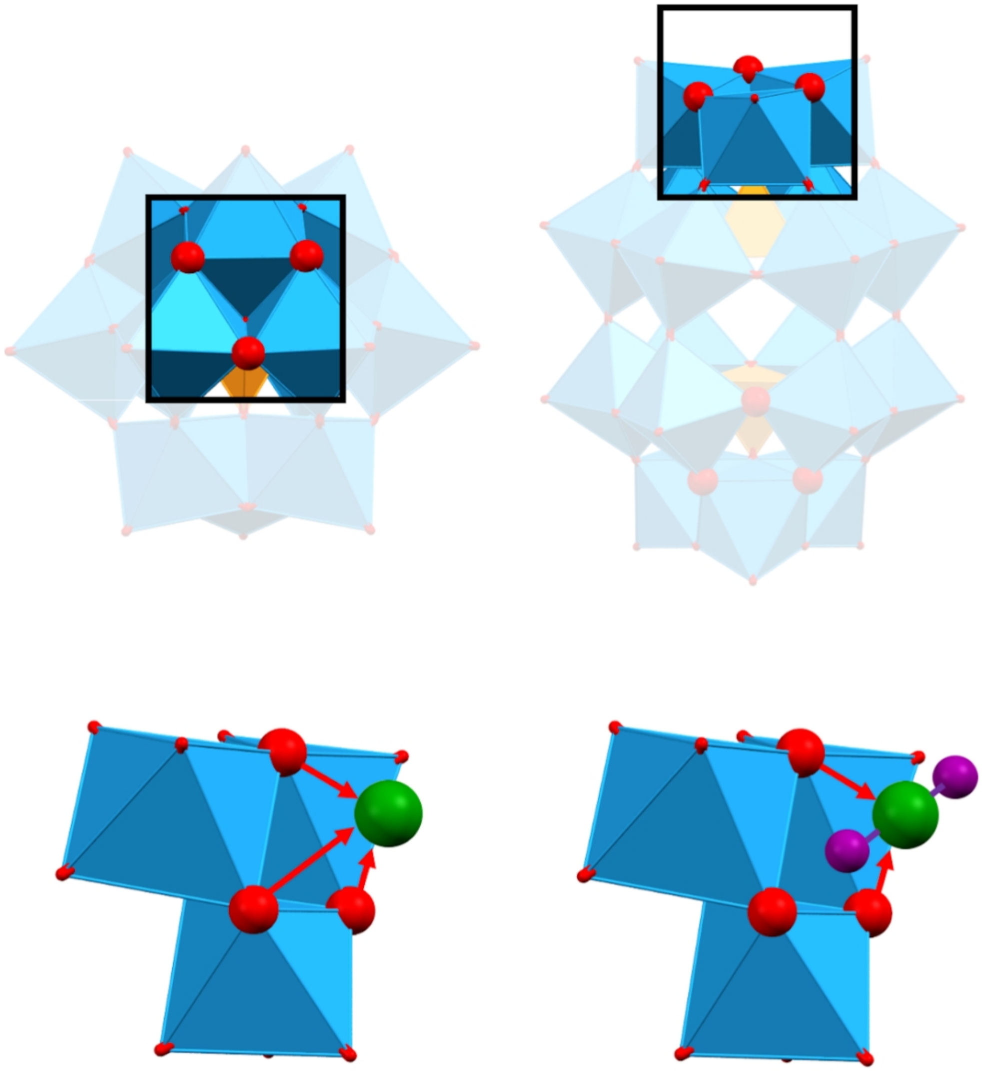
1. M. B. Jones and A. J. Gaunt, *Chemical Reviews*, 2013, **113**, 1137-1198.
2. L. S. Natrajan, A. N. Swinburne, M. B. Andrews, S. Randall and S. L. Heath, *Coordination Chemistry Reviews*, 2014, **266-267**, 171-193.
3. J. E. Birkett, M. J. Carrott, O. D. Fox, C. J. Jones, C. J. Maher, C. V. Roube, R. J. Taylor and D. A. Woodhead, *Chimia*, 2005, **59**, 898-904.
4. R. A Wigeland, T. H. Bauer, T. Fanning and E. E Morris, *Spent nuclear fuel separations and transmutation criteria for benefit to a geologic repository*, 2018.
5. M. Bunn, S. Fetter, J. P. Holdren and B. van der Zwaan, *The Economics of Reprocessing vs. Direct Disposal of Spent Nuclear Fuel*, Belfer Center for Science and International Affairs, Harvard Kennedy School, 2003.
6. M. P. Kelley, G. J. Deblonde, J. Su, C. H. Booth, R. J. Abergel, E. R. Batista and P. Yang, *Inorg Chem*, 2018, **57**, 5352-5363.
7. É. Ansoborlo, B. Amekraz, C. Moulin, V. Moulin, F. Taran, T. Bailly, R. Burgada, M.-H. Hengé-Napoli, A. Jeanson, C. Den Auwer, L. Bonin and P. Moisy, *Comptes Rendus Chimie*, 2007, **10**, 1010-1019.
8. T. J. Marks, *Science*, 1982, **217**, 989-997.
9. M. L. Neidig, D. L. Clark and R. L. Martin, *Coordination Chemistry Reviews*, 2013, **257**, 394-406.
10. S. T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 8604-8641.
11. P. L. Arnold, *Chem Commun (Camb)*, 2011, **47**, 9005-9010.
12. I. Karmel, R. Batrice and M. Eisen, *Inorganics*, 2015, **3**, 392-428.
13. E. Lu and S. T. Liddle, *Dalton Transactions*, 2015, **44**, 12924-12941.
14. J. Leduc, M. Frank, L. Jürgensen, D. Graf, A. Raauf and S. Mathur, *ACS Catalysis*, 2019, **9**, 4719-4741.
15. D. P. Halter, F. W. Heinemann, L. Maron and K. Meyer, *Nat Chem*, 2018, **10**, 259-267.
16. R. Faizova, F. Fadaei-Tirani, R. Bernier-Latmani and M. Mazzanti, *Angew Chem Int Ed Engl*, 2020, **59**, 6756-6759.
17. X. Zhang, P. Li, M. Krzyaniak, J. Knapp, M. R. Wasielewski and O. K. Farha, *Inorg Chem*, 2020, 10.1021/acs.inorgchem.1020c00850.
18. *Polyoxometalate Chemistry From Topology via Self-Assembly to Applications*, Kluwer Academic Publishers (Eds. M. T. Pope, A. Muller), 2002.
19. *Chem. Soc. Rev.*, 2012, **41**, Themed collection : Polyoxometalate cluster science (Eds. L. Cronin, Achim Muller).
20. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Springer Netherlands (Eds. M. T. Pope, A. Muller), 1994.
21. M. Fournier, C. Feumi-Jantou, C. Rabia, G. Hervé and S. Launay, *J. Mater. Chem.*, 1992, **2**, 971-978.
22. K. Wassermann, M. T. Pope, M. Salmen, J. N. Dann and H.-J. Lunk, *Journal of Solid State Chemistry*, 2000, **149**, 378-383.
23. A. V. Colusso, A. McDonagh and M. B. Cortie, *Surface and Interface Analysis*, 2018, **50**, 1384-1388.
24. G. Guedes, S. Wang, H. A. Santos and F. L. Sousa, *European Journal of Inorganic Chemistry*, 2020, **2020**, 2121-2132.
25. N. V. Izarova, M. T. Pope and U. Kortz, *Angew Chem Int Ed Engl*, 2012, **51**, 9492-9510.
26. P. Gouzerh and A. Proust, *Chem Rev*, 1998, **98**, 77-112.
27. J. W. Zhao, Y. Z. Li, L. J. Chen and G. Y. Yang, *Chem Commun (Camb)*, 2016, **52**, 4418-4445.
28. M. T. Pope, in *Structural Chemistry of Inorganic Actinide*

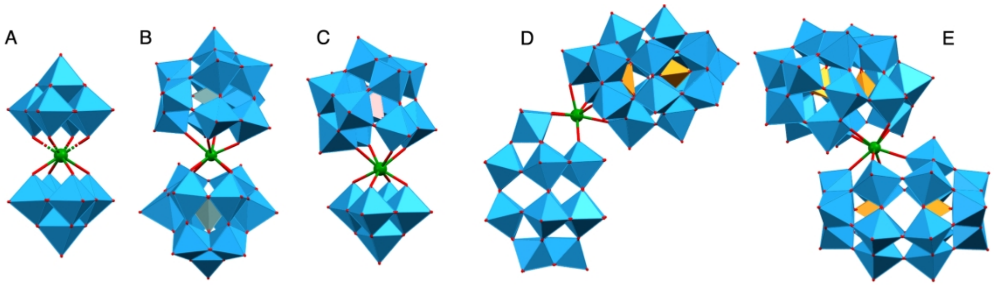
Compounds, eds. S. V. Krivovichev, P. C. Burns and I. G. Tananaev, Elsevier, Amsterdam, 2007, pp. 341-361.

29. P. C. Burns and M. Nyman, *Dalton Trans*, 2018, **47**, 5916-5927.
30. I. A. Charushnikova, A. V. Gogolev, M. S. Grigor’ev and A. M. Fedoseev, *Radiochemistry*, 2016, **58**, 457-465.
31. M. H. Alizadeh, S. P. Harmalker, Y. Jeannin, J. Martin-Frere and M. T. Pope, *Journal of the American Chemical Society*, 1985, **107**, 2662-2669.
32. I. Creaser, M. C. Heckel, R. J. Neitz and M. T. Pope, *Inorganic Chemistry*, 1993, **32**, 1573-1578.
33. M. R. Antonio and M. H. Chiang, *Inorg Chem*, 2008, **47**, 8278-8285.
34. M. Dufaye, S. Duval and T. Loiseau, *CrystEngComm*, 2020, **22**, 3549-3562.
35. K. Maher, J. R. Bargar and G. E. Brown, Jr., *Inorg Chem*, 2013, **52**, 3510-3532.
36. Y. Wang, M. Frutschi, E. Suvorova, V. Phrommavanh, M. Descostes, A. A. Osman, G. Geipel and R. Bernier-Latmani, *Nat. Commun.*, 2013, **4**, 2942.
37. A. Saito and G. R. Choppin, *Inorganic Chemistry*, 1991, **30**, 4563-4566.
38. A. Saito and G. R. Choppin, *Journal of Alloys and Compounds*, 1998, **271-273**, 751-755.
39. G. R. Choppin, *Journal of Nuclear Science and Technology*, 2002, **39**, 229-232.
40. C. E. VanPelt, W. J. Crooks and G. R. Choppin, *Inorganica Chimica Acta*, 2003, **346**, 215-222.
41. W. G. Klemperer and W. Shum, *Journal of the American Chemical Society*, 1977, **99**, 3544-3545.
42. V. W. Day, W. G. Klemperer and D. J. Maltbie, *Journal of the American Chemical Society*, 1987, **109**, 2991-3002.
43. L. A. Combs-Walker and C. L. Hill, *Inorganic Chemistry*, 1991, **30**, 4016-4026.
44. R. Contant, *Canadian Journal of Chemistry*, 1987, **65**, 568-573.
45. A. Tézé and G. Hervé, *Journal of Inorganic and Nuclear Chemistry*, 1977, **39**, 999-1002.
46. M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag Berlin Heidelberg, 1983.
47. A. B. Yusov and V. P. Shilov, *Radiochemistry*, 2007, **49**, 144-151.
48. M. N. Sokolova, G. B. Andreev and A. B. Yusov, *Inorganic Chemistry Communications*, 2011, **14**, 466-469.
49. R. D. Shannon, *Acta Crystallographica Section A*, 1976, **32**, 751-767.
50. R. D. Peacock and T. J. R. Weakley, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1971, 1836-1839.
51. R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A*, 1971, 1937-1940.
52. C. M. Tourné, G. F. Tourné and M. C. Brianso, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 2012-2018.
53. C. Tourné and G. Tourné, *Rev. Chim. Miner.*, 1977, **14**.
54. Y. Jeannin, *Comptes Rendus Chimie*, 2005, **8**, 999-1004.
55. M. N. Sokolova, G. B. Andreev and A. B. Yusov, *Inorganic Chemistry Communications*, 2011, **14**, 1089-1092.
56. A. B. Yusov, V. P. Shilov and A. M. Fedoseev, *Radiochemistry*, 2007, **49**, 135-143.
57. G. J. Deblonde, M. Sturzbecher-Hoehne and R. J. Abergel, *Inorg Chem*, 2013, **52**, 8805-8811.
58. S. Duval, S. Beghin, C. Falaise, X. Trivelli, P. Rabu and T. Loiseau, *Inorg Chem*, 2015, **54**, 8271-8280.
59. M.-H. Chiang, L. Soderholm and Mark R. Antonio, *European Journal of Inorganic Chemistry*, 2003, **2003**, 2929-2936.
60. A. B. Yusov, V. P. Shilov and A. M. Fedoseev, *Radiochemistry*, 2007, **49**, 152-155.
61. B. Keita, F. Girard, L. Nadjo, R. Contant, J. Canny and M. Richet, *Journal of Electroanalytical Chemistry*, 1999, **478**, 76-82.
62. M. T. Pope, *Inorganic Chemistry*, 1972, **11**, 1973-1974.
63. E. A. Erine, A. A. Baranov, A. Y. Volkov, V. M. Chistyakov and G. A. Timofeev, *Journal of Alloys and Compounds*, 1998, **271-273**, 782-785.
64. G. R. Choppin, *Radiochimica Acta*, 1983, **32**.
65. S. C. Termes and M. T. Pope, *Transition Metal Chemistry*, 1978, **3**, 103-108.
66. D. Chartier, L. Donnet and J. M. Adnet, *Radiochimica Acta*, 1998, **83**.
67. M. S. Milyukova, D. A. Malikov, E. V. Kuzovkina and B. F. Myasoedov, *Journal of Radioanalytical and Nuclear Chemistry Letters*, 1986, **104**, 81-89.
68. L. Bion, P. Moisy and C. Madie, *Radiochimica Acta*, 1995, **69**.
69. H. Idriss, *Surface Science Reports*, 2010, **65**, 67-109.
70. Z. R. Ismagilov, S. V. Kuntsevich, N. V. Shikina, V. V. Kuznetsov, M. A. Kerzhentsev, V. A. Ushakov, V. A. Rogov, A. I. Boronin and V. I. Zaikovsky, *Catalysis Today*, 2010, **157**, 217-222.
71. S. H. Taylor, C. S. Heneghan, G. J. Hutchings and I. D. Hudson, *Catalysis Today*, 2000, **59**, 249-259.
72. S. Lazareva, Z. Ismagilov, V. Kuznetsov, N. Shikina and M. Kerzhentsev, *Environmental Technology*, 2018, 1-9.
73. G. J. Hutchings, C. S. Heneghan, I. D. Hudson and S. H. Taylor, *Nature*, 1996, **384**, 341-343.
74. T. Campbell, M. A. Newton, V. Boyd, D. F. Lee and J. Evans, *J. Phys. Chem. B*, 2005, **109**, 2885-2893.
75. S. D. Pollington, A. F. Lee, T. L. Overton, P. J. Sears, P. B. Wells, S. E. Hawley, I. D. Hudson, D. F. Lee and V. Ruddock, *Chemical Communications*, 1999, 725-726.
76. P. L. Cottingham and L. K. Barker, *Product R&D*, 1973, **12**, 41-47.
77. R. K. Grasselli and J. L. Callahan, *Journal of Catalysis*, 1969, **14**, 93-103.
78. R. K. Grasselli, J. D. Burrington, D. D. Suresh, M. S. Friedrich and M. A. S. Hazle, *Journal of Catalysis*, 1981, **68**, 109-120.
79. A. P. Amrute, F. Krumeich, C. Mondelli and J. Pérez-Ramírez, *Chemical Science*, 2013, **4**, 2209-2217.
80. A. Ruiz Puigdollers, P. Schlexer, S. Tosoni and G. Pacchioni, *ACS Catalysis*, 2017, **7**, 6493-6513.
81. E. W. McFarland and H. Metiu, *Chemical Reviews*, 2013, **113**, 4391-4427.
82. D. M. Smyth, *Solid State Ionics*, 2000, **129**, 5-12.
83. C. Coperet, F. Allouche, K. W. Chan, M. P. Conley, M. F. Delley, A. Fedorov, I. B. Moroz, V. Mougel, M. Pucino, K. Searles, K. Yamamoto and P. A. Zhizhko, *Angew Chem Int Ed Engl*, 2018, **57**, 6398-6440.
84. S. L. Wegener, T. J. Marks and P. C. Stair, *Acc Chem Res*, 2012, **45**, 206-214.
85. M. Y. He, G. Xiong, P. J. Toscano, R. L. Burwell and T. J. Marks, *Journal of the American Chemical Society*, 1985, **107**, 641-652.
86. P. J. Toscano and T. J. Marks, *Langmuir*, 1986, **2**, 820-823.

87. O. A. Kholdeeva and R. I. Maksimovskaya, *Journal of Molecular Catalysis A: Chemical*, 2007, **262**, 7-24.
88. V. W. Day and W. G. Klemperer, *Molecular Engineering*, 1993, **3**, 61-78.
89. P. Putaj and F. Lefebvre, *Coordination Chemistry Reviews*, 2011, **255**, 1642-1685.
90. V. W. Day, C. W. Earley, W. G. Klemperer and D. J. Maltbie, *Journal of the American Chemical Society*, 1985, **107**, 8261-8262.
91. V. W. Day, W. G. Klemperer and D. J. Maltbie, *Organometallics*, 1985, **4**, 104-111.
92. P. L. Arnold, D. Patel, C. Wilson and J. B. Love, *Nature*, 2008, **451**, 315-317.
93. B. E. Cowie, J. M. Purkis, J. Austin, J. B. Love and P. L. Arnold, *Chem Rev*, 2019, **119**, 10595-10637.
94. S. Fortier and T. W. Hayton, *Coordination Chemistry Reviews*, 2010, **254**, 197-214.
95. M. K. Assefa, G. Wu and T. W. Hayton, *J Am Chem Soc*, 2020.
96. K.-C. Kim and M. T. Pope, *Journal of the American Chemical Society*, 1999, **121**, 8512-8517.
97. A. J. Gaunt, I. May, M. Helliwell and S. Richardson, *J Am Chem Soc*, 2002, **124**, 13350-13351.
98. C. Talbot-Eeckelaers, S. J. Pope, A. J. Hynes, R. Copping, C. J. Jones, R. J. Taylor, S. Faulkner, D. Sykes, F. R. Livens and I. May, *J Am Chem Soc*, 2007, **129**, 2442-2443.
99. R. Copping, C. Talbot-Eeckelaers, D. Collison, M. Helliwell, A. J. Gaunt, I. May, S. D. Reilly, B. L. Scott, R. D. McDonald, O. A. Valenzula, C. J. Jones and M. J. Sarsfield, *Dalton Trans*, 2009, 5609-5611.
100. R. Khoshnavazi, H. Eshtiagh-hossieni, M. H. Alizadeh and M. T. Pope, *Polyhedron*, 2006, **25**, 1921-1926.
101. R. Khoshnavazi, H. Eshtiagh-hosseini, M. H. Alizadeh and M. T. Pope, *Inorganica Chimica Acta*, 2007, **360**, 686-690.
102. K.-C. Kim, A. Gaunt and M. T. Pope, *Journal of Cluster Science*, 2002, **13**, 423-436.
103. A. J. Gaunt, I. May, R. Copping, A. I. Bhatt, D. Collison, O. Danny Fox, K. Travis Holman and M. T. Pope, *Dalton Transactions*, 2003.
104. J. M. Berg, A. J. Gaunt, I. May, A. L. Pugmire, S. D. Reilly, B. L. Scott and M. P. Wilkerson, *Inorg Chem*, 2015, **54**, 4192-4199.
105. A. J. Gaunt, I. May, D. Collison, K. Travis Holman and M. T. Pope, *Journal of Molecular Structure*, 2003, **656**, 101-106.
106. R. Copping, A. J. Gaunt, I. May, C. A. Sharrad, D. Collison, M. Helliwell, O. D. Fox and C. J. Jones, *Chem Commun (Camb)*, 2006, 3788-3790.
107. C. Boskovic, *Acc Chem Res*, 2017, **50**, 2205-2214.
108. J. G. West, T. A. Bedell and E. J. Sorensen, *Angew Chem Int Ed Engl*, 2016, **55**, 8923-8927.
109. J. N. Cross, T. H. Lee, C. J. Kang, Y. X. Yao, S. K. Cary, J. T. Stritzinger, M. J. Polinski, C. D. McKinley, T. E. Albrecht Schmitt and N. Lanata, *Chem Sci*, 2019, **10**, 6508-6518.
110. D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller and A. Du Chesne, *Chemistry - A European Journal*, 2000, **6**, 385-393.
111. A. Misra, K. Kozma, C. Streb and M. Nyman, *Angew Chem Int Ed Engl*, 2020, **59**, 596-612.
112. A. Arteaga, D. Ray, E. Glass, N. P. Martin, L. N. Zakharov, L. Gagliardi and M. Nyman, *Inorg Chem*, 2020, **59**, 1633-1641.
113. H. A. Neal, J. Szymanowski, J. B. Fein, P. C. Burns and M. Nyman, *European Journal of Inorganic Chemistry*, 2017, **2017**, 39-46.
114. C. Falaise, C. Volkringer, J. F. Vigier, A. Beaurain, P. Roussel, P. Rabu and T. Loiseau, *J Am Chem Soc*, 2013, **135**, 15678-15681.
115. N. P. Martin, C. Volkringer, N. Henry, X. Trivelli, G. Stoclet, A. Ikeda-Ohno and T. Loiseau, *Chem Sci*, 2018, **9**, 5021-5032.
116. L. Chatelain, R. Faizova, F. Fadaei-Tirani, J. Pecaut and M. Mazzanti, *Angew Chem Int Ed Engl*, 2019, **58**, 3021-3026.


Keggin
$[EM_{12}O_{40}]^{n-}$
Lacunary Keggin anions
Lindqvist
$[M_6O_{19}]^{n-}$
Lacunary
Lindqvist anion
Anderson
$[M'M_6O_{24}]^{n-}$
Wells-Dawson
$[E_2M_{18}O_{62}]^{n-}$
Lacunary Wells-Dawson anions
Dexter-Silverton
$[M'M_{12}O_{42}]^{n-}$
Decavanadate
$[V_{10}O_{28}]^{6-}$




A
B
C
D
E