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Trends and new directions in the crystal chemistry of actinide oxo-clusters incorporated in polyoxometalates

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The present highlight article deals with the incorporation of actinide cations into polyoxometalate (POM) moieties since the first example was structurally characterized and described in the literature at the beginning of the 70s. It illustrates the various structural types of topologies that can arise from the association of different polyoxometalates (molybdates or tungstates, Keggin- or Wells-Dawson-based entities, *etc.*) with the light actinide elements (mainly thorium and uranium). Nevertheless, some rare investigations have also been reported, performed with transuranium elements such as neptunium, plutonium, americium, curium and californium. The synthetic strategies for obtaining such molecular species, their crystal structure arrangements and their behavior in aqueous solution are discussed. The diverse varieties of actinide-POM assemblies are classified on the basis of the nature of the metal (Mo or W) and the vacancy states occurring in the polyoxometallic precursors, starting with the polyoxomolybdate family. The second series of polyoxotungstates has been intensively studied and is described more widely.

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1. Introduction

Université de Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du solide, F-59000 Lille, France. E-mail: sylvain.duval@univ-lille.fr, thierry.loiseau@univ-lille.fr; Fax: +(33) 3 20 43 48 95; Tel: +(33) 3 20 434 973 The chemistry of polyoxometalates (POMs) has been intensively studied during the past decades due to their structural diversities and fascinating varieties of atomic organizations with heteroelements in the construction of



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Maxime Dufaye received his bachelor's degree from the University of Valenciennes and his MSc in chemistry from the University of Lille, France. Afterward, he joined the group of Dr. Thierry Loiseau and prepared his PhD under his supervision with Dr. Sylvain Duval. He worked on the synthesis and characterization of polyanionic molecular species bearing actinide or lanthanide elements. After his PhD defense in 2019, he

moved to the Laboratory of Reactivity and Solid State Chemistry, headed by Dr. Mathieu Morcrette, at the University of Amiens as a research engineer and now focuses on the development of new electrode materials and their coating for solid-state batteries.



Sylvain Duval

Sylvain Duval has been an associate professor at the University of Lille since 2013. He received his PhD degree from Versailles-Saint-Quentin

University, France, in 2009 under the supervision of Prof. E. Cadot and Dr. C. Simonnet-Jegat in the field of supramolecular polyoxothiometalates and their solution stability studies. He then moved to Geneva, Switzerland, for a postdoctoral position between 2010 and 2013

in the group of Prof. A. Williams, where he worked on ligand synthesis and coordination chemistry of copper and iron cations. He is now interested in the crystallography and chemistry of polyoxometalates and poly-oxo clusters composed of tetravalent elements such as cerium, thorium or uranium. He pays particular attention to their solution behavior using various techniques such as NMR and SAXS. molecular entities with high nuclearities. POMs consist of discrete units composed of octahedrally coordinated metal oxides { MO_6 } occurring at their highest oxidation states (mainly W^{VI} , MO^{VI} , V^V and Nb^V).^{1,2} They result from the polycondensation reactions of the { MO_6 } units, either by olation or oxolation mechanisms, to form intermediate species with well-defined nuclearities around trigonal { XO_3 } or tetrahedral { XO_4 } mononuclear heterometalates, knowing that the ultimate step is the formation of infinite dense metallic oxide MO_x .

Based on their compositions, the different types of structural atomic arrangements resulting from these reactions can be divided into several families with specific names (Keggin, Wells–Dawson, Lindqvist, ...) related to the discoverer of a given molecular architecture.^{3–5} In these different series, the literature has shown that the most studied species derived from either the saturated Keggin $[XM_{12}O_{40}]^{n-}$ or Wells–Dawson $[X_2M_{18}O_{62}]^{m-}$ archetypes. Indeed, from these saturated species, it is possible to obtain a wide variety of molecular systems going from mono-lacunary polyoxometalate up to hexa-lacunary ones. Furthermore, starting from some of these polyvacant species, macro-cyclic compounds with complexing properties towards transition metals can easily be synthesized (Fig. 1).^{6,7}

One can also note that this structural richness arises mainly in the polyoxotungstate (POT) compounds, but much fewer results were described in the literature using polyoxomolybdates (POMos). This fact can be explained by the weaker stability of lacunary polyanions based on molybdate in comparison with the tungstate ones. For instance, the vacant POMos seem to easily reorganize themselves in aqueous solution to form saturated Keggin or



Thierry Loiseau

Thierry Loiseau is a research director at CNRS and received his PhD degree from Le Mans University, France, in 1994. He worked with Prof. G. Férey (Institut Lavoisier, University of Versailles, France) in the field of of openthe elaboration framework materials from 1991. His research interests concern the hydrothermal synthesis and structural characterization (XRD, NMR, in situ experiments) of organically templated aluminium

or gallium phosphates and more recently MOF-type porous aluminium carboxylates. He then moved to the University of Lille (2009) and now focuses on the chemistry of carboxylates, polyoxometalates and poly-oxo clusters bearing actinides, which include metals such as thorium or uranium, and their use in the treatment and recycling of nuclear waste. He is the author of more than 200 articles (h index of 55, >13 000 citations) and 4 patents. Wells–Dawson architectures, making it difficult to obtain lacunary species.⁸ The polyvacant polyoxometalate precursors can be used as inorganic ligands for the incorporation of a wide range of 3d–4d transition or 4f rare earth elements.^{1,9–14} These chemical combinations have been extensively described in the literature and are not the purpose of this review, which will be specifically devoted to the complexation of the 5f actinide elements.

The first relevance of the complexation of actinides with polyoxometalates appeared in 1971 with the publication of Spitsyn and co-workers.¹⁵ It was then followed by several research teams due to the interest in polyoxometalates as potential complexing agents for the separation or the storage of radioactive elements generated by military or industrial activities.¹⁶ Several article reviews were published between 1985 and 2002 focusing on the coordination behavior of actinides with polyoxometalate among other molecules and on the stability constants of formation of such compounds.17-19 Following this period, several worldwide research groups have continuously dedicated their work to the elaboration of such compounds. A book chapter was also written more than a decade ago by M. T. Pope, who drew up the inventory about the structural chemistry of vacant polyoxometalates bearing actinides.²⁰ The present review concerns the state of the art in the synthetic formation of polyoxometalate species, based on molybdate or tungstate, interacting with actinide elements and the recent research advances in this particular field.

2. Polyoxomolybdates

As mentioned in the introduction, vacant polyoxomolybdate compounds are much less explored than their polyoxotungstate counterparts. But, surprisingly, the first reported association between a polyanionic core and actinides was constituted of hexavalent molybdenum centers. resulting molecular systems with thorium(rv), The neptunium(IV) and uranium(IV) were structurally characterized between 1971 and 1978 and possess the formula $[An^{IV}Mo_{12}O_{42}]^{8-}$ (with $An^{IV} = Th^{IV}$, Np^{IV} and U^{IV}).^{15,21,22} All these molecules belong to the Dexter-Silverton type, discovered and described before, in 1968, by Dexter and Silverton with the cerium(iv) cation instead.²³ In this archetype, the single-incorporated tetravalent center behaves as a heteroelement with a surprisingly high twelve-fold coordination (Fig. 2a).

The $[U^{IV}Mo_{12}O_{42}]^{8^-}$ molecule was electrochemically studied and found to remain stable towards a reversible redox process of the uranium center from U^{IV} to U^V at a potential of +0.91 V vs. sce at pH 0. After 3–4 hours, degradation of the oxidized species (loss of the characteristic orange color of the solution) occurred and it was impossible to isolate the U^V bearing moieties by precipitation.¹⁶ Successful investigations were performed with the encapsulation of thorium(IV) and neptunium(IV) cations within the same molecular archetype.^{21,22} The uranium-containing molecule was also

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Fig. 1 Representation of some polyoxotungstates derived from the Keggin or the Wells–Dawson structural archetypes. (a) $\{XW_{11}O_{39}\}$, (b) $\{XW_{10}O_{36}\}$, (c) $\{A-XW_9O_{34}\}$, (d) $\{B-XW_9O_{34}\}$, (e) $[As_4W_{40}O_{140}]^{24-}$, (f) $\{\alpha_1-X_2W_{17}O_{61}\}$, (g) $\{X_2W_{15}O_{56}\}$, (h) $[P_2W_{12}O_{48}]^{14-}$, and (i) $[H_7P_8W_{48}O_{184}]^{33-}$.

fruitfully studied. It resulted in the formation of polymeric compounds by the addition of various cations (Th^{IV} , Er^{III} , V^V ,



Fig. 2 (a) Structural representation of the Dexter–Silverton polyoxomolybdate $[Mo_{12}O_{42}]^{12-}$ discrete anionic species incorporating a U^{IV} center (orange sphere) and (b) example of the interaction with Cu^{II} (cyan sphere) at the periphery of $[Mo_{12}O_{42}]^{12-}$ anions, which then form one-dimensional chains.

 ${\rm [U^{VI}O_2]^{2+}, Ni^{II}, Cu^{II}, Sc^{III}, Fe^{III}}$ linking the ${\rm [U^{IV}Mo_{12}O_{42}]^{8-}}$ entities (Fig. 2b).²⁴⁻³¹ Only recently, Nyman's team explored another similar interesting system³² related to the isolation of crystals of Na₅[NaU^{IV}(Mo₆P₄O₃₁H₇)₂], being the only molecular compound possessing reduced Mo^V centers interacting with actinides. Using SAXS, it could be demonstrated that these entities produce, in aqueous solution, fragments of polymeric ribbons of [NaU^{IV}(Mo₆P₄-O₃₁H₇)₂]_n⁵ⁿ⁻ species where n = 7, which is the predominant soluble species with a length of approximately 92 Å (Fig. 3).

The molybdate systems $[An^{IV}Mo_{12}O_{48}]^{8-}$ and $[NaU^{IV}(Mo_6-P_4O_{31}H_7)_2]_n^{5n-}$ are the only entities reported in the literature appearing to interact with actinide elements. The second category, related to the polyoxotungstate, has been much more studied with actinides and will be described in detail.

3. Polyoxotungstates

Due to the wide possibility of synthesizing numerous stable monovacant and polyvacant molecular species, the coordination properties of the polyoxotungstate family have been extensively explored with a large number of cations



Fig. 3 (a) Structural representation of the polymeric chain in compound $[NaU^{IV}(Mo_6P_4O_{31}H_7)_2]_n^{5n-}$ and (b) SAXS measurements showing the presence of polymeric ribbons with n = 7. Reprinted with permission from *Inorganic Chemistry*, 2016, **55**, 755–761 (ref. 32). Copyright 2016 American Chemical Society.

from the elements of the periodic table. Consequently, several reports about the interaction with actinides are thus described in the literature. They can be subdivided into the isopolyoxometalates, containing exclusively tungsten centers, and the heteropolyoxometalates, containing a central heteroelement (X = As, Bi, Sb, P, Si, ...) with a tetrahedral or trigonal geometry in addition to tungsten centers.

3.1 Isopolyoxotungstates

In the family of isopolyoxotungstates, the simplest compound derives from the Lindqvist-type $[W_6O_{19}]^{2^-}$ and is synthesized starting from the dissolution of $WO_4^{2^-}$ anions in water followed by acidification.⁴ The addition of actinide cations in an aqueous solution of tungstate $[WO_4]^{2^-}$ was first performed with U^{IV} and then followed by Th^{IV} and Np^{IV} in a narrow pH range between 5.5 and $6.5.^{33-35}$ It gave rise to the formation of isostructural 1:2 sandwich-type molecular systems with the formula $[An^{IV}(W_5O_{18})_2]^{8^-}$. In these double mono-lacunary Lindqvist molecules, the global molecular symmetry is D_{4d} , allowing the actinide cation with the tetravalent oxidation state to be at its center, with a regular eight-fold square antiprism (Fig. 4).

Thermal degradation of the thorium-containing compound results in the formation of Th_xWO_3 ($x \sim 0.1$) possessing a partially reduced tungsten center. This oxide was thought to be used as an inert matrix for actinide waste management.³⁶

3.2 Iso-heteropolytungstate hybrids

To our knowledge, there are only two iso-heteropolytungstate hybrid systems incorporating uranium(v) cations.^{37,38} The first one was synthesized in an aqueous solution at pH 4–4.5 by mixing Sb₂O₃, Na₂WO₄ and UCl₄ to give orange crystals among other impurities. It was found to be a molecular entity composed of two mono-lacunary POM units, corresponding to one protonated {HW₅O₁₈} moiety together with one

triprotonated $\{H_3Sb^{III}W_{17}O_{59}\}\$ entity. It forms the tetraprotonated anionic species $[(H_3Sb^{III}W_{17}O_{59})U^{IV}(HW_5O_{18})]^{11-}$ stabilizing one uranium(IV) cation with the classical square antiprism geometry. Several years later, in 2011, another molecule $[(B^{III}W_{11}O_{39})Np^{IV}(W_5O_{18})]^{11-}$ containing one neptunium(IV) cation was synthesized. In this case, the synthesis involved the $[WO_4]^{2-}$ anion and the preformed monovacant $\{B^{III}W_{11}O_{39}\}$ heteropolyanion (Fig. 5).

This latter neptunium(v)-containing isoheteropolytungstate hybrid $[(B^{III}W_{11}O_{39})Np^{IV}(W_5O_{18})]^{11-}$ was also dissolved in aqueous solution and analyzed by UV-vis



Fig. 4 Structural representation of the $[An^{IV}(W_5O_{18})_2]^{8-}$ Lindqvist-like species (An = Th^{IV}, U^{IV} and Np^{IV}).

spectroscopy. Three characteristic groups of signals were observed at 746-751 nm, 896-904 nm and 976-982 nm, assigned to a neptunium(iv) center in a square antiprismatic geometry in this specific neptunium-POM association. Nevertheless, the comparison with electronic spectra of the $[\mathrm{Np}^{\mathrm{IV}}(\mathrm{W}_{5}\mathrm{O}_{18})_{2}]^{8-}$ and $[\mathrm{Np}^{\mathrm{IV}}(\mathrm{B}^{\mathrm{III}}\mathrm{W}_{11}\mathrm{O}_{39})_{2}]^{14-}$ polyanions seems to show that the hybrid neptunium [(B^{III}W₁₁O₃₉)Np^{IV}(W₅- O_{18}]¹¹⁻ species is not stable and decomposes, following eqn (1), to form a mixture of two entities.^{39,40}

$$2[(B^{III}W_{11}O_{39})Np^{IV}(W_5O_{18})]^{11-} \rightarrow [Np^{IV}(W_5O_{18})_2]^{8-} + [Np^{IV}(B^{III}W_{11}O_{39})_2]^{14-} (1)$$

3.3 Heteropolytungstates

A wider variety of molecular systems can be found in the literature regarding the use of heteropolyanions for the complexation of actinides with different oxidation states (IV, V or VI). Distinctly from macromolecules (described in section 3.3.d), the first assemblies were obtained by using tetravalent actinides associated to monovacant POMs. On the one hand, the utilization of polyvacant anionic precursors with actinides(IV) was reported later in aqueous solution in 1999 and more recently their X-ray diffraction structure determinations have been described since 2015. All the lacunary POMs derive from the well-known Keggin $\{XM_{12}O_{40}\}$ and Wells-Dawson {X2M18O62} structural archetypes, for which one to several oxo-tungstate $\{WO_6\}$ units (up to 3) have been removed. On the other hand, the incorporation of the ${AnO_2}^{n+}$ actinul form is encountered only in polyvacant polyanionic entities, and no structural report was reported when using mono-lacunary species.



(a) Monovacant heteropolytungstate anions. In the late 70s, the incorporation of actinides(IV) has been observed in the monovacant POMs derived from the Keggin type, corresponding to the composition $[XW_{11}O_{39}]^{n-}$, with a wide range of central heteroelements: $X = Si^{IV}$, Ge^{IV} , P^{V} and B^{III} . The structural characterization indicated polyanionic molecules with a systematic 1:2 sandwich organization of $[An^{IV}(XW_{11}O_{39})_2]^{n-}$ type with $An^{IV} = Th^{IV}$, U^{IV} and Np^{IV,41-45} As expected, the actinide cation exhibited a typical Archimedean square antiprismatic geometry. This study was then completed by using other elements, such as Pu(IV), Am(III), Cm(IV) and Cf(IV), for which molecules of the general formula $[An^{(IV,III)}(XW_{11}O_{39})_2]^{n-}$ were identified in aqueous solution. In the case of the cations Pu(IV), Cm(IV) and Cf(IV), the coordination environment is probably similar to that found with the previous light actinides, but no single-crystal XRD characterization was performed to confirm this assessment. It is noteworthy that a redox reaction by the water solvent occurs in the case of the Cm(IV)- and Cf(IV)-containing species.^{46,47} In 1986, a study was extended with the use of the monovacant Dawson derivatives [PW₁₇O₆₁]¹⁵⁻. The first results were focused on aqueous solution investigations under strongly acidic conditions (from 0.1 M to 14 M HNO₃), in which the actinide and POM species have been combined in order to determine the decontamination ratios in biphasic mixtures (aqueous nitric acid with an alkyl-amine dissolved in either CH₂Cl₂, CHCl₃ or CCl₄) of various isotopes and cations: ²⁴⁹Bk, ²⁴¹Am, ²⁴³Cm, ¹⁴⁴Ce, ^{152–154}Eu, ¹³⁷Cs, ⁹⁰Sr, ²³²Th, and ²³⁵U elements.48-51 Since 2003, the related molecular moieties have been structurally characterized and similar 1:2 sandwich molecular systems of the formula $[An^{IV}(PW_{17}O_{61})_2]^{26-}$ were revealed with the series of tetravalent cations $An^{IV} = Th^{IV}$, U^{IV} , Np^{IV}, Pu^{IV} and Am^{IV,52,53} In the case of uranium(*iv*) and thorium(IV), it was noticed that the compounds could exist as syn and anti configurations in the presence of pure α_1 or α_2 POM isomers or with an α_1 - α_2 POM mixture (Fig. 6). ³¹P NMR spectroscopy on the uranium-based POM moiety shows that at least two species are present in aqueous solution and interconvert slowly on the NMR time scale.

(b) Divacant heteropolytungstate anions. Surprisingly, no molecular assembly was reported when actinides(iv) were associated to divacant polyoxotungstate units. However, the



Fig. 6 (a) Syn and (b) anti conformations of the $[An^{IV}(P_2W_{17}O_{61})_2]^{n-1}$ polyoxometalates (with $An^{IV} = Th^{IV}$, U^{IV}).

Fia.



Fig. 7 Structure of the $[{M(H_2O)}_4(U^{VI}O_2)_4(\mu-OH)_2(SiW_{10}O_{36})_4]^{22-}$ polyanion.

divacant γ -[SiW₁₀O₃₆]⁸⁻ polyanion was studied with the uranyl {U^{VI}O₂} cation, giving rise to the formation of a tetrameric inner core [{M(H₂O)}₄(U^{VI}O₂)₄(μ -OH)₂(SiW₁₀O₃₆)₄]²²⁻ (with M = Na⁺ and K⁺).⁵⁴ It consists of a ring-like subunit containing two dimers of corner-sharing seven-fold coordinated uranyl cations. Solution studies using ²⁹Si and ¹⁸³W NMR spectroscopy revealed the equimolar presence of a mixture of the tetrameric entity with another unidentified polyanion. The uranyl(v)@ γ -{SiW₁₀O₃₆} moiety was then found to decompose after approximately 12 hours to generate only the unidentified polyanion (Fig. 7).

Based on the relative intensities of the ²⁹Si and ¹⁸³W NMR signals, this unidentified entity is probably constructed with $[SiW_{10}O_{36}]^{8-}$ groups lying on mirror planes orthogonal to those of the tetrameric architecture.

(c) Trivacant heteropolytungstate anions. The literature related to the interactions of trivacant polyanions, derived from either Keggin or Dawson archetypes, is much more abundant with actinide elements. It concerns many studies describing the association of pentavalent or hexavalent actinyl cations with heteropolytungstate anions, while illustrations of such molecular compounds with the actinides(rv) were reported only recently. Due to the structural

diversity of An@POT assemblies, this part is subdivided as a function of the nature of the polyanion, considering the trivacant A or B isomers for the Keggin type or the Wells– Dawson phosphotungstate.

(c1) $[A-XW_9O_{34}]^{n-}$ -type polytungstate anions. Prior to the first structural characterization of actinide-trivacant polyanion groups research have proposed association, some interpretations using aqueous solution studies (electronic spectroscopy and photo-colorimetric titrations) and elemental analysis to determine the possible compositions from compounds' reactions using $[PW_9O_{34}]^{9-}$ and $[GeW_9O_{34}]^{10-}$ precursors with uranium(IV).55,56 They determined that these systems could structurally be closely related to the compound defined with a trinuclear subunit of cerium(IV), $[(Ce^{IV}O)_3(H_2O)_2(PW_9O_{34})_2]^{12-57}$ In 2015, Duval *et al.* reported the first two structural associations between the trivacant moiety $[SiW_9O_{34}]^{10-}$ with thorium(IV) and uranium(IV) cations (Fig. 8).

They showed that two distinct systems are organized in sandwich-type compounds, for which a set of trinuclear (with Th(IV)) or tetranuclear (with U(IV)) poly-oxo clusters interacts with two $[SiW_9O_{34}]^{10^-}$ polyanions to generate the molecules $[U_4^{IV}(\mu^3-O)_2(SiW_9O_{34})_2(CH_3COO)_2]^{10^-}$ and $[Th_3^{IV}(\mu^3-O)(\mu^2-OH)_3-(SiW_9O_{34})_2]^{13^-}$ in a 1 M acetate buffered aqueous solution.⁵⁸



Fig. 8 Structural representation of (a) $[Th_3^{IV}(\mu^3-O)(\mu^2-OH)_3(SiW_9O_{34})_2]^{13-}$ and (b) $[U_4^{IV}(\mu^3-O)_2(SiW_9O_{34})_2(CH_3COO)_2]^{10-}$. (c) ¹⁸³W NMR spectrum of the cerium model compound $[Ce_4^{IV}(\mu^3-O)_2(SiW_9O_{34})_2(CH_3COO)_2]^{10-}$ showing the five-line spectrum. Reprinted with permission from *Inorganic Chemistry*, 2015, **54**, 8271–8280 (ref. 58). Copyright 2015 American Chemical Society.

²⁹Si and ¹⁸³W NMR spectroscopy was performed on the aqueous solution containing the cerium(w) model compound isostructural to the (paramagnetic) system bearing the tetranuclear brick of uranium(IV). The stability of these molecules was analyzed upon re-dissolution of the crystals in water. The ¹⁸³W NMR spectrum indicated a five-line signal in agreement with the expected C_{2h} molecular symmetry and confirmed that the molecular organization of the tetranuclear brick of cerium(w) is kept in aqueous solution. Using actinyl cationic groups instead of tetravalent cations, several molecules were identified. Most of these compounds possess similar sandwich-like architectures. The first structurally characterized phosphotungstate anions were described in 1999 with the isolation of the species $[X_2(U^{VI}O_2)(PW_9O_{34})_2]^{12-1}$ (with $X = Na^+$ or K^+) from a uranyl-{PW₉O₃₄} mixture in aqueous solution.⁵⁹ For these molecules, the single uranyl group adopts a classical pentagonal bipyramidal geometry and the alkaline Na⁺, K⁺ cations play a role in stabilizing the crystal structure assembly as they also interact with the two vacancies of the polyanionic {PW9O34} moiety. The structurally analogous compounds $[Na_2(U^{VI}O_2)(AsW_9O_{34})_2]^{12-}$ $[Na_2(U^{VI}O_2)(SiW_9O_{34})_2]^{14-}$ were obtained using and arsenicotungstate or silicotungstate precursors, respectively. A neptunyl(vi) derivative was also characterized later, in 2002, with the same architecture, from the $[PW_9O_{34}]^{9-}$ precursor and was further characterized in aqueous solution following the $O \rightarrow Np^{VI}$ charge transfer band by UV-visible spectroscopy.^{54,60} The influence of the alkaline (Na⁺ or K⁺) or ammonium cations occurring in the neptunyl sandwich-like polyanion on their stability was also reported in 2015.⁶¹ The synthesis and luminescence properties of the closely related neptunyl(vi)- and plutonyl(vi)-containing system obtained from the [GeW₉O₃₄]¹⁰⁻ entity in water were investigated later with the generation of a similar single $[Np^{VI}O_2]^{2+}$ or $[Pu^{VI}O_2]^{2+}$ unit encapsulated between two trivacant polytungstate species.⁶² In the case of the neptunyl(vi)-containing molecule, the authors were able to show the interest of the polyanionic moieties in preventing the water quenching over the $\{Np^{VI}O_2\}^{2^+}$ luminescence. 63 In addition to this property, the ((Np^{VI} or Pu^{VI})O₂)[GeW₉O₃₄]¹⁶⁻ sandwich-like compounds are rapidly formed in solution in a near-quantitative yield and were consequently considered for a potential utilization in actinyl cation separation. In 2002, a more complex system incorporating a hypothetical central core of three uranyl centers was identified when the {PW9O34} precursor was used. In this work, the synthesis was performed in an aqueous solution at pH 3.5. However, the observation was based on elemental analysis and electronic spectroscopy and the occurrence of the three uranyl-centered cluster was not structurally characterized by means of the single-crystal XRD technique.⁶⁴ Later, in 2011, an interesting star-like molecule was synthesized by Mohadeszadeh, starting from the [A- $AsW_9O_{34}^{9-}$ polyanion.⁶⁵ He was able to structurally characterize an octahedral macromolecule [(NH₄)₁₂(U^{VI}O₂(H₂- $O)_{12}(AsW_9O_{34})_6]^{18-}$ for which the six trivacant $\{AsW_9O_{34}\}$ polyanionic moieties occupy the nodes in an octahedral

geometry fashion, allowing the encapsulation of twelve uranyl centers. The uranyl centers (organized in two trimers, bridged by μ^2 -OH ligands, and six monomers in a pentagonal bipyramidal geometry) are localized on the face of the octahedral architecture. This molecular association appears to be stabilized by the presence of twelve ammonium cations located within the octahedral cavity. Electronic spectroscopy was performed showing a classical $O \rightarrow U^{VI}$ charge transfer band at 428 nm, indicating a weakening of the $U^{VI} = O_{yl}$ bonds due to the strongly coordinating oxygen atoms of the vacancies of the polyanion. The $U^{VI} = O_{yl}$ bond distances are in the usual range of 1.70(3)-1.80(3) Å and thus appear unaffected by the coordinative environment.

(c2) $[B-X^{III}W_9O_{33}]^{n-}$ and $[B-X^VW_9O_{34}]^{n-}$ -type polytungstate anions. The polyanionic family containing central heteroatoms with a lone electronic pair, such as As^{III}, Sb^{III} or Bi^{III}, has been particularly intensively explored not only with transition elements but also with the uranyl(vi) cation. However, fewer structural characterizations were investigated using tetravalent uranium cations. The literature shows that the [XW₉O₃₃]ⁿ⁻ polyanion has been successfully complexed with hexavalent uranium to form various structural entities, with a large diversity of the central X heteroelement, such as As^{III}, Sb^{III}, Bi^{III}, Se^{IV} and Te^{IV}. The resulting polyanionic entities were obtained as sandwich-like molecules $[(U^{VI}O_2)_2(H_2O)_2(XW_9O_{33})_2]^{n-}$ (with X = Sb^{III} or Bi^{III}, n = 14 and X = Te^{IV}, n = 12) with a C_{2v} symmetry for which the two uranyl atoms are present as monomeric centers.⁶⁶ When the [As^{III}W₉O₃₃]⁹⁻ precursor is used, a distinct polyanionic entity is isolated with the assembly of three polyanionic units, for which two of them are reorganized in [As^{III}W₈O₃₀]⁹⁻ entities linked by one tungsten center. The three uranyl groups, possessing a classical pentagonal bipyramidal coordination geometry, are bridging the three polyanionic moieties on four of their equatorial positions, the fifth one being linked to a water molecule.⁵⁴ With X = Sb^{III} or Bi^{III}, the B-[XW₉O₃₃]⁹⁻ polyanions were successfully assembled in two molecular species encapsulating the pentavalent form $\{Np^{V}O_{2}\}^{+}$ of the neptunyl cation groups.67,68 In both polyanionic moieties, the three monomeric neptunyl centers are linked to a central $\{W_4O_{15}\}$ group sharing an oxygen atom to form the $[(Np_3^VW_4 O_{15}$)(H₂O)(XW₉O₃₃)₃]¹⁸⁻ compound (Fig. 9).



Fig. 9 (a) Structural representation of the compound $[(Np_3^VW_4O_{15})(H_2O)(XW_9O_{33})_3]^{18-}$ and (b) highlight of the central $[Np_3^VW^4O_{15}]^{9+}$ unit showing the $Np^V\!\!=\!\!O_{yl}\!-\!W^{Vl}$ interaction.

Highlight



Fig. 10 Structural representation of (a) $[(As^{III}W_9O_{33})_3(OAc)_2(U^{IV})_{5.5}(\mu^3-OH)_4(\mu^3-O)_4O(U^{VI}O)_{0.5}]^{19-}$, (b) $[(As^{III}W_9O_{33})_3(U^{VI}_3(U^{VI}O)_3)(\mu^3-OH)_4(\mu^3-O)_4]^{15-}$ and (c) $[(As^{III}W_9O_{33})_4(U^{IV})_6(\mu^3-OH)_4(\mu^3-O)_4]^{24-}$.

This $\{Np_3^VW_4O_{15}\}\$ block appears to be unique in the actinyl-polyanion molecular chemistry as it reports the existence of a particular $Np^V = O_{yl} - W^{VI}$ bonding (so-called cation-cation interaction)⁶⁹ that takes place between the three Np(v) centers (pentagonal bipyramidal geometry) with one octahedral $\{W^{VI}O_6\}\$ unit. The $Np=O_{yl}$ distances appear impacted by this interaction and are elongated (Np-O distance of 1.99(3) Å) in comparison with the uncoordinated shorter *trans*- O_{yl} atom (Np-O distances of 1.833(17) Å). In the same way, the central $\{WO_6\}\$ atom presents three elongated W-O distances of 2.03(3) Å to 2.05(3) Å when interacting with the neptunyl oxygen atoms and three shorter ones (W-O distances of 1.77(3) Å to 1.87(3) Å).

On the other hand, the fewer structural reports dealing with the use of uranium(IV) were first investigated in 2001 by using the tri-lacunary [Sb^{III}W₉O₃₃]⁹⁻ polyanion.⁷⁰ In the latter, the uranium(IV) atoms are found in a trinuclear subunit between two Sb^{III}-polytungstate precursors, with the resulting sandwich-like compound of an assumed formula [U₃^{IV}(Sb^{III}W₉- O_{33}]₂]⁶⁻. Spectroscopic evidence shows an interaction between the uranium(IV) cation and the Sb^{III}-polytungstate polyanion based on the shifts of the precursor v_{as} (W-O_{b,c}-W), $v_{as}(W=O_d)$ and $v_{as}(W-O_a)$ vibrations, but no single-crystal XRD structural data were obtained to confirm the formula assessment and the molecular arrangement of the system. Nevertheless, the [As^{III}W₉O₃₃]⁹⁻ polyanion was successfully used to complex uranium(n)-based hexanuclear clusters in the presence of an acetate buffer at pH 4.5 in aqueous solution (Fig. 10).⁷¹

Three distinct molecular species, $[(As^{III}W_9O_{33})_3(OAc)_2$ - $\begin{array}{l} (U^{IV})_{5.5}(\mu^3\text{-}OH)_4(\mu^3\text{-}O)_4O(U^{VI}O)_{0.5}]^{19^{-}}, \ \left[(As^{III}W_9O_{33})_3(U_3^{IV}(U^{VI}O)_3)\right] \\ (\mu^3\text{-}OH)_4(\mu^3\text{-}O)_4]^{15^{-}} \ and \ \left[(As^{III}W_9O_{33})_4(U^{IV})_6(\mu^3\text{-}OH)_4(\mu^3\text{-}O)_4\right]^{24^{-}}, \end{array}$ were thus structurally characterized. The first one crystalizes after a few hours and the second system then appears when the crystallization solution is left under air overnight. These first two molecules stabilize hexameric clusters with three {As^{III}W₉O₃₃} moieties. Interestingly, the hexameric cluster is composed of uranium centers at two different oxidation states. In the first compound, the hexanuclear core consists of one uranium center, substitutionally disordered between a tetravalent center and a hexavalent one, while in the second molecule, three uranium cations are at the tetravalent oxidation state and the other three are at the hexavalent one. The last compound of this series is obtained by decreasing the acetate buffer concentration and stabilized a "classic" purely uranium($_{IV}$) hexanuclear {U₆^{IV}O₄(OH)₄} brick. Very recently, the use of a trivacant analog polyanion, $[As^{V}W_{9}O_{34}]^{9-}$, with thorium(w) led to the formation of a complex molecular compound $[K_4{Th_3^{IV}(H_2O)_3(As^VO(\mu^2 - M_2O)_3(As^VO(\mu^2 - M_$ O_{3}_{2} { $Th_{3}^{IV}(H_{2}O)_{2}(As^{V}O(\mu^{2}-O)_{3})_{2}$ }{ $(As^{V}W_{10}O_{38})_{6}$ }³⁸⁻ defined from the octahedral arrangement of the As^V-polytungstate units. In this molecule, six divacant [As^VW₁₀O₃₈]¹¹⁻ entities, coming from the reorganization of the arsenicotungstic precursor $[As^{V}W_{9}O_{34}]^{9-}$, are connected to four $\{Th_{3}^{IV}As_{2}^{V}O_{n}\}$ (*n* = 25 or 26) groups (Fig. 11). Furthermore, four potassium cations appear to be embedded within the resulting cavity formed by the inorganic moiety. The latter might play a templating role, favoring the crystallization of this compound.⁷² SAXS measurements were performed on dissolved crystals of this molecule in aqueous solution. A shift between the experimental scattering data and the modelled curve clearly indicates that the molecular assembly is decomposed in aqueous solution, resulting in the generation of a simple 1:2 sandwich-like compound, which would imply two monovacant polytungstates [As^VW₁₁O₃₈]¹¹⁻ encapsulating one eight-fold coordinated thorium center.

(c3) The $[P_2W_{15}O_{56}]^{12-}$ polytungstate anion. The trivacant polyanions derived from the Wells–Dawson archetype have been relatively much less studied than their Keggin



Fig. 11 (a) Structural representation of the $\{Th_2^{V}(As^{V}W_9O_{34})_6\}$ molecular system, (b) SAXS analysis (dashed curve) and modelling (full line) of a solution of $\{Th_{12}^{V}(As^{V}W_9O_{34})_6\}$ in water using the structural model of the $\{Th_{12}^{V}(As^{V}W_9O_{34})_6\}$ system and (c) modelling (full line) considering a 1:2 sandwich-like compound. Reprinted with permission from *European Journal of Inorganic Chemistry*, 2019, 42, 4500–4505 (ref. 72). Published by John Wiley and Sons.

counterparts. Surprisingly, only the tri-lacunary $[P_2W_{15}O_{56}]^{12-}$ derivatives have been used with actinide elements. This polyanion possesses the same type of vacancy as encountered in the B isomer of the $[\alpha$ -PW₉O₃₄]⁹⁻ unit. The use of the uranyl cationic group with the Wells–Dawson trivacant unit, in a 3:2 stoichiometry, gave rise to the formation of the $[(U^{VI}O_2)_{12}(\mu^3-O)_4(\mu^2-H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$ entity with four $[P_2W_{15}O_{56}]^{12-}$ units organized around a T_d symmetry (Fig. 12).⁷³

The twelve uranyl cations, with a typical pentagonal bipyramidal geometry, are linked to each other in four independent $\{(U^{VI}O_2)_3O(H_2O)_3\}$ μ_3 -oxo-centered trinuclear bricks. Solution studies using ³¹P NMR spectroscopy in water give the expected two-line spectra (with chemical shifts of –2.95 ppm and –13.58 ppm), confirming the existence of the molecule in aqueous solution. Interestingly, the use of a mixture with a $3U/1P_2W_{15}$ stoichiometry reveals a two-line NMR spectrum with different chemical shifts (also affected by the pH) compared to those found in the T_d -symmetry-based original macromolecule. It probably indicates the presence of other $\{U^{VI}O_2\}$ – $\{P_2W_{15}O_{62}\}$ configurations in aqueous solution.

For now, the syntheses using actinide(IV) only lead to the formation of a molecule with a suggested $[(U^{\rm IV}O)_3({\rm H_2O})_6({\rm P_2-W_{15}O_{56}})_2]^{18^-}$ chemical formula isolated as a sodium salt. This species was characterized by elemental analysis and spectroscopic solution studies showing the adsorption band related to $U^{\rm IV} \rightarrow W^{\rm VI}$ charge transfer, but no structural analysis has yet confirmed its solid-state organization. 55

(d) Cryptand heteropolytungstate anions. Cryptand species like $[As_4W_{40}O_{140}]^{28^-}$, $[P_8W_{48}O_{184}]^{40^-}$ or the Preyssler anion $[P_5W_{30}O_{110}]^{15^-}$ are all derived from the previous polyvacant polyoxometalates. Their utilization introduces an alternative way in terms of complexation of actinide elements. Indeed, the occurrence of specific complexation sites within these cryptand molecules may offer a better controllable route to encapsulate actinide cations.

(d1) The $[P_5W_{30}O_{110}]^{15-}$ phosphopolytungstate anion. The $[P_5W_{30}O_{110}]^{15-}$ molecule was first discovered in 1970 with the erroneous formulation of the $\{P_3W_{18}\}$ type and was finally structurally characterized in 1985.^{74,75} It exhibits a cryptand configuration, described as a cyclic arrangement of five [PW₆O₂₂]³⁻ hexavacant entities derived from the Keggin structure, resulting in a central cavity. A sodium cation and a water molecule (which was discovered later by reexamination of the structure) lie within this inner void, centered on the five-fold symmetry axis of the molecule.⁷⁶ The non-labile Na⁺ cation can be removed using hydrothermal treatment in order to insert other metallic elements of approximately the same radius (~ 1 Å). By this way, actinide elements like uranium($_{IV}$), and later thorium(IV), americium(III) and curium(III), could be trapped within the cavity.77,78 The final actinide/POM ratio was one An(III or IV) to one $\{P_5W_{30}O_{110}\}$ species. Electrochemical studies on these molecular systems reveal that the presence of the actinide cation (Th $^{\rm IV}\!\!,\,{\rm Am}^{\rm III}$ or ${\rm Cm}^{\rm III}\!\!)$ within the $\{P_5W_{30}O_{110}\}$ cavity modifies the reduction potential of the tungsten(vi) centers of the polyanion, in comparison with the precursor {Na@P5W30O110}. This indicates that the sodium cation can be effectively exchanged with the various tetravalent elements mentioned above. Nevertheless, the cationic exchange of the central sodium atom with other elements is rather difficult, since a hydrothermal reaction at a temperature of 203-204 °C for 100 hours is required and this makes it particularly unpractical for a potential application in the separation of actinide elements.

(d2) The $[As_4W_{40}O_{140}]^{28-}$ arsenatopolytungstate anion. The $[As_4W_{40}O_{140}]^{28-}$ macromolecule was structurally identified in 1980.⁷⁹ It consists of four {As^{III}W₉O₃₃} fragments linked by four *cis*-di-oxo WO₂ subunits to generate a distorted cyclic tetrameric



Fig. 12 Structural representation of $[(U^{VI}O_2)_{12}(\mu^3-O)_4(\mu^2-H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$.



Fig. 13 Structural representation of the $[As_4W_{40}O_{140}]^{28-}$ showing the S_1 and S_2 complexation sites.

architecture with a global D_{2d} symmetry. The ring-like species possesses two types of coordination sites denoted S_1 and S_2 (Fig. 13) that can bind various alkali and alkaline earth elements or transition metals and lanthanides, respectively.⁸⁰

The reaction of $[As_4W_{40}O_{140}]^{28-}$ with $[UO_2]^{2+}$ uranyl cations has been performed and has given rise to a distinct molecular entity $[(U^{VI}O_2)_3(H_2O_6(W_3O_6)(AsW_9O_{33})_3]^{15-}$ due to decomposition of the cyclic precursor at pH 4. The latter is characterized by a C_{3v} symmetry showing the presence of three trivacant units stabilizing three isolated uranyl centers. An analogous molecule but with one lacking a tungsten center in the linking (W_3O_6) trimeric fragment was isolated at pH 7 to be $[(U^{VI}O_2)_3(H_2O)_5(W_2O_5)(AsW_9O_{33})_3]^{19-}$. This molecule remains reactive and addition of vanadium(v) was successfully performed on this vacancy.⁸¹ Thermal treatment at 725 °C under nitrogen performed on the $[(U^{VI}O_2)_3(H_2O)_6(W_3O_6)(AsW_9O_{33})_3]^{15-}$ ammonium salt leads to the formation of a tungsten bronze mixed oxide $U_{\sim 0.1}WO_3$. It was therefore noticed that the insertion of uranyl cations into the [As₄W₄₀O₁₄₀]²⁸⁻ species has been unsuccessful up to now from a direct reaction route. Comparatively, the interaction with uranium(IV) salts has been attempted by several research groups. In the first study in 1996,⁸² it was suggested that two octahedrally coordinated uranium atoms were incorporated within the cryptand but no structural investigation could confirm such an assessment. In 2002, a study of the mixture of different concentrations of uranium(IV) and [As₄W₄₀O₁₄₀]²⁸⁻ was undertaken in aqueous solution and showed that up to four uranium(IV) atoms could be incorporated within the cryptand-like molecule.

However, an important structural disorder related to the uranium(IV) positions has prevented a proper structural determination.⁵⁴ It was finally reported that a reaction of the uranium(w)/[As₄W₄₀O₁₄₀]²⁸⁻ solution with guanidinium chloride gave rise to the formation of the unexpected uranyl-containing molecule [Na(U^{VI}O₂)₃(µ-OH)(H₂O)₆(WO)As₄- $W_{40}O_{140}$ ¹⁸⁻. The oxidation reaction of uranium(w) into uranyl(vi) species was thus observed together with the addition of $\{WO\}$ units attached to the $\{As_4W_{40}O_{140}\}$ original core. The challenging investigation involving uranium(IV) was finally described in 2018 by Dufave et al.83 By systematically studying an addition of uranium(IV) varying from 1 to 10 equivalents per cryptand molecule, they were able to isolate three different crystal structures deriving from the $[As_4W_{40}O_{140}]^{28-}$ moiety. The first one was actually previously studied by Pope et al. and characterized by the occurrence of the disorder for uranium(IV) at the central "S2"-type sites. It was resolved with the presence of two uranium(IV) centers statistically located at the four S₂ complexation sites with an occupancy factor of 0.5. The other two crystal systems were found to incorporate either two or four uranium(iv) atoms located at the S₂ sites in an ordered manner. The ability of the $[As_4W_{40}O_{140}]^{28-}$ cryptand to selectively bind uranium cations was further explored with a Nd^{III}/U^{IV} mixture in the presence of cesium in order to favor their precipitation from the aqueous solutions. Surprisingly, the neodymium(III) cations were specifically complexed instead of the highly charged uranium(IV), opening an interesting route for the separation investigations of trivalent and tetravalent actinide mixtures.



Fig. 14 Schematic representation of the aggregation process (blackberry form) occurring upon dissolution of the $\{(U^{VI}O_2)_{7,2}P_8W_{48}O_{184}\}$ molecular polyanion. SAXS measurement (red and orange dots) showing the aggregation process is presented on the right. The black curve corresponds to the modelling based on the crystal data from the molecular $\{(U^{VI}O_2)_{7,2}P_8W_{48}O_{184}\}$ species alone.

(d3) The $[P_8W_{48}O_{184}]^{40-}$ polytungstate The anion. $[P_8W_{48}O_{184}]^{40-}$ wheel was first structurally described by Contant and Tézé in 1985 (ref. 7) and its complexation properties have been studied with several transition metals.⁸⁴⁻⁹² However, it was observed that it remains quite difficult to insert additional cationic species due to the presence of strongly anchored potassium cations coming from the chemical composition of the $K_{28}Li_5[H_7P_8W_{48}O_{184}]$ ·92H₂O precursor salt. As far as we know, there has been no literature report about the interactions of actinides with this macromolecule before the end of 2018. One can mention an approaching study with the isolation of the compound $[LiK_4(H_2O)_4\{(U^{VI}O_2)_4(\mu - O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]^{25-}$ obtained in 2008 by Kortz et al. from a slightly different synthetic strategy using the $[H_6P_4W_{24}O_{92}]^{18-}$ precursor (see section 4 below). Direct use of the $[P_8W_{48}O_{184}]^{40-}$ macrocycle with uranyl cations was first described by Duval et al. at the end of 2018.93 The compound was synthesized using hydrothermal treatment at pH 3.5 in the presence of formate ligands and LiCl to insert a maximum of 7.2 uranyl groups per $\{P_8W_{48}O_{184}\}$ unit on the periphery of the cavity. The uranyl centers appear to be highly disordered on two independent crystallographic sites with occupancy factors of 0.25 and 0.65 for the directly interacting uranyl with the $\{P_8W_{48}O_{184}\}$ core and for the neighboring one, respectively. Once dissolved in aqueous solution, SAXS and TEM studies show the good stability of the uranyl-containing phosphopolytungstate anionic moiety. Also pointed out was an interesting supramolecular aggregation process of these species in the form of spherical blackberry organization with a diameter of approximately 260 Å (Fig. 14). This particular aggregation was previously reported in a closely related system with a 20center copper cluster inside the cyclic precursor.94

One year later, Koronev *et al.* published two similar systems, $[(U^{VI}O_2)_7P_8W_{48}O_{184}]^{26-}$ and $[(U^{VI}O_2)_8P_8W_{48}O_{184}]^{24-}$, also incorporating a uranyl cationic group starting from the classical $K_{28}Li_5[H_7P_8W_{48}O_{184}]\cdot 92H_2O$ and the more recent $Li_{17}(NH_4)_{21}[H_2P_8W_{48}O_{184}]\cdot 85H_2O$ precursors, respectively.^{7,95,96} These two molecules were obtained at lower pH values (pH 1.5) and the crystallographic positions of the uranyl groups were determined to be close to those already observed in the first report.⁹³ The two compounds are stable once dissolved in water, and electrochemical studies apparently show the irreversible reduction of $\{U^{VI}O_2\}^{2+}$ groups into U^{IV} at a potential of -0.31 V (*vs.* As/AgCl).

Until now, the association of the $\{P_8W_{48}O_{184}\}$ macrocycle with the uranium(v) cation or with other actinide/actinyl groups has not been described in the literature.

4. Other chemical systems

In this review, we also have to mention other polyanionic molecules obtained with non-classical synthetic methods and derived from the previously described systems. For instance, Kortz's team obtained an interesting horseshoe architecture using uranyl cations and peroxide-type oxygen groups in the presence of the half-unit $[H_6P_4W_{24}O_{92}]^{18-}$ from the $\{P_8W_{48}\}$ macrocycle.⁹⁷ The resulting compound is constructed around the *in situ* formation of a $\{P_8W_{36}\}$ horseshoe-like polyanion incorporating two uranyl-centered $\{(U^{VI}O_2)_4(O_2)_4(H_2O)_2\}$ tetramers decorated with four peroxo ligands (Fig. 15).

The uranyl groups have a classical hexagonal bipyramidal geometry with two *trans*-dioxo atoms with typical short bond lengths of 1.73 Å to 1.83 Å. Four potassium cations directly connect these two peroxo-uranyl-based tetramers and are capped either by a lithium or a potassium additional cation. This molecule was also studied in aqueous solution, revealing its stability but also a slow exchange (on the NMR timescale) between the two hanging phosphates and "free" phosphates.

Another interesting class of molecular system was discovered in 2005 by Peter C. Burns et al.98 This research team specialized in the synthesis of the well-known actinyl (uranyl or neptunyl) peroxo cage clusters prepared in alkaline solution.⁹⁹ Later in 2012, they successfully synthesized uranylperoxide assemblies interacting with either polytungstate or polymolybdate entities. The interest is to work under more basic peroxide conditions, while polyanionic entities are mainly obtained in solutions below pH 7. In 2012, they obtained, at pH 8.8, a wheel-shaped molecule $[\{W_5^{VI}O_{21}\}_3]$ $O_2_2(\mu - O_2)_{3}^{30^{-}}$ as a mixed sodium-lithium salt. The uranyl centers in this molecule possess a hexagonal bipyramidal geometry with classical U=Ovl bond lengths of 1.8 Å. The {W₅O₂₁} subunit is composed of one square-pyramidal {W^{VI}O₅} tungsten atom surrounded by four octahedrally coordinated {W^{VI}O₆} atoms. These oxo-tungstic groups are alternated with uranyl peroxo dimers to form the molecular wheel.¹⁰⁰ Later, an alternative approach was successfully performed by using Keggin-type phospho-polyoxometalates (instead of [WO₄]²⁻ tungstate precursors) associated to uranyl and hydrogen peroxide at a pH of around 6. Six hybrid uranium-transition metal-peroxo cage clusters were isolated: the uranyl-peroxo polyhedra interact with monomers of tungstate or molybdate (depending on the precursor used) in which the uranium-transition metal nuclearity goes from $\{U_8^{VI}W_2P_{12}\}$ to $\{U_{50}^{VI}W_6P_{20}\}$ for tungsten-containing cages and from $\{U_8^{VI}Mo_4P_{12}\}$ to $\{U_{44}^{VI}Mo_2P_{16}\}$ for molybdenum ones. The somewhat great number of phosphor atoms comes from the addition of H₃PO₃ in the various syntheses.¹⁰¹ For all the molecules, the uranyl centers adopt the typical coordination environment with a hexagonal bipyramidal geometry. Here,



Fig. 15 Structural representation of the horseshoe complex $[\{(U^{VI}O_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2(P_6W_{36}O_{136})]^{30-}:$ (a) side view and (b) top view.

Table 1 Structurally characterized actinide-POM associations

Actinide cation	Binding polyoxometalate unit	Reference numbers
Th ^{IV}	$\{W_{-} \cap_{c_0}\}$	35
111	$\{PW_{i}=O_{i}\}$	52 53
	$\{XW_0O_{0,i}\}$ (X = Si ^{IV} , AS ^V)	58.72
	$\{P_{E}W_{20}O_{110}\}$	78
U^{IV}	$\{M_0, P_1, Q_2, H_2\}$	32
	$\{W_{\pi}O_{10}\}$	33
	$\{SbW_{17}O_{50}\}$	37
	$\{PW_{17}O_{61}\}$	52.53
U ^{VI}	$\{XW_{0}O_{34}\}$ (X = P ^V , Ge ^{IV} , Si ^{IV} , As ^V)	55, 56, 58
	{SbW ₉ O ₃₃ }	70
	$\{AsW_9O_{33}\}$	71
	$\{P_5W_{30}O_{110}\}$	77
	$\{As_4W_{40}O_{140}\}$	54, 82, 83
	${SiW_{10}O_{36}}$	54
	${XW_9O_{34}}$ (X = P ^V , Si ^{IV} , As ^V)	54, 59, 64, 65
	${XW_9O_{33}}$ (X = As ^{III} , Bi ^{III} , Te ^{IV} , Se ^{IV} , Sb ^{III})	54,66
	$\{P_2W_{15}O_{56}\}$	73
	$\{As_4W_{40}O_{140}\}$	81
	$\{P_8W_{48}O_{184}\}$	93, 95
	$\{P_4W_{24}O_{92}\}$	97
	$\{W_5O_{21}\}$	100
Np ^{IV}	$\{W_5O_{18}\}$	34
	$\{BW_{11}O_{39}\}$	38
	$\{PW_{17}O_{61}\}$	53
Np^{V}	${XW_9O_{33}} (X = Sb^{III}, Bi^{III})$	68
Np^{VI}	${XW_9O_{34}} (X = P^V, Ge^{IV})$	60-63
Am ^{IV}	${PW_{17}O_{61}}$	53
	$\{P_5W_{30}O_{110}\}$	78
Pu ^{IV}	${PW_{17}O_{61}}$	53
Pu ^{VI}	${GeW_9O_{34}}$	62
Cm ^{IV}	$\{P_5W_{30}O_{110}\}$	78

the originality of this geometry consists in the fact that two peroxo ligands on the uranyl groups are in a *trans*arrangement which is relatively rare in the uranyl peroxo cage family.¹⁰² Indeed, they are usually observed in *cis* configurations in most of Burns' uranyl peroxides cages. Interestingly, the transition metals inserted in the spherical uranyl peroxo clusters exhibit various coordination modes. They can be found as $[MO_3(OH)]^-$ (M = Mo or W) tetrahedra, $[WO_4(OH)]^{3-}$ square pyramids and $[WO_3(OH)_3]^{3-}$ octahedra. This shows the ability of these elements to be incorporated within the uranyl peroxo cages and may be stabilizing or constraining the occurrence of the *trans*-arrangement of the peroxo ligands around the uranyl centers.

5. Conclusion and remarks

Although polyoxometalate chemistry has been mainly devoted to the formation of systems incorporating 3d–4d transition metals or 4f lanthanide cations for various applications such as magnetism, luminescence or materials chemistry, the incorporation of actinide/actinyl cations within POM moieties has been much less explored. Indeed, the utilization of such materials for real applications remains quite complicated due to their intrinsic radiotoxicity. Only potential concepts such as their use in nuclear waste treatment by forming tungsten bronze for confinement or their coordination properties for the separation of heavy actinides (SESAME process) have been explored.¹⁰³ While some molecules have been studied, we could say from actual literature results that no real effort has been made to completely study the potentialities of such POM-actinide associations even if some research teams have started to regain interest in this topic (Table 1). The stabilization of tetravalent actinides by polyanions is relatively new and many chemical combinations still remain unknown, as well as with the actinyl cationic groups. Another strategy could lie in the addition of an organic ligand to the polyanion in order to modulate the condensation process of the actinide elements and to mimic their environmental behavior. This hybrid polyanion-organic linker approach was succinctly investigated with uranium(IV) elements and a little bit more exemplified with cerium(IV), which could be used as surrogate cations.^{58,104,105} Such associations would for sure give more structural versatility to the potential molecules and could provide a direction to new applications for these materials. Another class of rising systems in the polyanion domain is the so-called POMOF (polyoxometalate-based metal-organic framework) compounds, in which the polyanion serves as a node for the construction of the three-dimensional architecture in order to generate a MOF-like compound through spacer organic ligands. These molecules could thus serve as a trap for actinides, using actinide-POM as the node and, in addition, post modifications on the organic part could also help in complexing other actinides for trapping purposes. The chemical robustness of these systems could allow the emergence of new applications. For instance, a study on this topic showing a multi-purpose POMOF acting as a uranyl encapsulation for chemical and photocatalytic reduction of $\{U^{VI}O_2\}^{2+}$ in U^{IV} was recently published.¹⁰⁶

Conflicts of interest

There are no conflicts to declare.

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