CONCEPT

Covalency in Actinide Compounds

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Abstract: Covalency in actinides has emerged as a resounding research topic on account of the technological importance in separating minor actinides from lanthanides for spent nuclear fuel processing, and utilization of their distinct bonding properties has been realized as a route towards overcoming this challenge. Because of the limited radial extent of the 4*f* orbitals, there is almost no 4*f* electron participation in bonding in lanthanides; this is not the case for the actinides, which have extended 5*f* orbitals that are capable of overlapping with ligand orbitals, although not to the degree of overlap as in the *d* orbitals of transition metals. In this concept paper, we provide a general description of covalency in actinide compounds. After introducing two main approaches to enhance covalency, either by exploiting increased orbital overlap or decreasing energy differences between the orbitals causing orbital energy degeneracy, we show the current state of the field using several examples from the recent literature. We will conclude by proposing the use of actinide chalcogenides as a convenient auxiliary tool to study covalency in actinide compounds.

Introduction

Nuclear power is a rich source of energy that is capable of meeting society's ever-growing demand for abundant, low-carbon energy for the foreseeable future. The two major disadvantages of nuclear power use are related to the potential occurrence of accidents and the need for long-term storage of the spent nuclear fuel.[1] Risks of accidents at nuclear plants may be mitigated through further development of safety protocols and new types of fuels, e.g. accident tolerant fuels, while the long term storage of spent nuclear fuel relies on its separation into different waste streams and the creation of new stable host matrices for radionuclide sequestration. The PUREX process is commonly used for spent nuclear fuel reprocessing to remove uranium and plutonium, leaving behind a waste mixture that is composed of a wide variety of the elements, including minor actinides (all actinides in the waste except uranium and plutonium) and lanthanides.[2] Separation of the minor actinides from the nuclear waste can significantly decrease its level of radioactivity, reducing both thermal and radiation damage to the host matrices as well as facilitating the long-term storage of the waste. One way to dispose of highly active minor actinides, which exhibit high radioactivity as a result of the short half-lives of these elements and their daughter isotopes, is to transmutate them into safer isotopes using fast neutron reactors. Before the minor actinides can be disposed of, it is desirable to separate them from lanthanides, which can inhibit transmutation due to their high neutron capture cross sections. This makes separation of minor actinides, such as americium and curium, from lanthanides one of the major challenges in the currently utilized methods of spent nuclear fuel processing.

The difficulty in separating heavy actinides from the lanthanides stems from the similarity of their sizes and chemical properties.[3] Due to their localized nature, the core 4*f* electrons of the lanthanides make little contribution to chemical bonding with the surrounding atoms, and lanthanides exhibit predominantly +3 oxidation state chemistry.[4] In 5*f* electron systems, the valence electrons' behavior is more complicated and changes across the series. In the early actinides (U, Np, and Pu) the 5*f* orbitals extend far enough to participate in bonding, shaping the chemistry of these elements that exhibit species with predefined geometry, such as linear UO_2^{2+} and NpO_2^{+} cations. When crossing the actinide series, the 5*f* orbitals become more localized, and heavier actinides exhibit chemistry dominated by the trivalent state, very much like the lanthanide series. The similarity in size and oxidation states makes the design of ligands for minor actinide/lanthanide partitioning a difficult task, one that stands to benefit from exploitation of differences in their covalencies.

Covalency (and its opposite term, ionicity) often serves as an indication of bond strength in most classical non-f electron systems. While lanthanide cations are often considered as species that form predominantly ionic bonds with the ligand atoms, covalency in the actinide compounds is a much more complicated matter that continues to fuel debates over its nature in the current scientific literature.[5–7] There is a growing body of evidence that 5*f* orbitals participate in covalent bonding with the surrounding ligand atoms, and this matter has subsequently evolved from the particular topic of separation chemistry to a more fundamental research direction.[8] In this concept article, we briefly introduce covalency in 5*f* electron systems and the main challenges in its characterization. Intending this manuscript mainly for non-experts (there are a number of excellent reviews providing a more in-depth view on the subject[2,3,9]), we describe the general terms of chemical bonding in actinides, paying special attention to the roles of degeneracy of the energy states and orbital overlap in covalency. After discussing several, mostly organometallic, examples of the most recent studies in actinide covalency, we conclude by discussing potential routes of achieving covalent bonding in inorganic extended solids.

Covalency in actinide compounds

By definition, a covalent bond is created by the sharing of electrons between two atoms and concentrating electron density

between the two nuclei. The main features of a covalent bond are its directing nature, i.e. a strong preference for a predefined geometry for an atom forming covalent bonds, and high dissociation energies. The uranyl cation $[O{\equiv}U{\equiv}O]^{2+}$, which exhibits both of these features, is a good example of a covalently bound species from the realm of actinide chemistry. The participation of 5*f* orbitals in bonding promotes linear geometry of the uranyl cation (it is worth comparing to its 4*d* counterpart molybdenyl MoO_2^{2+}, which typically shows a significant deviation from linearity[10]). Short (about 1.79 Å[11]) U≡O bonds in the uranyl cations give rise to absorption bands in the infrared (IR) spectra of uranyl compounds at around 900 cm^{-1} for $\nu_{as}(UO_2)$, which serves as a good indication of their covalency (Figure 1).[12] Unlike the axial uranyl bonds, weaker ionic equatorial bonds (and therefore less covalent) are not observable in the mid-IR region. Therefore, most U(VI) compounds exhibit two sets of bonds, axial and equatorial, with predominant covalent and ionic contribution, respectively.

Covalency of a bond strongly correlates with the oxidation state of the metal atom. In general, the degree of covalency decreases as the oxidation state of the metal is decreased; good examples are U(IV) cations, which tend to form cubic (e.g. uraninite mineral) or irregularly shaped (most fluorides) polyhedra with long bonds of predominantly ionic nature. When reducing an actinide atom to the +3 oxidation state, the degree of covalency is decreased even further, and assessing bond covalency becomes even more challenging.[13] Furthermore, characterization of heavier actinides is intrinsically complicated; firstly, due to the actinide contraction (i.e. decreasing 5*f* orbital extension when traversing the actinide series) and therefore the unresolved role of 5*f* orbitals in bonding and, secondly, as a result of their radiotoxicity, which makes experimental manipulation with them very very demanding due to their short half-lives along with the great difficulties for many researchers to obtain such elements for their research program. This makes validation of the results more challenging as only limited number of laboratories have access to heavy actinides sources. This makes validation of the results more challenging as only limited number of laboratories have access to heavy actinides sources. Under these circumstances, computational methods assume significant importance in studying actinide complexes and overcoming experimental difficulties in working with them.[14] While there is a set of experimental techniques that provide valuable information on covalency in actinide compounds, the experiment is usually accompanied by computational data, which often provide better insights into the observed phenomena.

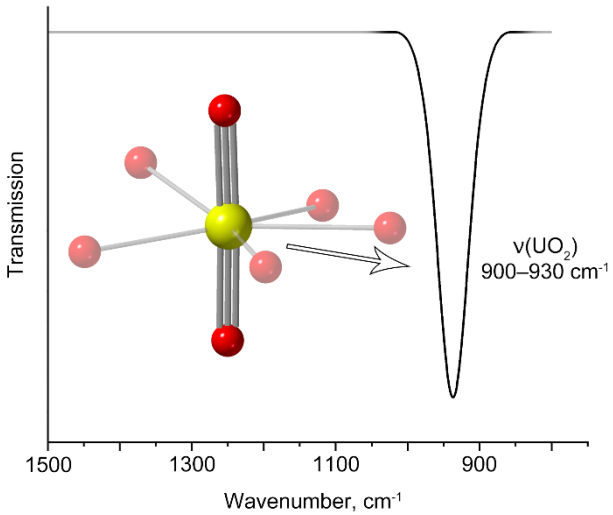

Figure 1. Schematic infrared spectrum of a uranyl-containing compound showing an absorption band at around 900–930 cm^{-1} that corresponds to antisymmetric stretching of the uranyl cation. The inset shows a pentacoordinated uranyl cation. The uranium atom forms multiple strong covalent bonds with the "-yl" O atoms, which give rise to the absorption band.

To assess covalency of a bond, it is helpful to assign a numeric value that is proportional to the degree of the covalent interaction. A convenient reference to covalency is the mixing coefficient λ, which can be expressed as:

$$\lambda = \frac{H_{ML}}{E_M^0 - E_L^0}$$

where H_{ML} is Hamiltonian matrix element between orbitals, which describes the overlap between the two orbitals, and E_M^0 and E_L^0 are orbital energies of the metal and ligand, respectively.[3] This equation suggests a seemingly clear route to inducing a more covalent bond by improving the orbital overlap and decreasing the energy difference between the orbitals, i.e. introducing orbital degeneracy. These two factors are independent but can compete with each other and covalency is usually driven by a combination of orbital overlap and orbital degeneracy. As a simplified example, one can consider a bond between a metal and O- or S-donor ligand. Due to the high electronegativity of the O atoms, there is a large energy gap between the metal and ligand orbitals, which serves to increase the magnitude of the denominator in the equation above and therefore minimizes the contribution to covalency from the orbital degeneracy factor. On the other hand, the smaller size of the oxygen atoms favors a larger orbital overlap, especially for π-bonds, thus increasing bond covalency through the orbital overlap factor. The opposite effect may be observed when a metal binds a S-donor ligand; in this case covalency may be dominated by orbital degeneracy due to a smaller difference in orbital energies rather than orbital overlap, which is typically lower for larger atoms. This concept is schematically depicted in Figure 2. Overlap stabilization can also be illustrated by comparing uranyl cation UO_2^{2+} with its hypothetical chalcogenide analogs US_2^{2+}, USe_2^{2+}, and UTe_2^{2+}. The uranyl cation is stabilized by orbital overlap between U and O atoms (due to the small size, O atoms achieve better overlap in π-bonding), while the chalcogenide counterparts would have much lower spatial overlap and therefore would not be stable. Indeed, there is no evidence of a contracted U=S bond in the solid state so far.

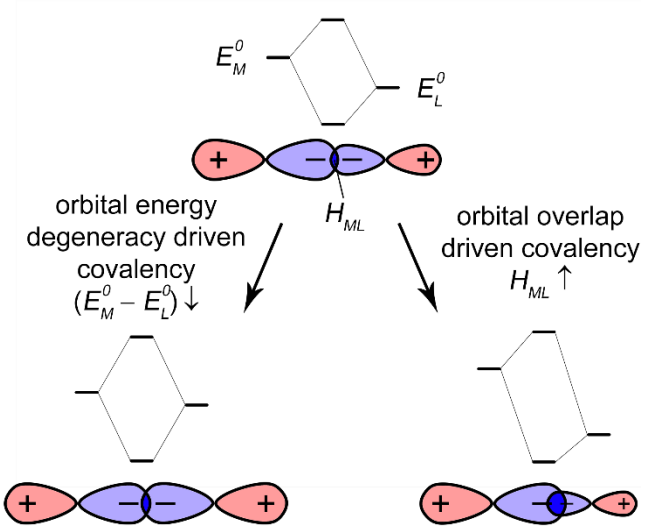

Figure 2. Representation of two major components that contribute to covalency of a bond: orbital energy degeneracy and orbital overlap. The former can be achieved by decreasing the orbital energy difference between the metal atom and a ligand atom though decreasing the ligand atom electronegativity. Enhanced orbital overlap can be achieved by the formation of multiple and/or short bonds with smaller atoms.

The overarching goal of the current research on actinide covalency is to develop principles that will enable us to design ligands with a controlled degree of covalency and ultimately with sufficiently high partitioning coefficients for selectivity of minor actinides in separations processes. This control requires an in depth understanding of the factors that govern contribution of orbital overlap and orbital energy degeneracy to covalency, which is the focus of most of the literature on this topic. In the following section we will illustrate the most recent advances in the field using several examples from the literature.

Covalency in Molecular and Organometallic Species

Chemists maintain traditional conceptual views on covalent bonding that are challenged by this notion of actinide covalency dictated by energy degeneracy as opposed to orbital overlap. While experimental techniques such as absorption spectroscopy provide effective means of probing metal-ligand bonding interactions, combining experimental approaches with computational efforts has contributed substantially toward fundamental understanding of the complexities of 5*f* systems. Such efforts are exemplified by the recent work of Su and coworkers, which investigated the actinide 5*f* and 6*d* contributions to An–Cl bond covalency in $AnCl_6^{2-}$ (An^{IV} = Th, U–Pu) anions via a comparison of ligand K-edge X-ray absorption spectroscopy (XAS) studies with DFT-calculated simulations of the XAS spectra across the series.[15] The clever selection of $AnCl_6^{2-}$, which adopts octahedral coordination geometry and is thus not subject to 6*d*/5*f* hybridization on account of selection rules, enabled the investigators to examine the individual orbital covalency contributions. It was revealed that while greater overall contributions to covalency were derived from the 6*d* orbitals, the 5*f* contribution increased from Th to Pu, opposite the expected trend based on reduced orbital overlap arising from the decrease in the 5*f* orbital radial extent. This result was reasoned through a consideration of perturbation theory, which establishes an inverse relationship between orbital mixing and the difference in energies between metal and ligand orbitals, indicating that in this case, orbital mixing was achieved by decreasing differences in energy between the An 5*f* and Cl 3*p* orbitals across the series from Th to Pu (Figure 3).

The ability to tune covalency as a function of ligand selection is an immensely valuable tool that can be applied to reveal fundamental differences in the electronic structures and bonding of the *f*-elements, which do not follow simple trends. In a recent report, Smiles and coworkers showed that cerocene, $Ce(C_8H_8)_2$, which is more appropriately described as Ce^{3+} coordinated by two $C_8H_8^{1.5-}$ ligands (Figure 4), participates in covalent bonding interactions between the C 2*p* and Ce 4*f* orbitals that are comparable to the degree of covalency exhibited by $U(C_8H_8)_2$.[16] This is a particularly intriguing finding considering the core-like nature of the 4*f* orbitals. Prior to this work, Minasian and coworkers performed a study that elucidated the orbital mixing of the partially occupied 5*f* and 6*d* orbitals in actinocene complexes of Th^{IV} and U^{IV} using carbon K-edge XAS and DFT methods.[17] Notably, in addition to the commonly recognized σ-, π-, and δ-bonding types, the investigators successfully identified intense transitions in the experimental XAS spectrum of $Th(C_8H_8)_2$ indicative of ϕ-orbital

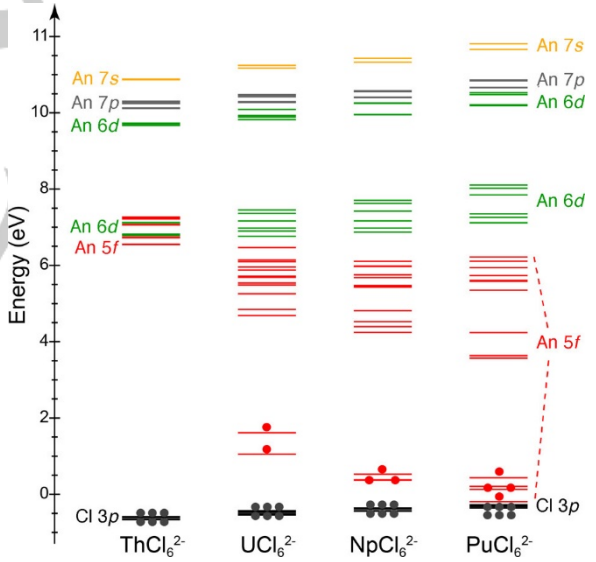

Figure 3. DFT calculated energy level diagram for $AnCl_6^{2-}$ complexes (An = Th, U, Np, and Pu). The energy of the An 5*f* orbitals decreases across the series, driving energy degeneracy covalency in the system. Reprinted with permission from reference [15]. Copyright 2018 American Chemical Society.

interactions, a rare form of bonding unique to the *f*-elements that had not previously been experimentally observed. It was determined that, contrary to the $AnCl_6^{2-}$ series, greater 5*f* orbital mixing was observed for $Th(C_8H_8)_2$ relative to $U(C_8H_8)_2$ on account of the suitable match in energies between Th 5*f* and $(C_8H_8)_2^{4-}$ orbitals and, correspondingly, the energy mismatch induced by the lowering of 5*f* energy levels in the U complex. Indeed, the ability to construct straightforward bonding generalizations among the actinides still eludes us, as is shown

in a recent study by the Bart group that sought to understand the bonding nature of a series of actinide DOPO-based complexes (An^{III} = Am–Cf ; $DOPO^-$ = 2,4,6,8-tetra-*tert*-butyl-1-oxo-1*H*-phenoxazin-9-olate, Figure 4) through a combination of techniques including absorption spectroscopy and electronic structure calculations.[6] Considering its ability to form highly covalent bonds in transition metal complexes, the redox-active $DOPO^-$ ligand was expected to enable covalent interactions in complexes containing the mid-actinide elements via energy degeneracy of the O and N 2*p* orbitals with the An 5*f* orbitals. However, the compounds were ultimately found to exhibit ionic bonding analogous to that of the isostructural lanthanide DOPO-based complexes.

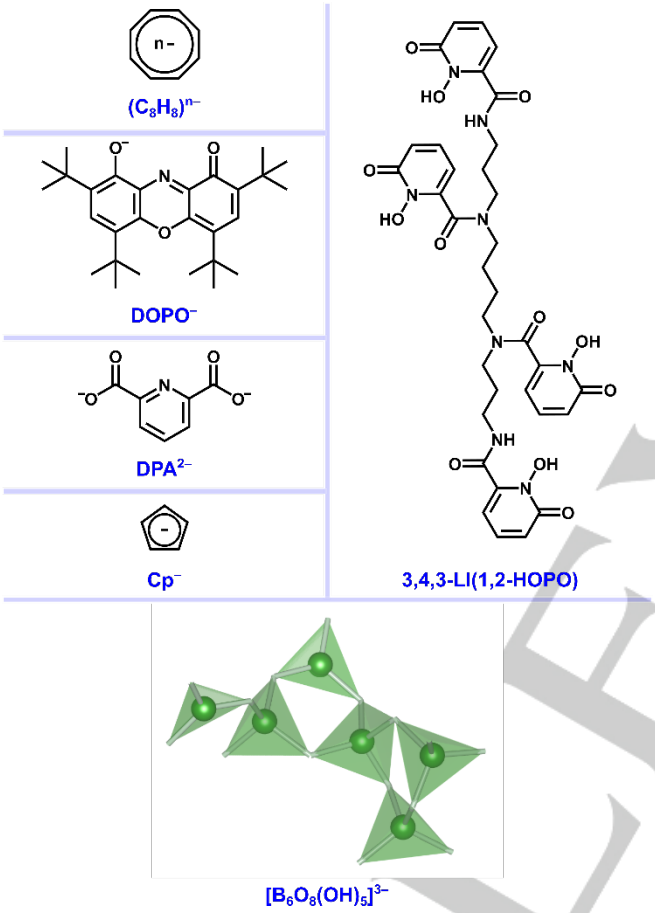

Figure 4. Structures of the ligands and inorganic building unit discussed throughout the text.

As an alternative approach to probe the covalency in actinide complexes, Kelley and coworkers examined the complexation behavior of a series of actinide dipicolinate (DPA^{2-}, Figure 4) complexes (An^{III} = Am–Cf) and through an assessment of their thermodynamic stability constants, the investigators effectively correlated an increase in the stability constants between Cm^{3+} and Bk^{3+} with enhanced An^{3+} 5*f* orbital bonding contributions in the actinide DPA-based complexes.[5] Electronic structure calculations provided an indication that this orbital mixing was facilitated by energy degeneracy with ligand orbitals rather than orbital overlap, an interpretation that was substantiated by the moderate differences in the measured stability constants as opposed to more significant differences that likely would have resulted in the case of orbital overlap. In a related computational study, Sadhu and Dolg used DFT to gain insight on how energy degeneracy driven covalency might be exploited to induce selective binding of Am^{3+} over Eu^{3+} via replacement of some of the hard donor O atoms with soft donor S atoms within the chelating ligand 3,4,3-LI(1,2-HOPO) (*N*,*N*'-(butane-1,4-diyl)bis(1-hydroxy-*N*-(3-(1-hydroxy-6-oxo-1,6-dihydropyridine-2-carboxamido)propyl)-6-oxo-1,6-dihydropyridine-2-carboxamide), shown in Figure 4.[18] The mixed hard-soft donor ligand was indeed determined to exhibit enhanced orbital mixing with Am^{3+} 5*f* orbitals in comparison to Eu^{3+} 4*f* orbitals on account of smaller metal-ligand energy differences. However, in this case covalency was induced at the expense of thermodynamic stability where the replacement of O, oxo group, with S resulted in reduced metal-ligand electrostatic interactions and hence, decreased metal-binding Gibbs free energies.

Although there are now a number of studies of actinides indicating that the lines between ionic and covalent bonding have indeed become blurred, the difference between covalent bonding driven purely by energy degeneracy versus that which involves an accumulation of electron density in the region between two bonded atoms remains, at least intuitively, less ambiguous. Serving as a cautionary reminder that computational results must be interpreted judiciously when investigating such effects, a report by Kaltsoyannis detailed the cases of $AnCp_3$ and $AnCp_4$ (An = Th–Cm, Cp = η^5-$C_5H_5^-$, Figure 4), finding them either to be increasingly more ionic or increasingly more covalent across the series depending on the computational method employed.[2] The results obtained from the investigator's application of the quantum theory of atoms-in-molecules (QTAIM), which had not been extensively utilized for actinides prior to this work, most reliably reproduced observed trends and highlighted the approach as a valuable tool for future computational studies. This conclusion was complemented by a recent computational investigation by Platts and Baker on the covalent bonding trends in $[UE_2]^{2+}$ (E = O, S, Se, and Te).[19] The investigators applied QTAIM analysis in conjunction with natural bond orbital and second-order perturbation analysis to show that while $[UO_2]^{2+}$ had the lowest bond order in comparison with the heavier chalcogenide analogs, which exhibited both smaller energy differences and enhanced sharing of electrons, the compromise between energy difference and orbital overlap was most favorable for the stabilization of the least covalent member of the series, $[UO_2]^{2+}$. In a broader context, this study demonstrates the merit in combining multiple computational methodologies to interpret and gain a more comprehensive bonding picture of 5*f* systems.

The soft donor approach to examining actinide covalency may be especially promising, where a combination of soft donor ligands and high oxidation state actinides could afford a valuable opportunity to tune covalency. The Mazzanti group has explored this possibility in their efforts to develop new synthetic routes to terminal uranium(V) sulfide complexes via metathesis reactions utilizing CS_2 or H_2S.[20] In pursuing routes to terminal sulfides rather than centrally bound sulfide groups, characterizations of the 5*f* contributions to U–S bonding may be more easily accomplished. Although the complexes in this study were found to have U–S covalent interactions arising from orbital overlap, it is interesting to contemplate how sulfide ligands might be utilized to induce energy degeneracy driven covalency in similar compounds containing heavier actinides. Overall, these examples show that not only is there immense fundamental value in

studying actinide species exhibiting non-classical covalency, it is also entirely feasible to do so through careful ligand selection that can be guided by computational analysis. Although currently there is no single generally accepted approach to ligand design, there exist numerous approaches to tune ligands for explorational studies. For example, the electronic structure of the ligand can be easily varied by the addition of electron donating or withdrawing groups, affecting the energy of the donor atoms and therefore the degeneracy and overlap between the ligand and metal atoms. Another strategy is to tailor the ligand's electronic structure by taking advantage of a given ligand's redox flexibility, i.e. withdrawing electron density to π^* orbitals. For example, this approach has been demonstrated successfully in the aforementioned case where DOPO can possess three charges, from –1 to –3. While there are certain benefits in using S as donor atoms, most research has focused primarily on O- and N-donor ligands. N-donor ligands are good candidates due to their softer nature compared to O-donor ligands, therefore promoting covalency and allowing their inclusion in heteroaromatic compounds, many of which are commercially available ligands with tunable denticity. A less studied alternative approach is the use of multidentate ligands with mixed donor atoms, which can be tuned by both the nature of the donor atom and the overall denticity of the ligand. The contracting radial extent of the 5*f* orbitals across the actinide series may present limitations to inducing covalent interactions with common ligands via orbital overlap. However, many of the examples discussed herein demonstrate that this limitation may be overcome by taking advantage of energy degeneracy-driven covalency, thereby providing a useful means to investigate the exotic bonding and electronic properties of these materials.

Studying Bonding in Inorganic Extended Structures

Organometallic complexes offer a convenient platform for studying covalency in actinide complexes, however, one can approach the same fundamental task from a different direction by using inorganic extended structures. Successful implementation of this approach has been demonstrated in recent years, where perhaps one of the most fascinating examples is that of the first Cf borate, $Cf^{III}[B_6O_8(OH)_5]$ (Figure 4).[21] In this study, the Albrecht-Schmitt group showed that the electronic properties of Cf(III) coordinated by highly polarizable polyborate anions were noticeably different from borate compounds of Pu(III) and Am(III), which also exhibit weak covalency driven by orbital overlap but do not exhibit changes in the behavior of their 5*f* electrons. The investigators' findings also indicated that the An(III) coordination can play a significant role in the properties of compounds.

Since there is not as much predictability of metal atom geometries in an extended solid-state structure, it is more challenging to achieve control over the covalency through orbital overlap. The orbital degeneracy, on the contrary, can be relatively easily tuned through the metal atom oxidation state and the nature of the atoms bound to it. To achieve higher covalency, one could take advantage of using a metal atom in its highest oxidation states to increase its electronegativity, and a "ligand" atom that has low electronegativity. Considering U as an example, one needs to achieve its highest +6 oxidation state while using low electronegative anions, such as sulfide or selenide, as counter-ions. At first glance this appears to be a relatively straightforward approach, however, it is indeed challenging to stabilize uranium in the +6 oxidation state in a sulfide environment due to the tendency of sulfides to reduce uranium from +6 to +4,[22,23] complicating the rational design of inorganic solid state materials with covalent An–Q bonding (An = actinide, Q = chalcogenide).

There are a handful of examples where uranium is stabilized in the +5 and +6 oxidation states in sulfides, including $A_6Cu_{12}U_2S_{15}$ (A = K, Rb, and Cs) and $K_2Cu_3US_5$ (Figure 5).[24–26] The $A_6Cu_{12}U_2S_{15}$ family was studied in detail by Ibers et al. and it was shown that these compounds, although containing uranium in the formal oxidation state of +6, are better described as a hybrid of $(A^+)_6(Cu^+)_{12}(U^{5+})_2(S^{2-})_{13}(S^-)_2$ and $(A^+)_6(Cu^+)_{12}(U^{6+})_2(S^{2-})_{15}$ oxidation state distributions. The reduced oxidation state of the uranium atoms was supported by magnetic susceptibility data, which showed a non-zero magnetic moment in all except one of the samples. After performing DFT calculations on the Rb-containing phase, the authors discussed the strong charge mismatch between the formal +6 oxidation state and the net volume oxidation states, which indicates a high covalent component in the U–S bonds within the US_6 octahedra of the structure. Moreover, the presence of antibonding f_{xyz} and $f_{z(x^2-y^2)}$

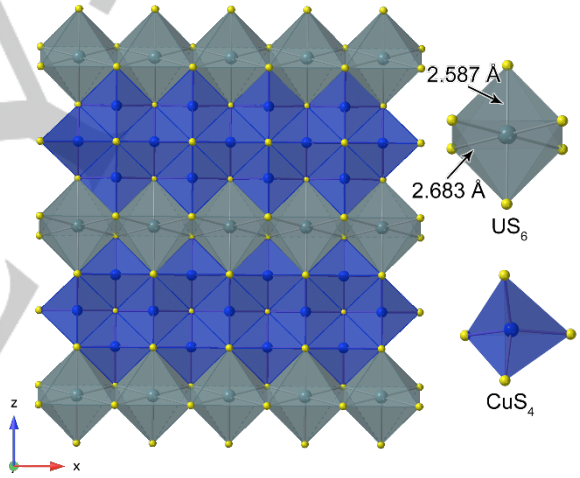

Figure 5. A view on the layers in $K_2Cu_3US_5$.[24] The uranium atoms in the formal +5 oxidation state adopt an octahedral coordination environment with rather short, 2.59 and 2.68 Å bond lengths.

orbitals at 0.6 and 0.9 eV above the Fermi level further suggests a strong covalent interaction between U and S atoms. This finding highlights a potential use of actinide chalcogenides as a promising class of compounds with which to study the covalency of 5f systems. Given that most of the chalcogenide phases with U(V) and U(VI) contain a d metal, often Cu and Ag, the most promising systems for exploratory crystal growth are the U–Cu–Q and U–Ag–Q (Q = S and Se) systems, which are highly suitable for creation of new compounds for studying covalency in actinide compounds and thus to shed light on the separation and isolation of the minor actinides.

Conclusion

Bonding in actinide complexes has attracted growing interest owing to challenges in minor actinide separation from lanthanides and fundamental interest in f orbital bonding. Given that 5*f* orbitals in actinides are not as localized as 4*f* orbitals in lanthanides, there exists 5*f* orbital driven covalency in the actinides, providing a tantalizing platform to study f orbital bonding. There are two main independent factors that drive covalency in complexes, orbital overlap and energy level degeneracy. In general, the orbital overlap is enhanced when a ligand containing atoms that are small in size is employed, whereas orbital energy level degeneracy can be achieved by using ligand atoms with lower electronegativity, which decreases when moving along the group in the Periodic table. Multiple recent studies discuss the source of covalency in actinide complexes, and although there persists a lack of complete understanding on how to control covalency in actinides, there is substantial work across both organometallic and inorganic fields that can eventually advance our understanding of this issue to the point where consensus is achieved.

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Keywords: actinides • covalency • complexes • extended structures

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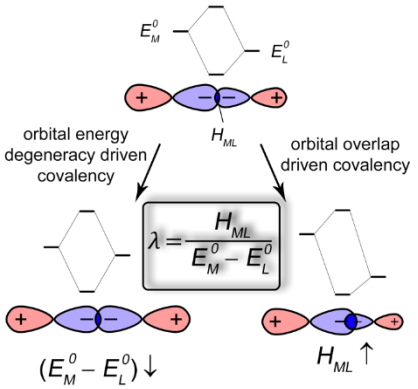
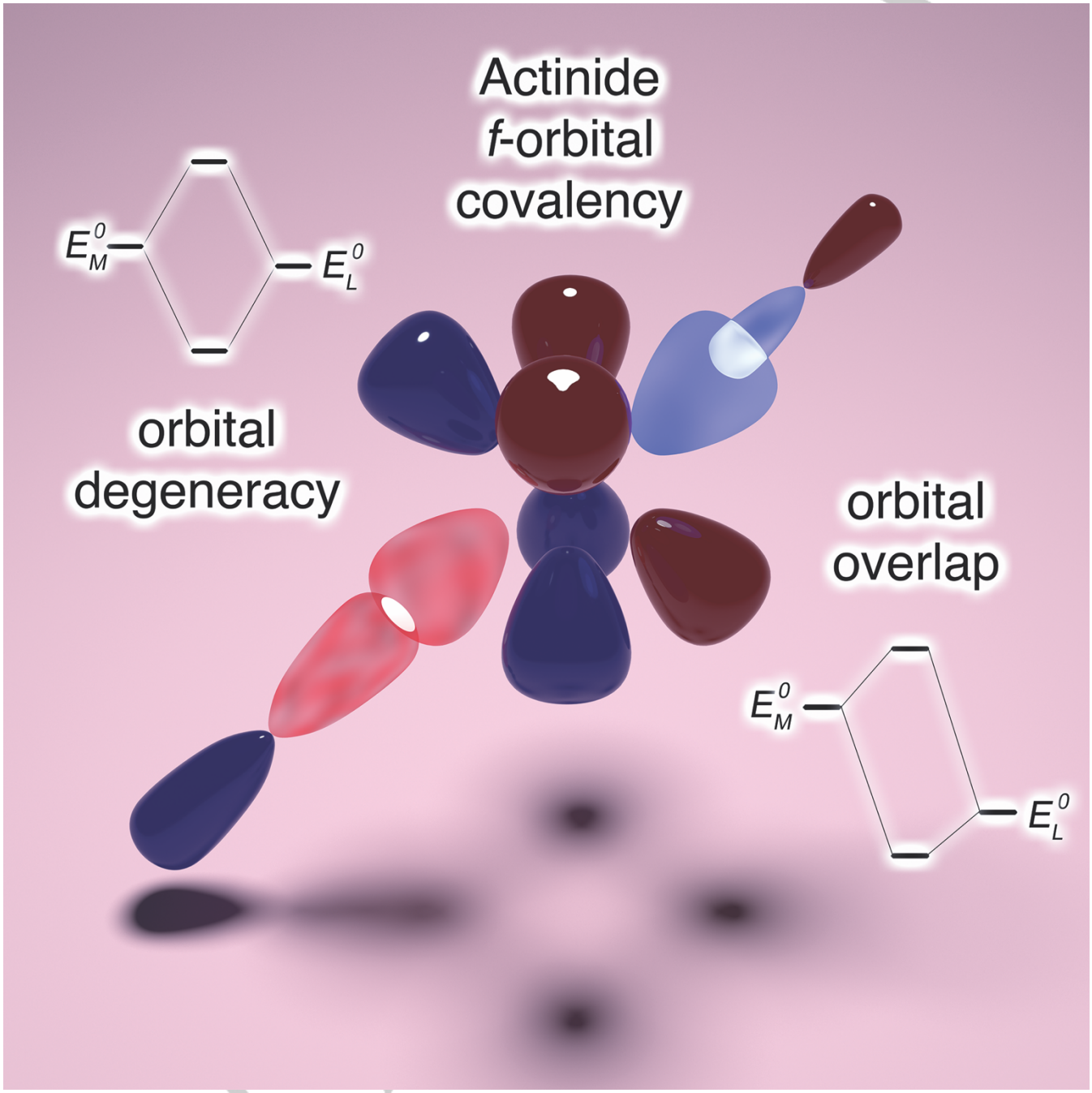
Entry for the Table of Contents



Organometallics Tricks for Actinide Extended Structures. Covalency in actinide complexes has long been studied for both fundamental interest and potential appication for minor actinides separation. In this concept, we introduce covalency in actinides and illustrate with several examples from current literature. We show that actinide chalcogenide extended structures may serve as auxillary platform for studying covalency.



Text for Fronts piece : This frontispiece illustrates two ways of achieving a higher degree of covalency in actinide compounds, one employing orbital energy degeneracy and the other employing orbital overlap between the 5f and ligand orbitals.