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Organometallic Neptunium Chemistry

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ABSTRACT

Fifty years have passed since the foundation of organometallic neptunium chemistry, and yet only a handful of complexes have been reported, and even fewer fully characterised. Yet increasingly, combined synthetic/spectroscopic/computational studies are demonstrating how covalently binding, soft, carbocyclic organometallic ligands provide an excellent platform for advancing the fundamental understanding of the differences in orbital contributions and covalency in f-block metal – ligand bonding. Understanding the subtleties are key to the safe handling and separations of the highly radioactive nuclei. This review describes the complexes that have been synthesised to date, presents a critical assessment on the successes and difficulties in their analysis, and the bonding information they have provided. Because of increasing recent efforts to start new Np-capable air-sensitive inorganic chemistry laboratories, the importance of radioactivity, the basics of Np decay and its ramifications (including the radiochemical synthesis of one organometallic) and the available anhydrous starting materials are also surveyed. The review also highlights a range of instances in which important differences in the chemical behaviour between Np and its closest neighbours, uranium and plutonium, are found.

Contents

1. Introduction

The first reported organometallic neptunium complexes are the cyclopentadienyl complexes Np(Cp)$_3$Cl and Np(Cp)$_4$ (Cp = η-C$_5$H$_5$),[1-3] and were made just a few years after the discovery of ferrocene, yet only a handful of complexes have been reported since, and even fewer fully characterised. The high radiotoxicity of Np compounds (which demands work on a small-scale) combined with restrictions on the availability of the metal (which is the most convenient preccursor to Np^{III} starting materials)[4] all compound the traditional difficulties associated with handling air-sensitive, highly paramagnetic organometallic early actinide complexes. The large number of valence orbitals and the effects of relativity mean that quantitative descriptions of the electronic structures for complexes of these large, relativistic, paramagnetic metals is still a matter of intense discussion. An understanding of the subtleties is key to the safe handling and separations of the highly radioactive nuclei, and will be crucial for the low cost, long-term management of the civil nuclear waste legacy and the development of geological repositories.[5-7]

Combined synthetic/spectroscopic/computational reports are demonstrating with increasing frequency how in the absence of protic and hydrolysable ligands and solvents, discrete molecular complexes in a variety of formal oxidation states, with covalently binding, organometallic ligands that form actinide-ligand σ-, π-, δ- and even ϕ-(back)bonding interactions provide an excellent platform for advancing the fundamental understanding of the differences in orbital contributions and covalency in f-block metal – ligand bonding.[8,9] For example, recent quantitative carbon K-edge X-ray absorption spectroscopy (XAS) analyses on the organometallic actinocenes An(COT)$_2$ (An = Th, U; COT = η-C$_8$H$_8$), provided the first experimental evidence for extensive ϕ-orbital interactions in thorocene (observation of a C1s to Th-C antibonding $2e_{3u}$ ($5f$–ϕ)), and remarkably little in the U analogue (where the interaction is more closely with the $2e_{2u}$)[10] providing an important caveat that different orbitals will not necessarily show the same trends in orbital mixing across the actinide series. [11] Different behaviour is seen again for the electronic structure of the recently published plutonocene derivative Pu(1,3-COT'')(1,4-COT'') (COT'' = η-C$_8$H$_6$(SiMe$_3$)$_2$).[12] Neptunium is also a very sensitive nucleus for Mössbauer spectroscopic studies of the electronic influences of ligand bonding on a Np cation.

Progress in anaerobic transuranic chemistry trails far behind that of uranium and thorium due to the limited number of appropriate radiological research facilities worldwide, scarcity of pure transuranic elements and a skills shortage, and the relative lack of Np studies compared to the other early actinides has been highlighted.[4] An excellent indicator for the progress of modern molecular chemistry are structurally characterized complexes added into the *Cambridge Structural Database* (CSD), as originally pointed out for single crystal structural determinations of plutonium complexes.[13] Figure 1 shows the small number of transuranic compounds (a), and even smaller number of organometallic derivatives (b) listed in the database, but includes some incomplete datasets so the real numbers are actually lower than presented.

This review sets out what is already known of neptunium's organometallic chemistry, highlighting how surprisingly different it can be from that of its neighbours, uranium and plutonium, and suggests what might be possible in the future from this metal cation that can exhibit so many oxidation states, such variable and high coordination numbers, and yet about which so little reaction chemistry is known yet.

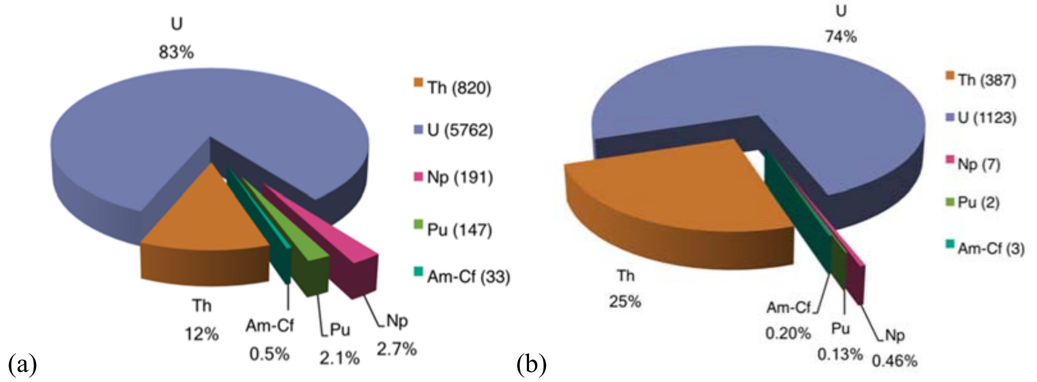


Figure 1. Pie-charts showing the fraction and number of structurally characterised actinide complexes in the Cambridge Structural Database (WebCSD, update 9th February 2017) ordered by: (a) element, (b) element entries that contain an An-C bond.

1.1 Synthetically important isotopes of neptunium

The only neptunium ($_{93}$Np) available on Earth is man-made since any primordial neptunium is no longer present. The element has twenty four radioisotopes;[14] the most stable are ^{237}Np ($t_{1/2} = 2.144(7) \times 10^6$ y), ^{236}Np ($t_{1/2} = 1.54(6) \times 10^5$ y) and ^{235}Np ($t_{1/2} = 396.1(12)$ d), whilst all the remaining have half-lives of under 4.5 days, with a majority below 50 min.[15] The longest-lived nuclide, ^{237}Np, has a half-life of 2117(24) times shorter than the age of the Earth thus no primordial neptunium is present today. This notwithstanding, accurate α-ray measurements of concentrated uranium ores allowed the direct detection of natural ^{237}Np at the maximum mass ratio to ^{238}U of 1.8×10^{-12}; the result of the neutron activation and decay products.[16] The isotope ^{237}Np is typically produced from the β decay of ^{237}U ($t_{1/2} = 6.749(16)$ d); spent commercial uranium fuel rods in about 0.03 % of the total material, and about 5 % of that of plutonium. Around 50 000 kg of the element is produced annually, in essentially pure from spent fuel via the PUREX (**P**lutonium **U**ranium **R**edox **E**xtraction) waste separation process.[17] The long half-life of ^{237}Np make it a major contributor to the total radiation dose remaining after spent civil nuclear waste has been stored for tens of thousands to millions of years. Additionally, if plutonium has not been recovered prior to disposal of waste then additional ^{237}Np will form from ^{241}Pu via α–decay, prolonging the long term radiotoxicity of the waste.

The complicated behaviour of Np in the PUREX process is a clear demonstration of the importance of the ability to understand and control the solution phase chemistry and speciation of neptunium. Neptunium ions cause problems in the PUREX separation process as the soluble, non-extractable neptunyl(VI) $[NpO_2]^{2+}$ and neptunyl(V) $[NpO_2]^+$ ions are in equilibrium with the extractable Np^{IV} resulting in a distribution of Np between the organic and aqueous phases.[18] This means that in the early stages of partitioning about 75 % of the initial Np content of the feed is co-extracted as $[NpO_2]^{2+}$ with the uranium (as U^{VI}).[19] It would be preferable to control its oxidation state to Np^{IV} so that it can be co-extracted with Pu(IV). The so-called 'pentavalent' form, $[NpO_2]^+$, is also more environmentally mobile than the other actinide 'yl' anions, posing further potential risks.[19,20]

1.2 Radiological concerns with handling neptunium

Compounds of ^{237}Np are more chemotoxic[20] than those of plutonium,[16] but significantly less radioactive (specific activities for α decaying isotopes: $a(^{237}\text{Np}) = 0.7\ \text{mCi} \cdot \text{g}^{-1}$ and $a(^{239}\text{Pu}) = 62.1\text{mCi} \cdot \text{g}^{-1}$). The ^{237}Np radioisotope shows primarily α emission ($Q\alpha = 4.958$ MeV). The accompanying γ-ray radiation is weak (29 and 86 keV) but ^{237}Np decays to ^{233}Pa ($t_{1/2} = 26.97$ days, $a = 21\ \text{kCi} \cdot \text{g}^{-1}$), which in turn is a potent β emitter ($Q^{-} = 0.570$ MeV) and a strong γ-ray emitter. After approx. 189 days (7 half-lives) the concentration of the ^{233}Pa daughter approaches 34.6 ppb, increasing the equivalent gamma dose rates to almost five times that of the parent isotope.[21] For ^{237}Np complexes, the radiation toxicity from γ-radiation is negligible, but as for all radionuclides emitting α-particles any bodily ingestion or injection of the nuclide must be avoided. Accordingly, synthetic neptunium chemistry must be carried out with suitable radioprotection, usually in negative pressure gloveboxes under an inert atmosphere to protect from fire. Because the negative pressure mode of glove-box use allows higher oxygen and moisture ingress compared to a standard glove box, the handling of highly sensitive organometallic complexes can be facilitated by the use of a Schlenk line and Schlenk techniques inside the box. In contrast to plutonium and later actinide samples, where radiolysis effects are often visually apparent after days to weeks, the degradation of ^{237}Np complexes due to autoradiolysis is insignificant over a timescale of many months, and although the ^{237}Np isotope is fissile, the mass required to achieve criticality is 63.6 kg, so is not a practical concern.[22]

Thus in the early preparative reports arising from experiments in the original radiological facilities with only limited access to simple analytical tools and spectrometers, standard characterisation methods are focused on vibrational spectroscopies such as FIR, IR, UVvisible and Raman, and gravimetric methods (titration for metal and halide), with occasional reports of ^{1}H NMR spectroscopic analysis. In recent years, more laboratories have gained access to NMR, EPR and single crystal XRD capabilities, but the radiological concerns in safe manipulation of transuranium elements that demand double or even triple encapsulation of samples still presents problems for data acquisition on more sensitive samples (thermal and air/moisture). Low-temperature analyses remain considerably more technically challenging than normal. Between the 1960's and 80's two different laboratories also collected Mössbauer spectra of a variety of neptunium complexes, in the anticipation of better understanding the M-L bonding from analysis of the metal. More recently, variable temperature SQUID magnetometry has become an analytical method of choice to study these high f^{n} complexes.

1.3 Redox properties

The redox properties of the element play a pivotal role in neptunium chemistry as it conventionally exhibits five oxidation states in compounds, from +3 to +7, with +5 the most common in aqueous media.[23] This very wide range means that there is much important and relevant chemistry still to explore in a protic, aerobic environment. In the meantime, two recent instances of thermally unstable, highly-coloured compounds that suggest that Np$^{\text{II}}$ is chemically accessible offer organometallic chemistry a chance to contribute much to the fundamental structure and bonding.[24] It is now clear that early actinides and to a lesser extent the rare earths, particularly in the lower formal oxidation states,[25] exhibit strongly ligand-dependent ground electronic configurations,[26] and the formal, aqueous redox potentials are poor predictors of the accessibility of a particular oxidation state in well-controlled coordination environment.[27] However, there are hardly any reports of measured redox potentials for transuranic complexes in non-aqueous media, and no studies yet of a set of comparable complexes where the An$^{\text{IV}}$/An$^{\text{III}}$ couple could be compared for U, Np, and Pu (the two most common oxidation states found in organo-neptunium chemistry). The standard potentials (V vs. SHE, I = 0, acidic conditions) are: U$^{\text{IV/III}}$ -0.553 (± 0.004);

$Np^{IV/III}$ +0.219 (± 0.010); and $Pu^{IV/III}$ +1.047 (± 0.003).[28,29] The literature available on kinetically inert organometallic complexes agree that U^{IV} is more common and stable than U^{III}, with the redox potentials of $Np(Cp)_4$ and $Np(Cp_3)Cl$ around 0.7V below those for the U analogues,[30] and the stability of the An^{IV} halides with respect to decomposition into An^{III} and elemental halogen decreases in the order U > Np > Pu.[31] This means that commonly used organometallic ligands may be strongly influential in changing the preferred formal oxidation state of organo-neptunium complexes, allowing spontaneous reduction of a Np^{IV} centre during a ligand exchange reaction.[32]

1.4 Magnetic properties

Neptunium has seven valence electrons and the common Np^{IV} oxidation state provides a high spin state Kramers' ion ($5f^3$, $^4I_{9/2}$). This has the potential to provide more magnetically interesting properties than those of the corresponding U^{IV} ($5f^2$, $^3H_4$) ion in its complexes. The propensity of these large metal cations to form clusters with strong and covalent metal oxo bridges also offers routes for magnetic exchange and has already led to some coordination complexes with interesting magnetic properties, albeit in higher formal oxidation states which provide a lower total spin that is achievable for most organometallics. The most interesting recent example is the air-sensitive, oxo-coupled trinuclear $Np^{VI/V}$ neptunyl complex $[(Np^{VI}O_2Cl_2)\{Np^{V}O_2Cl(THF)_3\}_2]$ that is the first polymetallic transuranic complex to exhibit slow relaxation of the magnetisation with a high (140 K) energy barrier and strong magnetic coupling between the cations. The superexchange-mediated coupling (10.8 K) is an order of magnitude larger than in related 4f-systems.[33]

Indeed, the recognition that f-block metal cations have high spin numbers and strong anisotropies has led to much research aimed at combining them into single molecule magnets, SMMs, molecules posessing an energetically isolated high-spin ground state that exhibit slow relaxation of the magnetic moment, and could have applications in spintronic devices.[34-38] Actinides are favored over lanthanides as the greater covalency in their bonding offers a greater chance of the control of directionality and stronger magnetic communication. The SMM properties of the actinocene sandwich $Np(COT)_2$ is discussed in the section on COT complexes below.

1.5 Neptunium halide starting materials

This is a particularly important consideration for the development of organo-neptunium chemistry since only certain forms of Np are available to particular radiolabs. Anhydrous actinide(III) halides (AnX_3, X = Cl, Br, I) are polymeric and poorly soluble.[39,40] This nothwithstanding, the *in situ* reaction of suspended $NpCl_4$ with sodium amalgam in diethyl ether produces a reactive, high-surface area form of $NpCl_3$, that warrants further characterisation, or solvation studies as it has already proved its efficacy for metathesis reactions.[41] Unlike the many synthetically useful solvated uranium(III) halides, for neptunium, only $[NpI_3(THF)_4]$[42] has been reported, and its synthesis is from the metal which is generally not available to radiological facilities. Notably, in contrast to the synthesis of the isostructural $UI_3(THF)_4$ the Np does not require activation prior to the reaction with I_2, and forms the thermally-stable product in very good yield.[43]

For neptunium(IV) the anhydrous $NpCl_4$ continues to play a pivotal role in the synthetic chemistry because of three particular properties: 1) good solubility in polar, aprotic organic solvents, 2) excellent ligand salt metathesis and reductive chemistry, and 3) the relative ease of conversion of aqueous Np^{IV} chloride solutions into anhydrous solvates such as $NpCl_4(DME)_2$, which is a soluble, molecular complex and will no doubt become a key entry point for organoneptunium chemistry going forward.[44] The neptunate(IV)

$[NEt_4]_2[NpCl_6]$,[45] has also been used with good effect, and another analogue, $[PPh_4]_2[NpCl_6]$, has been very recently reported.[46] Finally, unsolvated $NpCl_4$ offers the rather special opportunity to build an essentially closed recycling loop for neptunium within a research laboratory since high-temperature vacuum sublimation procedures can yield pure $NpCl_4$ on a gram-scale from mixtures containing less volatile Pu and related elements.

1.6 The qualitative and quantitative study of actinide-ligand bonding and covalency

The electronic structures of complexes of the actinides are complicated and difficult to predict, and orbital populations do not necessarily follow simple trends across the 5f series for a given set of complexes. This is due to relativistic effects, electron correlation, and crystal-field effects. There is an ongoing debate as to the nature and extent of covalency in f-block M-L bonds as it is important for the safe and efficient separation, manipulation, recovery, and prediction of behaviour of these (in many cases) rare, expensive, and important elements.

Many techniques have been explored in an effort to better quantify the orbital occupation of the metals' valence electrons. Experimental methods have increasingly taken advantage of both reactivity trends and physical techniques, often involving the comparisons of sets of isostructural complexes. Analyses of sets of single crystal X-ray diffraction data, and on the degree and strength of binding of donor molecules have been studied in depth to reveal trends and breaks in the 5f-series.[47,48] Atom-specific analyses have focused on NMR and EPR where appropriate spin-active nuclei or unpaired electrons are available,[49] XANES (X-ray absorption edge spectroscopy) of certain elements in bound ligands,[50] XAS (X-ray absorption spectroscopy) on the metal nucleus,[51] and crucially here, Mössbauer spectroscopy. As ^{237}Np is a Mössbauer- active nucleus this spectroscopy, like NMR spectroscopy, can probe minute changes in the Np centre's energy levels brought about by ligated atoms, and the results of studying many Np complexes are summarised in Section 6. Many of these experimental outputs are only interpretable through the use of computational methods, but these have become significantly more powerful in the last decade, allowing the discussion to become much more involved and to start to open up even more complicated arguments such as how to define covalency.[5]

In addition to classical carbon-binding ligands, other sets of compounds with increasingly 'soft' or electronegative donor atoms have been made and studied to explore the covalency changes in the bonding. The most notable neptunium complexes explored to this end are the chacogenide-based diselenophosphinate $Np^{IV}(Se_2PPh_2)_4$ which was compared with Ln^{III} and An^{III} and An^{IV} congeners,[48] and the dithiphosphinates $Np^{IV}(S_2PPh_2)_4$ and $Np^{IV}(S_2P(^tBu_2C_{12}H_6))_4$ which were compared with An^{III} and An^{IV} congeners.[52] A pair of non-aqueous halides have been made, with the chloride $[(Tren^{TIPS})NpCl]$ having been structurally characterised.[53] The opportunity to use An-L multiple bonding to study covalent bond overlap is offered by the unprecedented bis(imido) Np complex $[Np^V(NDipp)_2(tBu_2bipy)_2Cl]$[54] which provides a fascinating comparison with the highly unusual U analogues such as $[U^{VI}(NPh)_2(THF)_2I_2]$ [55] that are being reported with increasing frequency.

1.7 Previous reviews of actinide and transuranic organometallics

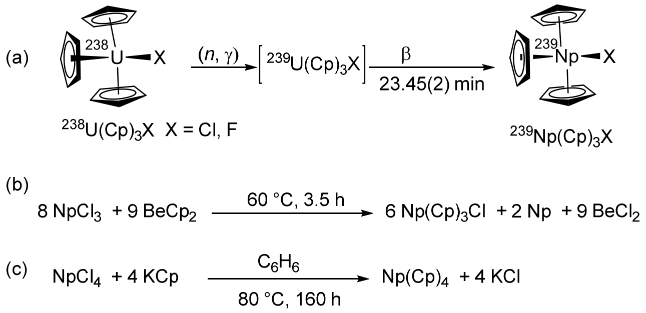
Three early reviews included organometallic actinide complexes made in the 1960's and '70s,[56,57,58] with one written for a more generalist audience.[59] The last review of organometallic Np compounds appeared in 1986.[60] Element-specific surveys have been recently published for non-aqueous uranium[61-64] and plutonium[65] along with more general discussions of synthetic and structural actinide coordination and organometallic chemistry,[66-68] and two book chapters in the multi-volume 'Chemistry of the Actinide and Transactinide Elements' cover the element,[69] and organoactinide chemistry.[70] A non-element specific listing of the year's reported organometallic actinide complexes reported during each previous year is published annually.[71]

2. Cyclopentadienyl and substituted cyclopentadienyl ligands

Np(IV)

Early organoactinide chemistry relied on the ubiquitous cyclopentadienyl ligand, $Cp = (C_5H_5)^-$, due to its enormous success in transition metal chemistry, and rich structural and electronic diversity. Remarkably, organoneptunium chemistry originated from a radiochemical rather than a chemical synthesis: Baumgärtner, Fischer and Laubereau subjected the uranium complex $[^{238}U(Cp)_3X]$ to thermal neutrons, inducing transmutation to neptunium in the pioneering synthesis of $^{239}Np(Cp)_3X$ (X = Cl, F) (Scheme 1a).[1]

Scheme 1. Nuclear and solvent-free syntheses of Np^{IV} cyclopentadienyl complexes.



The activation reaction $^{238}U(n,\gamma)^{239}U$ followed by β-decay of the new isotope proceeds cleanly according to ^{239}Np γ-ray spectrometry (*ca.* 90 % yield conversion of U to Np). It is interesting that the nuclear recoil displacement[72] of the radioisotope did not destroy the molecule, and the authors were able to demonstrate both the volatility and thermal stability of the new $Np(Cp)_3X$ complexes. Concurrently, the first chemical preparations of $^{237}Np(Cp)_3X$ (X = Cl, and F) were reported, using molten $Be(Cp)_2$ as a reactant and solvent[73] in reactions with $NpCl_3$, $NpCl_4$ or NpF_3, Scheme 1b. The clean formation of $Np^{IV}(Cp)_3$ -containing products contrasts to the analogous uranium chemistry that exclusively forms UCp_4. Vibrational spectroscopy was used heavily in the early organoneptunium chemistry studies, as in both IR and FIR regions provide assignable bands for the carbocyclic ligands bound to a heavy central ion. Both the vibrational spectra in the IR (600-4000 cm^{-1}) and the FIR (40-400 cm^{-1}), where the skeletal vibrations are visible, are useful in the characterisation of An-Cp complexes and comparison of their molecular symmetry, and often the bonding in these molecules has been shown to contain both π-aromatic and σ-ionic interactions by careful comparison with spectra of the lighter congeners (Th, U).

The chemical properties of $Np(Cp)_3Cl$ closely match those of its uranium analogue. Halide exchange reactions proceed most readily from the use of ammonium salts,[74] affording $Np(Cp)_3X$, X = Br, I, SCN, ½ SO_4, NC_4H_4, $AlCl_4$, O^tBu, O^iPr, OPh, $O^iC_3F_7$.[75] Although it is not clear that the complexes have yet been fully characterised, variable temperature magnetic analyses of a subset, $Np(Cp)_3X$, X

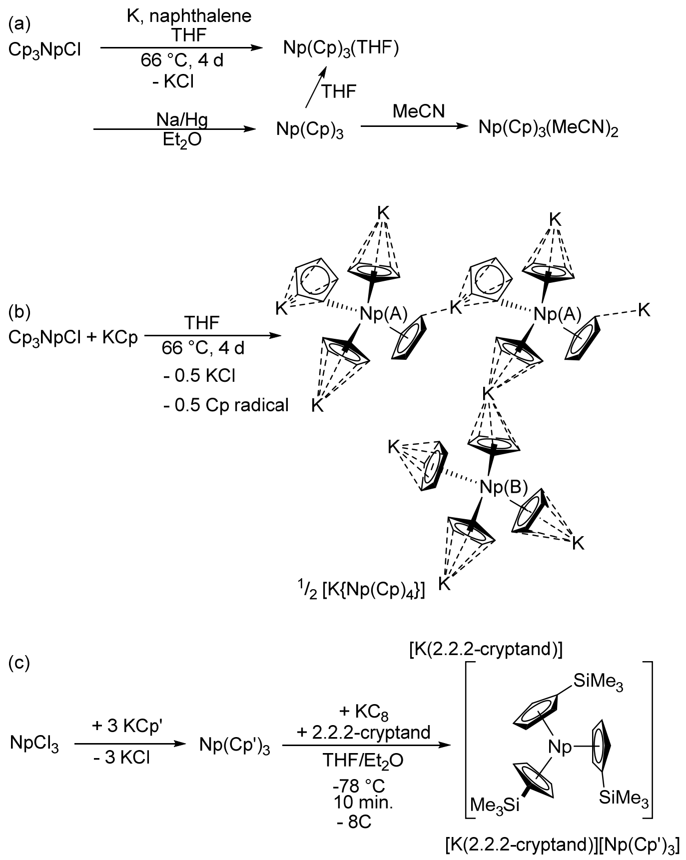
= F, Cl, Br, I, ½ SO_4, Cp) were also undertaken. They discuss the crystal field splitting of the $^4I_{9/2}$ ground state of Np^{IV} in the different complexes, and the possibility of a dimeric structure of the fluoride, which has very a different temperature dependance, and much higher values, of the magnetic susceptibility than the others.[76] For this study, the fluoride $Np(Cp)_3F$ was prepared from the iodide in a sold state synthesis,by treating the monchloride with an excess of NaF at 300 °C for 40 h, followed by a THF extraction of the product. The monochlorido $Np(Cp)_3Cl$ forms the hydrated cation $[Np(Cp)_3]^+$ in dilute or semi-concentrated aqueous mineral acids under strictly oxygen-free conditions,[75] or the thiocyanate-solvated anion in the salt $[AsPh_4][Np(Cp)_3(NCS)_2]$.[77] (The authors also point out they were unable to isolate the neutral $Np(Cp)_3(NCS)(NCMe)$ although evidence for its formation in solution was obtained.) Red-brown solutions of the cation, or $Np(Cp)_3Cl$ react with ferric chloride only very sluggishly to produce ferrocene,[78] suggestive of the similar bond energy in An^{IV}-(η^5-Cp) interaction for An = U, Np, and contrasting with the rapid ligand exchange of the Th analogue.[79] The single crystal X-ray structure of $Np(Cp)_3(OPh)$ was the first, and until very recently the only reported structure of a tris(Cp)-Np containing complex.[80] It is isostructural with the previously reported uranium analogue $[U(Cp)_3(OPh)]$[81] and is best described as a flattened tetrahedron, showing approx. C_{3v} symmetry at the metal site with the O donor at the C_3 axis. Electrochemical analyses on $An(Cp)_3Cl$ (An = U, Np) show reversible one-electron reduction at $E_{1/2}$ = -1.80 V for U and -1.29 V for Np (*vs.* Fc^+/Fc in THF),[26] confirming that the Cp-supported Np(IV) complexes are significantly easier to reduce.

Baumgärtner *et al.* reported the first homoleptic organoneptunium complex, tetrakis(η^5-cyclopentadienyl)neptunium(IV), $Np(Cp)_4$, from the reaction of $NpCl_4$ with excess KCp in benzene solvent, Scheme 1c.[3] The S_4 symmetry with four identical Cp rings around the Np^{IV} centre assigned from combined IR[3] and FIR(far infra-red)[82] spectroscopic and powder X-Ray diffraction[83] data for the reddish brown crystals, and supported by a computational study,[8] has now been confirmed by single-crystal X-ray diffraction.[41] The computed Np-Cp centroid distance of 2.563 Å compares with the experimentally observed value of 2.551 Å (and values of 2.606 Å for Th, and 2.588 Å for U), continuing the expected trend of shortening An-Cp bonds with increasing An^{4+} atomic number. Across the row of the isostructural $An(Cp)_4$ (An: Th, U, Np), in line with the actinide contraction, the cell volume decreases from 802 $Å^3$ (Th) to 786 $Å^3$ (U) to 775 $Å^3$ (Np). A concomitant shrinking of the entire molecule is evidenced by a decrease in An - Cp ring centroid distances, from 2.606 Å for Th,[84] to 2.588 Å for U,[85] and 2.551 Å for the Np complexes described here, again shorter. The shrinking parallels the decrease of the ionic radii;[86] this implies that the nature of the bonding in the complexes in this row is comparable and even if covalency plays a role it does not affect the bond lengths in the complexes significantly. Interestingly, an analysis of the skeletal vibrations in IR and FIR regions for the simple series of $An^{IV}Cp_4$ complexes (An = Th, Pa, U, Np) revealed not only the two expected oscillations out of total of four normal active oscillations in the IR, but also a weak vibration band at ca. 250 cm^{-1}, suggestive of a lowering of the symmetry from the expected parent T_d across the whole series. This small deviation could either originate from an actual D_{2d} symmetry, or S_4,[87] and was confirmed by subsequent investigations that found a non-zero electrical dipole moment in solution.[82] Further fitting of the low temperature magnetic susceptibility data[88,89] and also the optical spectra for the uranium analogue also suggested both D_{2h} distortion,[87] whereas the single crystal X-ray diffraction analysis of UCp_4 and photoelectron spectroscopy (using $U(Cp^{Me})_4$ as a surrogate, $Cp^{Me} = C_5H_4Me$)[90] indicated S_4 symmetry for both. Our recent single crystal X-ray diffraction analysis of $NpCp_4$ confirmed the previous findings for the isostructural nature with the uranium analogue.[41]

Np(III)

Many routes to solvated and base-free $U^{III}(Cp)_3$ complexes exist, but until very recently only the THF solvate of $Np^{III}(Cp)_3$ had been reported, made from treating $[Np(Cp)_3Cl]$ with potassium metal and catalytic naphthalene in refluxing THF for a few days. The isolated product was assigned as the tris THF solvate $Np(Cp)_3(THF)_3$ based on metal analysis,[78] but IR, FIR and UV-vis-NIR spectroscopic analysis suggested the 1:1 Lewis base adduct $Np(Cp)_3(THF)$ constitution, analogous to that of uranium.[91] Attempts to desolvate it by heating samples *in vacuo* led to significant decomposition.[78] We used a minor modification of Zanella *et al.*'s strategy[92] (sodium amalgam instead of sodium hydride as reductant) to make the unsolvated Np^{III} complex $Np(Cp)_3$ (Scheme 2).[41]

Scheme 2. Syntheses of $An(Cp)_3$ complexes, related Np^{III} derivatives and the thermally unstable putative Np^{II} derivative, including a drawing of $K[Np(Cp)_4]$ showing the two types of Np coordination geometries labelled (A) and (B).



The Np^{IV} complex $Np(Cp)_3Cl$ is cleanly reduced by sodium amalgam in diethyl ether, forming the pale green diethyl ether solvate $Np(Cp)_3(OEt_2)$ that loses solvent readily, affording $Np(Cp)_3$ in excellent yield. This compares with a maximum yield of around 40 % achieved so far from the four different synthetic routes used to make $U^{III}(Cp)_3$ complexes. The unsolvated $Np(Cp)_3$ crystallises in a monoclinic cell, and contains polymeric zig-zag chains of the $\{An^{III}(\eta^5\text{-}Cp)_2\}$ units bridged through alternating $\mu\text{-}\eta^5,\eta^1$-bound cyclopentadienyl groups.[41] This is directly comparable to the structures of the unsolvated $LnCp_3$ (Ln = Ce, Ho, Dy)[93] $SmCp_3$,[94] and $LaCp_3$.[95] Another, orthorhombic form of $SmCp_3$ has however also been reported.[96] In the polymeric form the neptunium complex is only very sparingly soluble in non-coordinating solvents but samples dissolve slowly in Et_2O, THF, or MeCN forming solvates.[41]

The utility of the Cp anion as a reductant is well documented in preparative inorganic chemistry, as the homolysis of the M-hydrocarbyl bond provides one reducing electron to the metal and releases the organic radical which can dimerise or be solventquenched. The recognition of this transformation in transuranic chemistry may be of wider interest as it enables research labs in facilities to access lower formal oxidation states of these metals without using pyrophoric Group 1 elements or amalgams that preclude the incineration of lab waste.

Although the neutral complex $Np(Cp)_4$ has been reported several times to form in the reaction between $NpCl_4$ and excess KCp in THF,[41] benzene,[3] or toluene[97] solution, the reaction between $Np(Cp)_3Cl$ and KCp cleanly affords the Np^{III} ate product $K[Np(Cp)_4]$, the first actinide(III) tetrakis-cyclopentadienyl complex, instead of the anticipated $Np(Cp)_4$, Scheme 2. The solid state structure of $K[Np(Cp)_4]$ is unique in containing two different types of metal-Cp coordination geometries in the same crystal, labelled as Np(A) and Np(B) in Scheme 2. This Np^{III} product could provide an explanation for the disagreements in the Mössbauer studies on covalency. Adrian observed that Mössbauer spectra of the $Np(Cp)_4$ targets provided by Bohlander contained two low intensity bands arising from the unidentified impurities.[98]

Finally, these complexes present an unusual opportunity to observe a metal cation with two different formal oxidation states in an identical coordination geometry: In $Np^{IV}Cp_4$ and $KNp^{III}Cp_4$ there exists a Np centre that has four η^5-coordinated Cp rings around the Np cation. In $NpCp_4$ the mean Np-ring centroid distance is with 2.551(1) Å, which is about 0.08 Å shorter than the distance in the equivalent Np centre in $K[NpCp_4]$ (in which it is 2.635(1) Å). This direct comparison provides an organometallic datapoint showing the radius of Np^{III} being 0.08 Å larger as for Np^{IV}.[41]

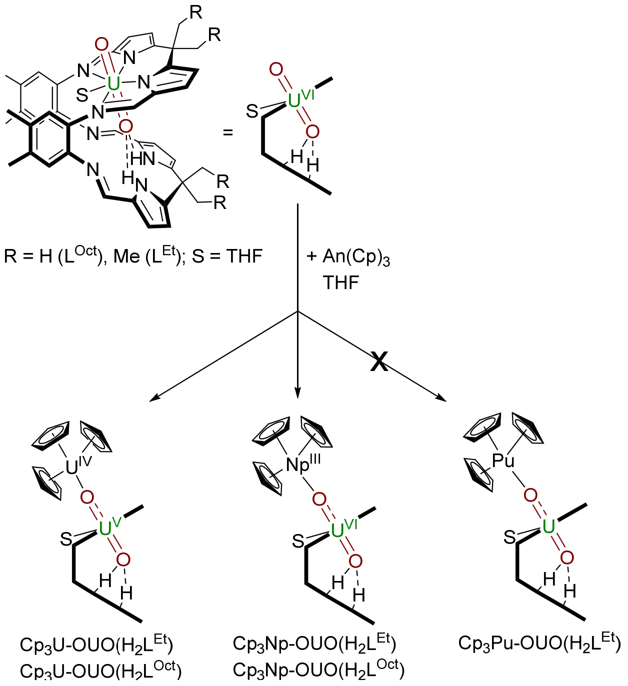
Np(II)

Reports of the new formal oxidation state for uranium, in the form of the U^{II} 'ate' complex $[K(2.2.2\text{-cryptand})][U(Cp')_3]$, $[K(2.2.2\text{-cryptand})][U(Cp'')_3]$ and $[K(2.2.2\text{-cryptand})][Th(Cp'')_3]$ ($Cp' = C_5H_4SiMe_3$; $Cp'' = C_5H_3(SiMe_3)_2$) spurred a search for the neptunium analogue. Reduction of $Np(Cp')_3$ by KC_8 in the presence of 2.2.2-cryptand affords black solutions and unstable crystals at -78 °C that were tentatively suggested to be a neptunium(II) complex $K(2.2.2\text{-cryptand})[Np(Cp')_3]$, like the U^{II} and Th^{II} complexes $K(2.2.2\text{-cryptand})[Th/U(Cp')_3]$, Scheme 2, and that is thermally unstable above -10 °C. Unfortunately, radiological concerns precluded mounting of the putative Np^{II} crystals on the diffractometer head at low temperatures and the diffraction data from the crystals mounted were too poor for a structural determination. However, in line with the presumed increasing stability of lower formal oxidation states across the row, the Pu analogue $K(2.2.2\text{-cryptand})[Pu(Cp'')_3]$ with additional $SiMe_3$ substituents, was reported around the same time, having been found to be sufficiently thermally stable at -35 °C to be structurally characterised by X-ray diffraction.[99] All these compounds are extremely reactive with standard radiologically protective materials such as teflon-liners required for spectroscopy tubes, increasing the technical difficulty of these studies.

Heterobimetallic complexes

A systematic study on the ability of the $An^{III}(Cp)_3$ (An = U-Pu) complexes to reductively functionalize the *exo*-oxo group of the uranyl(VI) dication in $(UO_2)(THF)(H_2L)$, where $(H_2L)^{2-}$ is a doubly-deprotonated tetrapyrrolic, Schiff-base macrocycle, afforded $(Cp)_3AnOUO(THF)(H_2L)$ complexes with four structurally characterised analogues afforded with different peripheral substituents on L, Scheme 3.[91]

Scheme 3. Reductive oxo-metalation of uranyl complexes by $AnCp_3$ (An = U, Np, Pu).



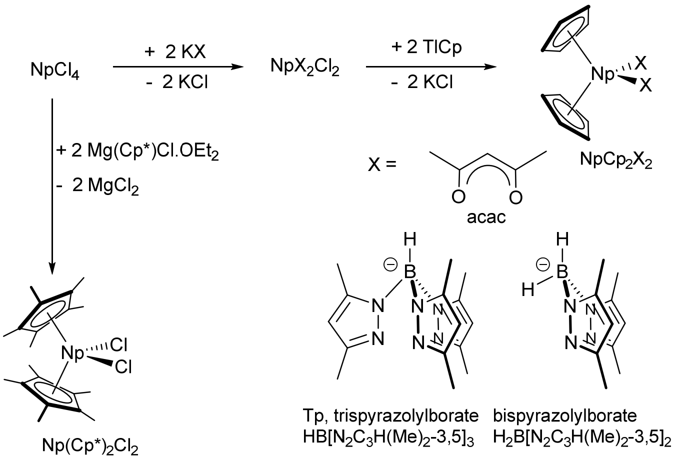
For the more reducing U^{III} ion, the oxo group provides a capable bridge between the two actinide cations,[38] with the Np coordination forming the first heterobimetallic transuranic organometallic complex. Although the many techniques used to assign formal oxidation states are not all in agreement, in combination, and with support from DFT calculations, they show that the extent of electron transfer to the uranyl is U>Np>Pu. There is no clear magnetic communication between the actinide centers, the U^{IV}-U^{V} complex $(Cp)_3UOUO(THF)(H_2L)$ is a single ion magnet (arising from the uranyl(V) f^1 centre), with a relaxation barrier of 19 cm^{-1}. A strong donor-acceptor interaction, or perhaps even non-integral formal oxidation states for Np and U are probably most appropriate for the $Cp_3Np(UO_2)$ molecule $(Cp)_3NpOUO(THF)(H_2L)$, and any interaction between the Pu^{III} and U^{VI} is too weak to be observed in the presence of coordinating THF solvent.

Bis(cyclopentadienyl) complexes

To avoid the formation of mixtures of $Np(Cp)_3Cl$ and $Np(Cp)Cl_3(L)_2$ (L=coordinating solvent),[100] two chlorides must be first be replaced by a larger polydentate anion such as acetyl acetonate (acac), bis(1-pyrazolyl)borate ($H_2B(pz)_2$) or tris(1-pyrazolyl)borate, ($HB(pz)_3$) anions. Alternatively, the Grignard reagent of the larger Cp* (C_5Me_5) ligand can be used to make the purple dichloride

$Np(Cp^*)_2Cl_2$ directly, albeit in low yield (16 %) Scheme 4.[101] The authors note the similarity in the PXRD (powder X-ray diffraction) pattern with the stable U^{IV} analogue, implying that it has not been reduced to $Np^{III.}$. They also note the reversible one-electron reduction of $Np(Cp^*)_2Cl_2$ in MeCN occurs at $E_{1/2}$ -0.68V vs SCE, which compares with the value of -1.30V for of $U(Cp^*)_2Cl_2$. These differences neatly mirror the difference between the aqueous $Np^{IV/III}$ and $U^{IV/III}$ couples (-0.063 V and -0.849 V respectively).

Scheme 4. Routes to stable bis(Cp) and mono(Cp) Np^{IV} complexes.



Mono(cyclopentadienyl) complexes

The synthesis of $Np(Cp)Cl_3(L)_2$ (L = O=PMePh$_2$) was reported early in the history of organoneptunium chemistry and included a rare single crystal X-ray structural study.[102] The Np coordination geometry is crowded but approximately octahedral with *mer*- chloride ligands and *cis*-phosphine oxide coordination. The Cp(centroid)-Np-Cl/O bonds are closer to 100° than 90°. A facile ligand redistribution occurs for larger L, forming mixtures of $Np(Cp)_3Cl$ and $NpCl_4L_2$ but stable adducts are formed for L = dmf, MeCONPr$^i_2$, EtCONPr$^i_2$, OPMe$_3$ and OPMe$_2$Ph) were isolated and assigned similar structures to $Np(Cp)Cl_3(O{=}PMePh_2)_2$ by IR spectroscopy.

3. Complexes with σ-bound hydrocarbyl ligands

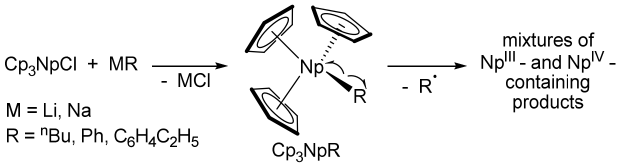
The syntheses of the solvated actinide triiodides $AnI_3(THF)_4$ (An = U, Np, Pu) from the metals has been a milestone in synthetic uranium chemistry.[42] Reports of preliminary investigations of the reactivity of $NpI_3(THF)_4$ suggested it reacts with three equivalents of $LiCH(SiMe_3)_2$ in hexanes to afford the homoleptic alkyl $Np[CH(SiMe_3)_2]_3$ to be targeted.[103] Comparisons with the U and Pu analogues make this a fascinating reagent worthy of further investigation.

Tetraalkylactinides(IV) such as UR_4 (R = Me, ^{n}Bu, 2-*cis*-2-butenyl, 2-*trans*-2-butenyl, ^{t}Bu, iPr, neopentyl)[104] containing coordinatively unsaturated An^{IV} centres are generally unstable with respect to α- and/or β-hydride elimination reactions, the sterically protection afforded by Cp ligands has allowed some heteroleptic σ-bound organometallic complexes to be isolated, albeit in moderate yields. Unlike the robust Th^{IV} and U^{IV} analogues, salt metathesis reactions between $Np(Cp)_3Cl$, and carbanionic alkyl- or aryl-lithiums LiR (R = Me, Et, ^{n}Bu, Ph) form the target $Np^{IV}(Cp)_3R$ (R = ^{n}Bu, Ph) in 40-60 % yield and together with some $Np(Cp)_4$, unidentified

Np^{III} side-products suggest that the Np^{IV}-C alkyl or aryl bond homolysis in the parent complex is a relatively facile process, even for Cp-supported Np^{IV}.[41,97] It may be that significant amounts of $Np(Cp)_3$ are being formed in these processes,[41] and as such might warrant re-investigation.

The alkynide complexes $[Np(Cp)_3]_2(\mu\text{-}C{\equiv}C)$ and $Np(Cp)_3(C{\equiv}CH)$ have been reported during Mössbauer studies but without full synthetic or characterising data.[98,105]

Scheme 5. Synthesis of $[(Cp)_3AnR]$ complexes.



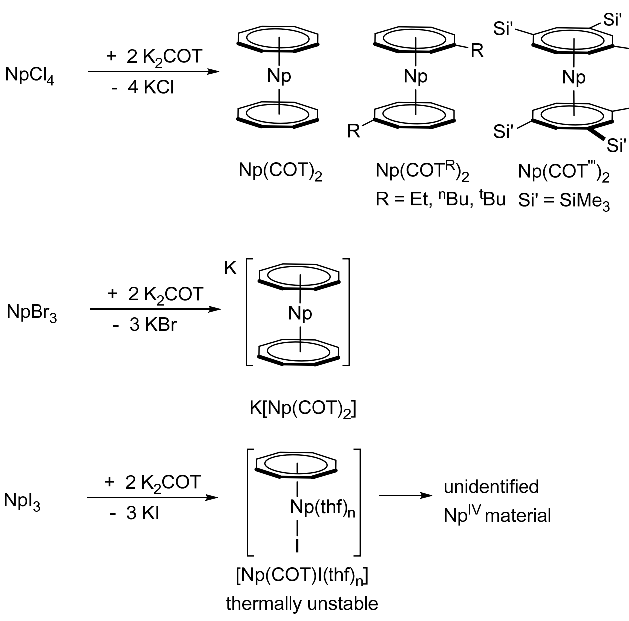
Studies on the thermal decomposition of the solids $An(Cp)_3Me$, An = Th, U, Np, showed the stability trend: Th >> U > Np, in accordance with the decreasing trend in An^{IV}/An^{III} reduction potential, i.e. increasing stability of the An^{III} state. The thorium complex decomposes at 167 °C with a half-life of 97 h, while $UCp_3(^nBu)$ starts to decompose, albeit more slowly (a half life of 1130 h), in toluene solution heated to 97 °C. Further comparisons are complicated because of the identification of different decomposition mechanisms and products.[106] Studies on the kinetics of the alcoholysis reaction in which $Np(Cp)_3Me$ is dissolved in EtOH show a considerable inertness, with the IR bands for both unreacted starting material as well as the alkoxide product $Np(Cp)_3(OEt)$ both present after 15 h at room temperature. The uranium analogue UCp_3Me reacts instantly with methanol.[75,107] This reactivity mirrors the hydrolysis of the bis([8]annulene) complexes of early actinides (see below).[108,109]

4. Cyclooctatetraene and substituted cyclooctatetraene complexes

Np(IV)

The large, cyclic aromatic cyclooctatetraene dianion, COT = $C_8H_8^{2-}$, has proven ideally suited to stabilising sandwich complexes of the f-block, and excellent treatises on the original actinide sandwich, uranocene, have been written.[110,111] ‘Neptunocene’ $[Np(COT)_2]$, is prepared by combining two equivalents of K_2COT with one equivalent of $NpCl_4$ in a non-polar solvent, Scheme 6.[112] The complex is water- but not oxygen- stable, in line with the high-hapticity of the ligand.

Scheme 6. Syntheses of neptunocene and derivatives.



On the basis of IR spectroscopy and powder X-ray diffraction data the compound was assigned the same D_{8h} bis(η^8-COT) sandwich structure as uranocene with confirmation from subsequent single crystal X-ray analyses.[113,114]

Table 1 Comparison of calculated An-COT centroid distance (r(An-COT)), An^{4+} ionic radius and the ratio between the two. An=Th-Am. (Data from references [113-115].)

An	**r(An-COT) (Å)**	**An^{4+} ionic radius (Å)**	**r(An-COT)/An^{4+} ionic radius**
Th	2.002	0.94	2.130
Pa	1.933	0.90	2.148
U	1.907	0.89	2.143
Np	1.890	0.87	2.172
Pu	1.870	0.86	2.174
Am	1.861	0.85	2.189

The early An sandwich complexes are isostructural and their geometric data can be directly compared with neptunocene. Progressing from Th to Np no real pattern appears in the C-C bond lengths on the COT ligand, but the An-ring centroid distance decreases from Th (2.0036(5) Å) to U (1.9264(5) Å) and to Np (1.9088(3) Å).[64,116] Very recently the structure of Pu(1,3-COT")(1,4-COT") (COT" = $C_8H_6(SiMe_3)_2$) has been reported;[12] the An-ring centroid distances are 1.89 and 1.90 Å. A computational analysis was also undertaken in order to suggest the reason for an unanticipated ring-migration of one of the silyl substituents. Alongside the recent report on the structures of An(1,4-COT")$_2$ (An = Th, U; COT" = $C_8H_6(SiMe_3)_2$),[117] and the anticipated corresponding Np complex, this will provide another set of complexes An(COT")$_2$ for comparisons across the series An = Th, U, Np, and Pu.

A computational analysis on An(COT)$_2$ (An= Th-Cm), predicts the shortening of the An-COT distance continues through to Am, but the trend does not correlate with the decrease in An^{4+} ion radius (Table 1) and is explained by the variations in the covalent nature of the M-COT bonding.[118] Further spectroscopic investigations suggested stronger covalent M-L bonding in Np(COT)$_2$ than in either U(COT)$_2$ or Th(COT)$_2$, in agreement with the large isomer shift of 19 mm s^{-1} found in the ^{237}Np Mössbauer spectrum, and which corresponds to a formal oxidation state of *ca.* 3.5 for Np.[112] This could indicate a multiconfigurational ground state like Ce(COT)$_2$ which is a mixture of Ce^{III}(COT$^{1.5-}$)$_2$ and Ce^{IV}(COT^{2-})$_2$. Cerocene and related organometallics where the *f*-electron is metal-localised but polarises nearby 'conducting' electrons on the aromatic ligand, to give an effective magnetic singlet, are discrete models for the 'Kondo effect',[119] a key concept in condensed matter physics that can be used to understand metallic systems with strongly interacting electrons such as heavy fermion materials, superconductors, quantum dots, and the unusual magnetic delta-phase of plutonium.[120]

Analogues with ring substituents have also been made and compared to the parent: a single ethyl or n-butyl substituent in Np(η-C$_8$H$_7$Et)$_2$ and Np(η-C$_8$H$_7$^{n}Bu)$_2$ respectively affords increased solubility in benzene and toluene, Scheme 6,[121] but no noticeable difference to the isomer shift in the Mössbauer spectrum. Powder x-ray diffraction suggests that the crystal structure of the three hydrocarbyl derivatives are different to each other but isostructural with the uranium and plutonium sandwich counterparts. The hexachloroneptunate(IV) [(NEt$_4$)$_2$(NpCl$_6$)] proved an excellent starting material for the reaction to afford di-*tert*-butylneptunocene, Np(COT^{tBu})$_2$, whilst silylated substituents impart improved solubility and air-stability to Np(C$_8$H$_5$(SiMe$_3$)$_3$-1,3,5)$_2$ compared to neptunocene, Scheme 6.[122]

The parent neptunocene, which has rigorous D_{8h} symmetry Np(COT)$_2$, exhibits intriguing magnetic memory effects at low temperatures, Figure 2, and provided the first experimental proof that the 5*f* ions can provide stronger magnetic anisotropy and larger coercive fields than 4*f* ions in SMMs.[113] Even at the maximum field of 14 T and the lowest attainable temperature of 1.8 K, the resultant magnetic moment (0.8 μ_B) remains largely unsaturated and corresponds to *ca.* half of the expected value for $J_z = \pm 5/2$ doublet. At temperatures above 10 K and applied fields of below 2 T, the graph of the function $\ln(\tau) = f(1/T)$ become essentially linear and surprisingly low thermal activation barrier of $\Delta = 41$ K and $\tau_0 = 1.1 \times 10^{-5}$ s was obtained. This could be due to a field-induced nuclear spin mediated electron crossing, only observable below 2 T. At 1.8 K and applied fields of 5 T and above, the slow relaxation of magnetization becomes independent of frequency and butterfly-shaped hysteresis loops develop by 14 T, suggesting that the primary mechanism of relaxation at low temperatures is nuclear spin-induced quantum tunneling (Figure 2). Interestingly, the isoelectronic f^3 U^{III} complex K[U(COT)$_2$] shows no detectable SMM behaviour,[123] presumably due to the net difference in crystal field splitting but also possibly due to distortions in the molecular symmetry. In fact, it was the magnetic splitting observed in the ^{237}Np Mössbauer spectra that inspired the measurement of magnetic susceptibility of Np(COT)$_2$ in an applied magnetic field.

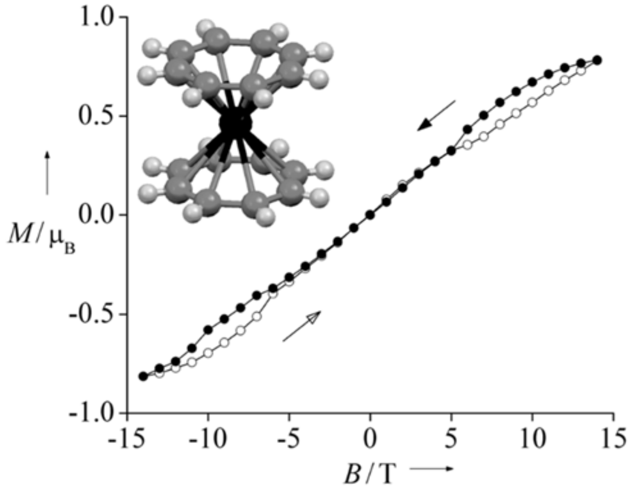


Figure 2. Hysteresis of isothermal magnetization of Np(COT)$_2$ at 1.8 K; datapoints for increasing (decreasing) magnetic field are depicted with empty (full) circles. The molecular structure is depicted in the inset; neptunium (black), carbon (grey), hydrogen (light-grey). Reproduced with permission from ref. 113 Copyright 2011, John Wiley and Sons.

Np(III)

Red-purple K[Np(COT)$_2$].2THF can be made directly from NpBr$_3$ and K$_2$COT in THF, Scheme 6; it is air and moisture sensitive, and is readily oxidised to Np(COT)$_2$.[124] It is assumed to adopt a sandwich structure with either D_{8h} symmetry (eclipsed rings like neptunocene) or D_{8d} symmetry (staggered rings) since the asymmetric parameter of the quadrupole-split Mössbauer spectrum is zero, which indicates that the Np^{3+} ion sits on an n-fold axis with n>3. According to the Mössbauer isomer shift, the bonding is less covalent than in Np(COT)$_2$. This was suggested to be due to a poorer ability of the 'more hidden' 5f orbitals in the larger Np^{III} centre to overlap favourably with the COT ring orbitals. The piano-stool complex Np^{III}(COT)I·*x*THF (*x* was undetermined) may be made from combining equimolar NpI$_3$ and K$_2$(COT) in THF, although the product decomposes on work-up to an unknown Np^{IV}-containing material, Scheme 6. A two-step colour change suggests that K[Np(COT)$_2$] is formed first, prior to reacting with the remaining NpI$_3$ to produce the green-brown Np^{III}(COT)I(THF)$_n$. Prior to decomposition, which is accelerated by removal of donor solvent, the material was shown to have an isomer shift of +3.83 cm s^{-1} in the Mössbauer spectrum, closer to that of K[Np(COT)$_2$] than NpI$_3$.[125]

5. Other cyclic aromatic ligands

Cycloheptatrienyl adducts

Although uranium and thorium cycloheptatrienyl (CHT, [C_7H_7]) complexes are readily accessible, the Np analogue, Np(η-C_7H_7)$_2$ has only been computationally investigated.[126] The CHT ligand is interesting for two reasons – the D_{7h} point group is very rare, and the question of the choice of formal charge for the ligand in a complex is also open to debate, since a planar, Huckel-aromatic ligand can be formulated from either a 6e$^-$ [C_7H_7]$^+$ cation or a 10e$^-$ [C_7H_7]$^{3-}$ limiting forms. The comprehensive survey of neutral and charged [An(η-C_7H_7)$_2$]^q (An = Th, Pa, U, Np, Pu, Am; q = -2, -1, 0, +1) showed the importance of fδ- as well as dδ-symmetry orbitals in the bonding with the pπ-orbitals of the CHT rings, and that most redox reactivity will involve primarily ligand-based electrons.

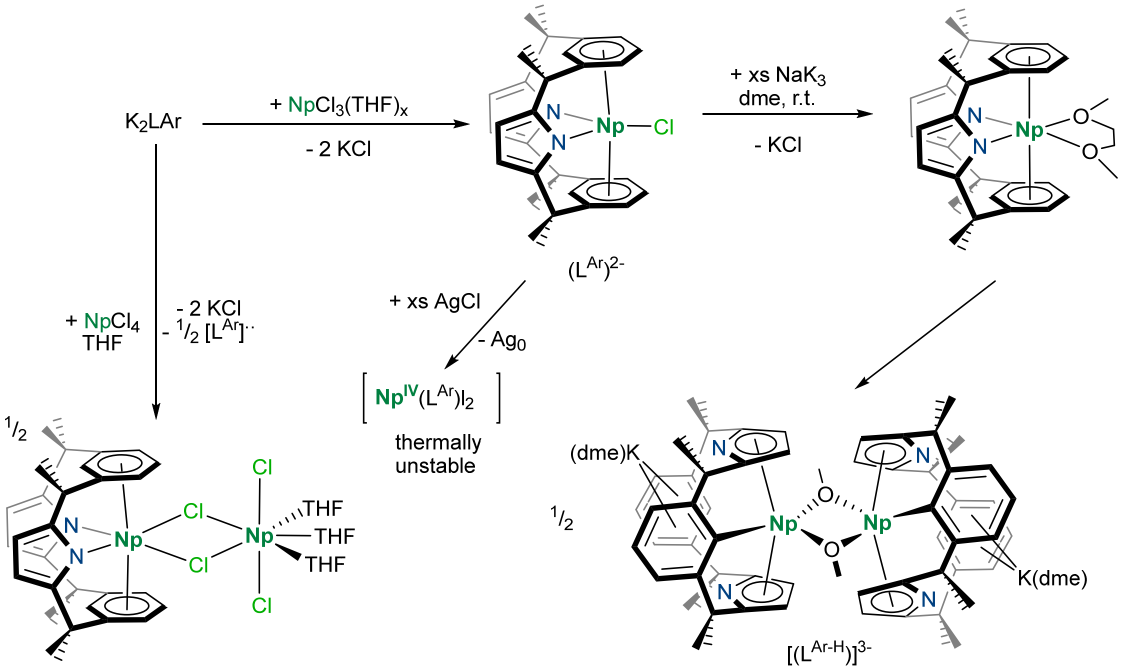
Arenes

Np(III)

Although metal-bis(arene) complexes are widely recognised across the periodic table, including for the rare earth elements,[127,128] and uranium bis(benzene) has been computationally predicted to be isolable,[129] no formally An(0) complex has yet been reported. Perhaps the closest bonding situation to this motif so far is provided by the two arenes in the small, flexible dianionic *trans*-calix[2] benzene[2]pyrrolide macrocycle, (L^{Ar})$^{2-}$ which can bind in an η^6:η^6-fashion with a Np to ring centroid distance of 2.601 Å in Np(L^{Ar})Cl.[20] A coarse comparison of the centroid distances in a series of aromatics is now possible: The neptunium – ring centroid distance in Np^{IV}(COT)$_2$ is 1.898 Å,[109] that in Np(Cp)$_4$ is 255.1 Å,[41] those in K[Np(Cp)$_4$] are 2.527, 2.516, 2.493 2.631, and 2.645 Å (ave. 2.562 Å),[41] and that in Np(L^{Ar})Cl, 2.601 Å.[20] We reported mono- and dinuclear neptunium(III) complexes Np(L^{Ar})Cl and Np$_2$(L^{Ar})Cl$_4$(THF)$_3$, Scheme 7; both complexes adopted η^6:κ^1:η^6:κ^1 bis(arene) sandwich structural motif (Figure 3 for Np(L^{Ar})Cl) for a single Np^{III} ion, which is similar to the previously reported complexes of Sm^{III} and U^{III}.[130,131] The Np^{IV} analogue Np(L^{Ar})Cl$_2$ was not thermally stable, in contrast to the U^{IV} system, attributed again to spontaneous Np-X ligand bond homolysis.

Alternatively, or additionally, depending on the metal:ligand ratio and formal oxidation state of the metal, the two pyrrolide groups can bind η^5:η^5- to electronically mimic the bis(cyclopentadienyl) ligand set.[132]

Scheme 7. Syntheses of Np^{III} L^{Ar} adducts Np(L^{Ar})Cl and Np_2(L^{Ar})Cl_4(THF)$_3$ and reduction with NaK_3 to form a putative Np^{II} complex Np^{II}(L^{Ar})(DME) , which gradually decomposes into the Np^{III} aryl complex [K(DME)Np(L^{Ar-H})(OMe)]$_2$.



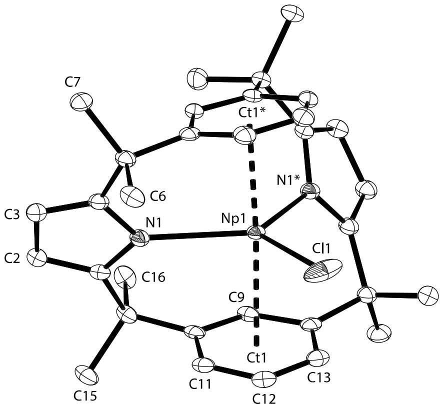


Figure 3. Displacement ellipsoid drawing of Np(L^{Ar})Cl with hydrogen and lattice solvent atoms omitted for clarity.

Np(II)

Further redox studies confirmed the ability of this ligand to support low oxidation state metal centres. In particular, the reduction of the red complex Np(L^{Ar})Cl with NaK_3 in DME produces near-black solutions suggestive of the formation of a formally Np^{II} complex, Np^{II}(L^{Ar})(DME), Scheme 7. Unfortunately, the small black crystals of [Np^{II}(L^{Ar})(DME)], diffracted X-rays too weakly to determine the solid state structure. In the absence of excess NaK_3, solutions of the putative Np^{II}(L^{Ar})(DME) gradually (over *ca* 90 mins at room temperature) reoxidises to the red-brown, metallated (L^{Ar-H})$^{3-}$ neptunium(III) complex, [K(DME)Np^{III}(L^{Ar-H})(OMe)]$_2$, featuring a ‘metallocene-type’ η^5-bound pyrrolide binding; the first crystallographically characterized ‘metallocene-type’ geometry measured for Np^{III}.

A variable temperature magnetic analysis of $Np(L^{Ar})Cl$ found a significant slowing down of the magnetization dynamics below 10 K, signifying that the onset of single molecular magnetism behaviour should occur below 2 K. The trinuclear neptunyl coordination complex $[\{Np^{VI}O_2Cl_2\}\{Np^{V}O_2Cl(THF)_3\}]$ has previously been shown to exhibit slow relaxation of magnetisation and sizeable inter-Np superexchange,[33] so finding this behaviour in a Np^{III} complex may offer opportunities for high f^n systems to be generated.[123] A combination of experimental and QTAIM computational comparisons of $M(L^{Ar})X$ (M = Sm, U, Np; X = Cl, I) show significant differences (up to 17%) in orbital contributions to M-L bonds between the Ln and An analogues. There have been recent discussions over the way in which covalent overlap can be defined in the M-L bond; either in terms of spatial orbital overlap, or through the existence of metal and ligand orbitals that have the same energy, and are therefore able to mix. In this case, the Np-ligand bonding arises from spatial orbital overlap with the more diffuse 5f orbitals.[24] The metal content of the metal-arene π bonding orbitals is remarkably similar in the Sm, U, and Np model complexes, (6 to 8 %) and is largely d-based, in agreement with that proposed for the hypothetical $U(C_6H_6)_2$.[133] For comparison, these values are about half that in the classical d-block $W(\eta^6\text{-}C_6H_6)_2$ (calculate to have 16 % metal 5d character in the e_{1g} metal-ring π bonding orbitals).

6. Mössbauer studies of the Np nucleus in organometallic complexes

The isomer shift in the ^{237}Np Mössbauer spectrum of a compound depends on the shielding of the 6s orbital by electron density in the inner orbitals, including in particular, the 5f, with an increase in the value of the isomer shift observed with either a decrease in Np oxidation state or increase in electron donation from the ligands.[98] Spectra of a number of organometallic Np^{IV} as well as some Np^{III} complexes have been reported, Table 2.

The isomer shift for $Np(Cp)_3Cl$ recorded by Adrian of 0.6 mm s^{-1} (the other reported measurement of +14 mm s^{-1} had a particularly large error of ±10 mm s^{-1} associated) is larger than that of $NpCl_4$ (-3.4 mm s^{-1}) confirming that Cp is a better electron donor for the Np^{IV} ion than chloride, and that there is appreciable covalency in the Np-Cp bonding.[75,78,134] However, disagreements in the isomer shift value for the homoleptic $Np(Cp)_4$ complex; +7.2 mm s^{-1}[78,97] vs 17.9(1) (referenced to $NpAl_2$ at $\delta = 0$; reported originally as +31.8 mm s^{-1} vs Am metal)[98,105] stalled further discussions. The latter measurements were made on a spectrometer at the Kernforschungszentrum Karlsruhe, GmbH, which was regarded at the time as state-of-the-art in terms of accuracy and resolution, but the samples always contained impurities. Our current knowledge of the propensity of organo-Np^{IV} to be reduced to Np^{III} (see below) therefore suggest the sample contained both Np^{III} and Np^{IV} Cp complexes, and that these compounds warrant re-investigation. We now know that the colour and solubility properties of $K[Np(Cp)_4]$ and $Np(Cp)_4$ are almost identical (see below).

The effects of incorporating Cp ligand ring-substituents can be explained by reduced overlap of carbon and Np orbitals arising from steric crowding: The average Np-C bond length in $Np(Cp)_3(OPh)$ of 2.73 Å increases to 2.81 Å in $Np(Cp)_4$, exactly as seen in U analogues.[81]

Orbital overlap is even more restricted in the bis(cyclopentadienyl) complexes $Np(Cp^{Me})_2(acac)_2$ (-5.3 mm s^{-1}) ($Cp^{Me} = C_5H_4CH_3$) and $Np(Cp)_2(HB(pz)_3)_2$ (-4.6 mm s^{-1}) for which the isomer shifts are very similar to the parent chlorides ($Np(acac)_2Cl_2$; -4.2 mm s^{-1} and $Np(HB(pz)_3)_2Cl_2$; -6.0 mm s^{-1}).[4,100] Neptunocene has a very large isomer shift (19.4 mm s^{-1}) as it has short Np-C distances (2.63 Å, Np-ring centroid 1.899 Å) compared with the average Np- Cp ring centroid distance in $Np(Cp)_3(OPh)$ of 2.466(3) Å,[114] and that of 2.551(1) Å in $Np(Cp)_4$,[41] exactly as seen in U analogues.[81] The The existence of a multiconfigurational ground state that affords some Np^{III} character to neptunocene (see below) was not discussed at the time.

When the absorbing ^{237}Np nucleus relaxes faster than the 62-ns half-life of the excited state, the spectra become poorly resolved or uninterpretable, limiting the utility of the technique. The use of bulkier ligands was shown to reduce the relaxation problem,[134] although the observation that $Np(Cp^{Me})_4$ has the same isomer shift as its parent $Np(Cp)_4$ within experimental error suggests that perhaps only a limited utility for this technique in teasing out subtle differences.

Even though only limited conclusions can be drawn from the above data due to sample availability and purity, and spectrometer technology, Np Mössbauer spectroscopy is clearly a powerful method to determine the 6s electron density at the Np nucleus for different compounds. The study of a wider range of organometallic compounds with modern spectrometers should enable a much deeper understanding of electronic structure and covalency in the early actinides.

Table 2 Mössbauer isomer shifts for organometallic Np^{IV} and Np^{III} complexes

Compound	**Isomer shift^a δ (mm s^{-1})**	**Reference**
$NpCl_4$	-3.4	135
$Np(COT)_2$	19.1(2)	75
$Np(Cp)_4$	7.2(2)	78
$Np(Cp)_4$	17.9(1)^b	98
$Np(Cp^{Me})_4$	7.1(7)	97
$Np(Cp^{Me})_3(BH_4)$	14.5(40)	97
$Np(Cp)_3Cl$	0.6	100
$Np(Cp)_3Cl$	14(10)	78
$Np(Cp)_3I$	-3.9	100
$Np(Cp)_3Ph$	17.4	100
$Np(Cp)_3(n\text{-}Bu)$	2.7(7)	97
$Np(Cp^{Me})_3(O^iPr)$	9.3(7)	97

$Np(Cp)_3(O^tBu)$	8.6(30)	97
$Np(Cp)_3(O^iPr)$	8.6(20)	97
$Np(Cp)_3(O^iC_3F_7)$	7.9(20)	97
$Np(Cp)_3(p\text{-}(C_6H_4C_2H_5))$	4.2(28)	97
$Np(Cp)_3C_2H$	11.0	100
$Np(Cp)_3(NCS)$	8.1	100
$[Np(Cp)_3)_2]_2C_2$	20.1	105
$Np(Cp)_3(NC_4H_4)$	19.7	105
$[Np(Cp)_3]_2SO_4$	1.9	105
$[Np(Cp)_2[HB(pz)_3]_2$	-4.6(7)	100
$Np(Cp)_2(Cl)_2$	-2.7(2)	100
$Np(Cp^{Me})Cl_3 \cdot 2THF$	-3.1(7)	97
$NpCl_3$	35.4	78
NpI_3	33.3	125
$NpI_3 \cdot 6THF$	33.2	125
$NpCp_3 \cdot 3THF$	36.4	78
$NpCp_3(THF)$	35.4	78
$Np(C_9H_7)_2 \cdot x THF$	35.5(2)	97
$K[Np(COT)_2] \cdot 2THF$	39.2	124
$Np(COT)I \cdot x THF$	38.3	125

a) $NpAl_2$ standard set at $\delta = 0$.[136] b) the value reported of 31.75 was referenced against Am metal, and has been converted here to enable comparisons.

7. Concluding remarks

Contemporary organometallic actinide chemistry is already playing a key role in the fundamental understanding of electronic structure and bonding in the actinides, a poorly understood area of the periodic table. Organoneptunium chemistry has had a long, slow infancy, but technological advances such as paramagnetic multinuclear NMR spectroscopy and high-resolution single crystal X-ray diffraction are enabling an increased take-up as clearly much work has to be done to understand the fundamental properties of this important, environmentally mobile, and (radio)toxic element. The most recent advances in miniaturisation of spectrometers such that they can be placed in a glove box (FTIR, Uvvis, NMR spectroscopy), or coupled to a box via fibre-optic or needle (UVvis spectroscopy, Mass spectrometry) have the potential to eliminate the double containment requirements for sample analysis. Although keeping the spectrometers clean is of paramount importance, these may enable timely analyses of much more reactive and labile complexes, with a desirable associated increase in speed.

The $\mathrm{Np}^{\mathrm{III/IV}}$ redox interconversion is more closely balanced than that of $\mathrm{U}^{\mathrm{III/IV}}$ which is heavily weighted towards U^{IV}. Spontaneous reduction chemistry of organo-$\mathrm{Np}^{\mathrm{IV}}$ complexes is a more common reaction process that was originally envisaged, but a fine balance in redox potentials for cyclopentadienyl ligand – supported complexes should enable many $\mathrm{Np}^{\mathrm{IV}}$ and $\mathrm{Np}^{\mathrm{III}}$ organometallic complexes to be isolated. The utility of the Cp anion as a reductant is well documented in preparative inorganic chemistry, but the development of this transformation in transuranic chemistry, where the manipulation of Group 1 element reducing agents and amalgams, may place additional burdens on safety or disposal procedures, may be of wider interest. Furthermore, the recent efforts to isolate complexes with formal oxidation state $\mathrm{Np}^{\mathrm{II}}$ fall in line with work to isolate 'ate' complexes containing formal $\mathrm{Th}^{\mathrm{II}}$, U^{II}, and $\mathrm{Pu}^{\mathrm{II}}$ cations. These very low oxidation state targets should be more readily accessible for both Np and Pu than the earlier actinides.

No redox reactivity studies, for example the activation of small molecules such as H_2, CO, and N_2 by $\mathrm{Np}^{\mathrm{III}}$, have yet been reported (*c.f.* $\mathrm{U}^{\mathrm{III}}$), but academically-interesting reactions that could be made to turnover can be envisaged because of the closer balance of the III/IV couple as mentioned above. The homoleptic alkyl complex $\mathrm{Np[CH(SiMe_3)_2]_3}$ that has been mentioned in preliminary studies might be an ideal candidate for this, but there are many other strongly binding non-Cp based organometallic ligands that could also provide either spectator or reactive ligands, such as benzyl, or amino-benzyl, aryl, N-heterocyclic carbene, or other ylid derivatives like $[\mathrm{CH{=}CPPh_3}]^-$.

Single or diatom-bridged ligands that mediate strong metal-metal magnetic coupling are potentially exciting targets for these high f^n-systems, with the oxo atom and acetylide units being the most obvious well-defined, and therefore simplest, initial candidates for study. The combined experimental/computational study of simple molecular magnetic systems is usually extremely helpful for the understanding of more complicated phenomena in materials. The alkynide complexes or their analogues may also provide precursors for neptunium carbide materials, which could be interesting comparators for the uranium carbide materials that are potential future nuclear fuels.

Perhaps most importantly to the f-block chemist, the extent, and indeed the definition, of covalency in the actinide-ligand bond continues to exercise, and these single-ion complexes with soft and derivatisable carbocyclic ligands offer routes to study subtle trends and differences between metals and ligand substitution patterns. The series of compounds that were originally made for Mössbauer studies warrant further investigation in this respect, particularly if more modern instrumentation is to become available. Combined experimental-computational studies offer powerful, mutually helpful, approaches to understand electronic structures and ways in which ligands can manipulate them.

The study of high f^n-containing discrete molecules has yielded fascinating magnetic properties for the 4f series, such as molecules that exhibit very high spin-inversion barriers that generates single molecule magnet behaviour. Early results on neptunium complexes suggest there may be even more interesting spin-systems to be discovered from further reduction chemistry or from coupling multiple low oxidation state nuclei. Molecular spintronics is a burgeoning area and there may be many more unusual spin systems to be explored and developed in neptunium chemistry.

In terms of size and one-electron redox couples neptunium fits neatly between uranium and plutonium, its two more famous neighbours. However, it is now clear that there are many instances when its organometallic chemistry proceeds differently, and often the products have interesting properties. Understanding the subtleties and learning to control its chemistry in an anaerobic environment will help the general understanding of structure and bonding, and contribute to understanding speciation in the more complicated protic, aerobic, and potentially more hazardous areas of waste and environmental transuranic chemistry. Of the small number of examples now made, neptunium is already showing a rich ligand and redox reactivity manifold. We suggest that the fact that neptunium's chemistry has been generally overlooked is reason enough for it to be studied.

Now is a good time for organometallic Np chemistry to come of age.

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9. Abbreviations

Ar	aromatic, arene (generic)
ATR	attenuated total reflectance
CCI	cation-cation interactions
COT	cyclooctatetraenediyl dianion
Cp	cyclopentadienyl anion
Cp'	(trimethylsilyl)cyclopentadienyl anion
Cp''	1,3-bis(trimethylsilyl)cyclopentadienyl anion
Cp^*	pentamethylcyclopentadienyl anion
Ct	centroid, spatial centre between
DME	1,2-dimethoxyethane
Py	pyridine
$t_{1/2}$	half-life
DFT	density functional theory
TRU	transuranic element

10.References

(1) Baumgärtner, F.; Fischer, E. O.; Laubereau, P. Über die Existenz von Tri-cyclopentadienyl-neptunium(IV)-halogenid. *Die Naturwissenschaften* **1965,** *52*, 560-560.

(2) Fischer, E. O.; Laubereau, P.; Baumgärtner, F.; Kanellakopulos, B. Tricyclopentadienylneptunium-chlorid. *J. Organomet. Chem.* **1966,** *5*, 583-584.

(3) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B.; Laubereau, P. Tetrakis(cyclopentadienyl)neptunium(IV). *Angew. Chem. Int. Ed.* **1968,** *7*, 634-634.

(4) Ibers, J. Neglected neptunium. *Nat. Chem.* **2010,** *2*, 996.

(5) Kaltsoyannis, N. Does covalency increase or decrease across the actinide series? Implications for minor actinide partitioning. *Inorg. Chem.* **2013,** *52*, 3407-3413.

(6) Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. Bonding in tris(η^5-cyclopentadienyl) actinide complexes. 2. The ground electronic configurations of "base-free" Cp_3An complexes (An = thorium, protactinium, uranium, neptunium, plutonium). *J.Am. Chem. Soc.* **1989,** *111*, 2756-2758.

(7) Kirker, I.; Kaltsoyannis, N. Does covalency really increase across the 5f series? A comparison of molecular orbital, natural population, spin and electron density analyses of AnCp3 (An = Th-Cm; Cp = [small eta]5-C5H5). *Dalton Trans.* **2011,** *40*, 124-131.

(8) Tassell, M. J.; Kaltsoyannis, N. Covalency in $AnCp_4$ (An = Th-Cm): a comparison of molecular orbital, natural population and atoms-in-molecules analyses. *Dalton Trans.* **2010,** *39*, 6719-6725.

(9) Pepper, M.; Bursten, B. E. The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry. *Chem. Rev.* **1991,** *91*, 719-741.

(10) Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L.; Shuh, D. K.; Tyliszczak, T. New evidence for 5f covalency in actinocenes determined from carbon K-edge XAS and electronic structure theory. *Chem. Sci.* **2014,** *5*, 351-359.

(11) Neidig, M. L.; Clark, D. L.; Martin, R. L. Covalency in f-element complexes. *Coord. Chem. Rev.* **2013,** *257*, 394-406.

(12) Apostolidis, C.; Walter, O.; Vogt, J.; Liebing, P.; Maron, L.; Edelmann, F. T. A structurally characterized organometallic plutonium(IV) complex. *Angew. Chem. Int. Ed.* **2017,** *in press*.

(13) Gorden, A. E. V.; Shuh, D. K.; Tiedemann, B. E. F.; Wilson, R. E.; Xu, J.; Raymond, K. N. Sequestered Plutonium: $[Pu^{IV}\{5LiO(Me\text{-}3,2\text{-}HOPO)\}_2]$—The First Structurally Characterized Plutonium Hydroxypyridonate Complex. *Chem. Eur. J.* **2005,** *11*, 2842-2848.

(14) Wang, M.; Audi, G.; Wapstra, A. H.; Kondev, F. G.; MacCormick, M.; Xu, X.; Pfeiffer, B. The Ame2012 atomic mass evaluation. *Chin. J. Phys. C* **2012,** *36*, 1603-2014.

(15) Bhat, M. R. In *Nuclear Data for Science and Technology*; Qaim, S. M., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 1992.

(16) Thompson, R. C. Neptunium: The Neglected Actinide: A Review of the Biological and Environmental Literature. *Radiat. Res.* **1982,** *90*, 1-32.

(17) Herbst, R. S.; Baron, P.; Nilsson, M., *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Elsevier, 2011.

(18) Drake, V. A. In *Science and Technology of Tributyl Phosphate Vol. III*; Schulz, W. W.;Burger, L. L.;Navratil, J. D., Eds.; CRC Press: Boca Rayton, Florida, 1990.

(19) Kienzler, B.; Vejmelka, P.; Römer, J.; Fanghänel, E.; Jansson, M.; Eriksen, T. E.; Wikberg, P. Swedish-German actinide migration experiment at ASPO hard rock laboratory. *J. Contam. Hydrol.* **2003,** *61*, 219-233.

(20) Icopini, G. A.; Boukhalfa, H.; Neu, M. P. Biological Reduction of Np(V) and Np(V) Citrate by Metal-Reducing Bacteria. *Environ. Sci. Tech.* **2007,** *41*, 2764-2769.

(21) NucleonicaGmbH, *Nucleonica Nuclear Science Portal (*www.nucleonica.com*)*; Nucleonica GmbH: Karlsruhe, Germany, 2014.

(22) Weiss, P. Neptunium Nukes? *Science News* **2002,** *162*, 259.

(23) Nash, K.; Madic, C.; Mathur, J. N.; Lacquement, J.,Neptunium; in The Chemistry of the Actinide and Transactinide Elements, 4th ed.; Joseph J. Katz;Morss, L. R.;Edelstein, N. M.;Fuger, J., Eds.; Springer: Netherlands, 2010; Vol. 5.

(24) Dutkiewicz, M. S.; Farnaby, J. H.; Apostolidis, C.; Colineau, E.; Walter, O.; Magnani, N.; Gardiner, M. G.; Love, J. B.; Kaltsoyannis, N.; Caciuffo, R.et al. Organometallic neptunium(III) complexes. *Nature Chem.* **2016,** *8*, 797-802.

(25) Evans, W. J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. *Organomet.* **2016,** *35*, 3088-3100.

(26) Marks, T. J.; Ernst, R. D.,Scandium, Yttrium and the Lanthanides and Actinides; in Comprehensive Organometallic Chemistry; Elsevier, 1982.

(27) Martinot, L.; Fuger, J.,Standard Potentials in Aqueous Solutions; in; Bard, A. J.;Parsons, R.;Jordan, J., Eds.; Marcel Dekker: New York, 1985.

(28) Capdevila, H.; Vitorge, P. Temperature and ionic strength influence on U(VI/V) and U(IV/III) redox potentials in aqueous acidic and carbonate solutions,. *J. Radioanal. Nucl. Chem. Art.* **1990,** *143*, 403-414.

(29) Lemire, R. J.; Fuger, J.; Nitsche, H.; Potter, P.; Rand, M. H.; Rydberg, J.; Spahiu, K.; Sullivan, J. C.; Ullman, W. J.; Vitorge, P.et al., *Chemical Thermodynamics of Neptunium and Plutonium*; Elsevier: Amsterdam, 2001.

(30) Sonnenberger, D. C.; Gaudiello, J. G. Cyclic voltammetric study of organoactinide compounds of uranium(IV) and neptunium(IV). Ligand effects on the M(IV)/M(III) couple. *Inorg. Chem.* **1988,** *27*, 2747-2748.

(31) Konings, R. J. M.; Morss, L. R.; Fuger, J.,Thermodynamic Properties of Actinides and Actinide Compounds; in The Chemistry of the Actinide and Transactinide Elements; Lester R. Morss, N. E., Jean Fuger, Ed.; Springer Science, 2010; Vol. 4.

(32) Choppin, G.; Liljenzin, J.-O.; Rydberg, J.; Ekberg, C. Radiochemistry and Nuclear Chemistry. *Radiochem. Nucl. Chem.* **2013**, 753-788.

(33) Magnani, N.; Colineau, E.; Eloirdi, R.; Griveau, J. C.; Caciuffo, R.; Cornet, S. M.; May, I.; Sharrad, C. A.; Collison, D.; Winpenny, R. E. P. Superexchange coupling and slow magnetic relaxation in a transuranium polymetallic complex. *Phys. Rev. Lett.* **2010,** *104*, 197202.

(34) Rinehart, J. D.; Long, J. R. Exploiting single-ion anisotropy in the design of f-element single-molecule magnets. *Chem. Sci.* **2011,** *2*, 2078-2085.

(35) Chatelain, L.; Walsh, J. P. S.; Pécaut, J.; Tuna, F.; Mazzanti, M. Self-assembly of a 3d-5f trinuclear single-molecule magnet from a pentavalent uranyl complex. *Angew. Chem. Int. Ed.* **2014,** *53*, 13434-13438.

(36) Arnold, P. L.; Hollis, E.; Nichol, G. S.; Love, J. B.; Griveau, J. C.; Caciuffo, R.; Magnani, N.; Maron, L.; Castro, L.; Yahia, A.et al. Oxo-functionalization and reduction of the uranyl ion through lanthanide-element bond homolysis: Synthetic, structural, and bonding analysis of a series of singly reduced uranyl-rare earth $5f^n$-$4f^n$ complexes. *J.Am. Chem. Soc.* **2013,** *135*, 3841-3854.

(37) Arnold, P. L.; Hollis, E.; White, F. J.; Magnani, N.; Caciuffo, R.; Love, J. B. Single-electron uranyl reduction by a rare-earth cation. *Angew. Chem. Int. Ed.* **2011,** *50*, 887-890.

(38) Mougel, V.; Chatelain, L.; Pecaut, J.; Caciuffo, R.; Colineau, E.; Griveau, J.-C.; Mazzanti, M. Uranium and manganese assembled in a wheel-shaped nanoscale single-molecule magnet with high spin-reversal barrier. *Nature Chem.* **2012,** *4*, 1011-1017.

(39) Taylor, J. C.; Wilson, P. W. The structure of uranium(III) trichloride by neutron diffraction profile analysis. *Acta Crystallogr., Sect. B: Struct. Sci.* **1974,** *30*, 2803-2805.

(40) Levy, J. H.; Taylor, J. C.; Wilson, P. W. The structure of uranium(III) triiodide by neutron diffraction. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975,** *31*, 880-882.

(41) Dutkiewicz, M. S.; Apostolidis, C.; Walter, O.; Arnold, P. L. Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding. *Chem. Sci.* **2017,** *8*, 2553-2561.

(42) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. A convenient entry into trivalent actinide chemistry: synthesis and characterization of $AnI_3(THF)_4$ and $An[N(SiMe_3)_2]_3$ (An = U, Np, Pu). *Inorg. Chem.* **1994,** *33*, 2248-2256.

(43) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. Lewis base adducts of uranium triiodide: a new class of synthetically useful precursors for trivalent uranium chemistry. *Inorg. Chem.* **1989,** *28*, 1771-1773.

(44) Reilly, S. D.; Brown, J. L.; Scott, B. L.; Gaunt, A. J. Synthesis and characterization of $NpCl_4(DME)_2$ and $PuCl_4(DME)_2$ neutral transuranic An(IV) starting materials. *Dalton Trans.* **2014,** *43*, 1498-1501.

(45) Eisenberg, D. C.; Streitwieser, A.; Kot, W. K. Electron transfer in organouranium and transuranium systems. *Inorg. Chem.* **1990,** *29*, 10-14.

(46) Minasian, S. G.; Boland, K. S.; Feller, R. K.; Gaunt, A. J.; Kozimor, S. A.; May, I.; Reilly, S. D.; Scott, B. L.; Shuh, D. K. Synthesis and Structure of $(Ph_4P)_2MCl_6$ (M = Ti, Zr, Hf, Th, U, Np, Pu). *Inorg. Chem.* **2012,** *51*, 5728-5736.

(47) Cary, S. K.; Vasiliu, M.; Baumbach, R. E.; Stritzinger, J. T.; Green, T. D.; Diefenbach, K.; Cross, J. N.; Knappenberger, K. L.; Liu, G.; Silver, M. A.et al. Emergence of californium as the second transitional element in the actinide series. **2015,** *6*, 6827.

(48) Jones, M. B.; Gaunt, A. J.; Gordon, J. C.; Kaltsoyannis, N.; Neu, M. P.; Scott, B. L. Uncovering f-element bonding differences and electronic structure in a series of 1 : 3 and 1 : 4 complexes with a diselenophosphinate ligand. *Chem. Sci.* **2013,** *4*, 1189-1203.

(49) Formanuik, A.; Ariciu, A.-M.; Ortu, F.; Beekmeyer, R.; Kerridge, A.; Tuna, F.; McInnes, E. J. L.; Mills, D. P. Actinide covalency measured by pulsed electron paramagnetic resonance spectroscopy. *Nat. Chem.* **2017,** *9*, 578-583.

(50) Löble, M. W.; Keith, J. M.; Altman, A. B.; Stieber, S. C. E.; Batista, E. R.; Boland, K. S.; Conradson, S. D.; Clark, D. L.; Lezama Pacheco, J.; Kozimor, S. A.et al. Covalency in lanthanides. An X-ray absorption spectroscopy and density functional theory study of $LnCl_6^{x-}$ (x = 3, 2). *J.Am. Chem. Soc.* **2015,** *137*, 2506-2523.

(51) Butorin, S. M.; Kvashnina, K. O.; Smith, A. L.; Popa, K.; Martin, P. M. Crystal-Field and Covalency Effects in Uranates: An X-ray Spectroscopic Study. *Chem. Eur. J.* **2016,** *22*, 9693-9698.

(52) Macor, J. A.; Brown, J. L.; Cross, J. N.; Daly, S. R.; Gaunt, A. J.; Girolami, G. S.; Janicke, M. T.; Kozimor, S. A.; Neu, M. P.; Olson, A. C.et al. Coordination chemistry of 2,2[prime or minute]-biphenylenedithiophosphinate and diphenyldithiophosphinate with U, Np, and Pu. *Dalton Trans.* **2015,** *44*, 18923-18936.

(53) Brown, J. L.; Gaunt, A. J.; King, D. M.; Liddle, S. T.; Reilly, S. D.; Scott, B. L.; Wooles, A. J. Neptunium and plutonium complexes with a sterically encumbered triamidoamine (TREN) scaffold. *Chem. Comm.* **2016,** *52*, 5428-5431.

(54) Brown, J. L.; Batista, E. R.; Boncella, J. M.; Gaunt, A. J.; Reilly, S. D.; Scott, B. L.; Tomson, N. C. A linear trans-bis(imido) meptunium(V) actinyl analog: $Np^V(NDipp)_2(tBu_2bipy)_2Cl$ (Dipp = 2,6-$iPr_2C_6H_3$). *J.Am. Chem. Soc.* **2015,** *137*, 9583-9586.

(55) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. Synthesis of Imido Analogs of the Uranyl Ion. *Science* **2005,** *310*, 1941-1943.

(56) Gysling, H.; Tsutsui, M. Organolanthanides and Organoactinides. *Adv. Organomet. Chem.* **1971,** *9*, 361-395.

(57) Legin, E. K. Uranocene and its actinoid analogues. *Radiokhimiya* **1979,** *21*, 565-578.

(58) Hayes, R. G.; Thomas, J. L. organommetallic compounds of lanthanides and actinides. *Organometallic Chem. Rev. A-Subject Reviews* **1971,** *7*, 1-&.

(59) Marks, T. J. Actinide Organometallic Chemistry. *Science* **1982,** *217*, 989-997.

(60) Mishin, V. Y.; Sidorenko, G. V.; Suglobov, D. N. A review of organo neptunium chemistry. *Radiokhimiya* **1986,** *28*, 292–300.

(61) Liddle, S. T. The Renaissance of Non-Aqueous Uranium Chemistry. *Angew. Chem. Int. Ed.* **2015,** *54*, 8604-8641.

(62) LaPierre, H. S.; Meyer, K. Activation of small molecules by molecular uranium complexes. *Progr. Inorg. Chem.* **2014,** *58*, 303-416.

(63) Baker, R. J. The coordination and organometallic chemistry of UI_3 and $U\{N(SiMe_3)_2\}_3$: Synthetic reagents par excellence. *Coord. Chem. Rev.* **2012,** *256*, 2843-2871.

(64) Arnold, P. L. Uranium-mediated activation of small molecules. *Chem. Comm.* **2011**.

(65) Gaunt, A. J.; Neu, M. P. Recent developments in nonaqueous plutonium coordination chemistry. *Comp. Rend. Chim.* **2010,** *13*, 821-831.

(66) Jones, M. B.; Gaunt, A. J. Recent developments in synthesis and structural chemistry of nonaqueous actinide complexes. *Chem. Rev.* **2013,** *113*, 1137-1198.

(67) Behrle, A. C.; Walensky, J. R.,Actinides: Organometallic Chemistry; in Encyclopedia of Inorganic and Bioinorganic Chemistry; Scott, R. A., Ed.; John Wiley & Sons, Ltd: Chichester, UK, 2014.

(68) Edelmann, F. T. Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2014. *Coord. Chem. Rev.* **2016,** *306*, 346-419.

(69) Yoshida, Z.; Johnson, S. G.; Kimura, T.; Krsul, J. R.,Chapter 6, Neptunium; in The Chemistry of the Actinide and Transactinide Elements; Morss, L. R.;Edelstein, N. M.;Fuger, J., Eds.; Springer Netherlands: Dordrecht, 2011.

(70) Burns, C. J.; Eisen, M. S.,Chapter 25. Organoactinide Chemistry: Synthesis and Characterization; in The Chemistry of the Actinide and Transactinide Elements; Morss, L. R.;Edelstein, N. M.;Fuger, J., Eds.; Springer Netherlands: Dordrecht, 2011.

(71) Edelmann, F. T. Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2016. *Coord. Chem. Rev.* **2017,** *338*, 27-140.

(72) Harbottle, G.; Sutin, N. The Szilard–Chalmers Reaction in Solids. Part I. Chemical Effects of Nuclear Recoil. *J. Phys. Chem.* **1958,** *62*, 1344-1351.

(73) Laubereau, P., 1966.

(74) Dornberger, E.; Klenze, R.; Kanellakopulos, B. Über eine neue präparative methode zur synthese metallorganischer verbindungen. *Inorg. Nucl. Chem. Lett.* **1978,** *14*, 319-324.

(75) Bohlander, R., Kernforschungszentrum Karlsruhe G.m.b.H. (Germany, F.R.). Inst. fuer Heisse Chemie; Karlsruhe Univ. (T.H.) (Germany, F.R.). Fakultaet fuer Chemie, 1986.

(76) Stollenwerk, A.; Klenze, R.; Kanellakopulos, B. Magnetic susceptibility of some organometallic compounds of neptunium(IV). *J. Phys. Colloques* **1979,** *C4*, 179-180.

(77) Bagnall, K. W.; Plews, M. J.; Brown, D.; Fischer, R. D.; Klahne, E.; Landgraf, G. W.; Sienel, G. R. Anionic tris(cyclopentadienyl)actinide(IV) complexes. *Dalton Trans.* **1982**, 1999-2007.

(78) Karraker, D. G.; Stone, J. A. Moessbauer and magnetic susceptibility studies of uranium(III), uranium(IV), neptunium(IV) compounds with the cyclopentadiene ion. *Inorg. Chem.* **1972,** *11*, 1742-1746.

(79) Reynolds, L. T.; Wilkinson, G. π-cyclopentadienyl compounds of uranium-IV and thorium-IV. *J. Inorg. Nucl. Chem.* **1956,** *2*, 246-253.

(80) De Ridder, D. J. A.; Apostolidis, C.; Rebizant, J.; Kanellakopulos, B.; Maier, R. Tris(η^5-cyclopentadienyl)phenolatoneptunium(IV). *Acta Cryst. C* **1996,** *52*, 1436-1438.

(81) Spirlet, M. R.; Rebizant, J.; Apostolidis, C.; Van den Bossche, G.; Kanellakopulos, B. Structure of tris(η5-cyclopentadienyl)phenolatouranium(IV). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990,** *46*, 2318-2320.

(82) Kanellakopulos, B.; Maier, R.; Heuser, J. Molecular structure and charge distribution in organometallics of the 4f and 5f elements I: Dipole moment and charge distribution of the actinoid(IV) tetracyclopentadienides, An(C5H5)4. *J. Alloys Compd.* **1991,** *176*, 89-96.

(83) Kanellakopulos, B.; Bagnall, K. W.,Inorganic Chemistry - Series One: Lanthanides and Actinides vol. 7; in M.T.P. International Review of Science; Bagnall, K. W., Ed.; Butterworth & Co Publishers Ltd (February 1972), 1972.

(84) Maier, R.; Kanellakopulos, B.; Apostolidis, C.; Meyer, D.; Rebizant, J. Molecular structure and charge distribution in organometallics of the 4f and 5f elements V: crystal and molecular structure of tetrakis(ν5-cyclopentadienyl)-thorium(IV) and the temperature dependence of its electrical dipole moment. *J. Alloys Compd.* **1993,** *190*, 269-271.

(85) Burns, J. H. The molecular and crystal structure of tetracyclopentadienyluranium(IV). *J. Organomet. Chem.* **1974,** *69*, 225-233.

(86) Raymond, K. N.; Eigenbrot, C. W. Structural criteria for the mode of bonding of organoactinides and -lanthanides and related compounds. *Acc. Chem. Res.* **1980,** *13*, 276-283.

(87) Amberger, H. D. Zur elektronenstruktur metallorganischer komplexe der f-elemente. *J. Organomet. Chem.* **1976,** *110*, 59-66.

(88) Amberger, H. D.; Fischer, R. D.; Kanellakopulos, B. The Electronic Structure of Organometallic Complexes Involving f-Electrons, II Magnetic Susceptibility and Crystal Field Splitting of Uranium(IV)-tetracyclopentadienide. *znb* **1976,** *31*, 12.

(89) Amberger, H. D.; Fischer, R. D.; Rosenbauer, G. G. Zur Elektronenstruktur hochsymmetrischer Komplexe der Lanthaniden und Actinoiden, I Magnetismus und Schwingungsspektren von Tris(tetraäthylammonium)-hexaisocyanato-ytterbium(III) / The Electronic Structure of Highly-Symmetrical Lanthanide and Actinide Complexes, I Magnetism and Vibrational Spectra of Tris(tetraethylammonium)-hexaisocyanate-ytterbium(III). *znb* **1976,** *31*, 1.

(90) Bursten, B. E.; Casarin, M.; DiBella, S.; Fang, A.; Fragala, I. L. Photoelectron spectroscopy of f-element organometallic complexes. 6. Electronic structure of tetrakis(cyclopentadienyl)actinide complexes. *Inorg. Chem.* **1985,** *24*, 2169-2173.

(91) Arnold, P. L.; Dutkiewicz, M. S.; Zegke, M.; Walter, O.; Apostolidis, C.; Hollis, E.; Pécharman, A.-F.; Magnani, N.; Griveau, J.-C.; Colineau, E.et al. Subtle interactions and electron transfer between U^{III}, Np^{III}, or Pu^{III} and uranyl mediated by the oxo group. *Angew. Chem. Int. Ed.* **2016,** *55*, 12797-12801.

(92) Zanella, P.; Rossetto, G.; De Paoli, G.; Traverso, O. Reduction of (η5 -C5H5)3UCl with sodium hydride: the preparation and spectral studies of (η5 -C5H5)3U and (η5 -C5H5)3 U·OC4H8. *Inorg. Chim. Acta* **1980,** *44*, L155-L156.

(93) Baisch, U.; Pagano, S.; Zeuner, M.; Schmedt auf der Günne, J.; Oeckler, O.; Schnick, W. Synthesis, structure, and dynamics of tris(η5-cyclopentadienyl)lanthanides and bis(η5-cyclopentadienyl)[bis(trimethylsilyl)amido]cerium(III). *Organomet.* **2006,** *25*, 3027-3033.

(94) Wong, C.-H.; Lee, T.-Y.; Lee, Y.-T. The crystal structure of tris(cyclopentadienyl)samarium(III). *Acta Crystallogr., Sect. B: Struct. Sci.* **1969,** *25*, 2580-2587.

(95) Eggers, S. H.; Kopf, J.; Fischer, R. D. On the metal coordination in base-free tris(cyclopentadienyl) complexes of the lanthanoids. 2. The x-ray structure of tris(cyclopentadienyl)lanthanum(III): a notably stable polymer displaying more than three different lanthanum-carbon interactions. *Organomet.* **1986,** *5*, 383-385.

(96) S.Eggers; W.Hinrichs; J.Kopf; R.D.Fischer; Xing-Fu, L. CYPESM02: tris(η^5-cyclopentadienyl)samarium(III). *CSD Communication* **1992**.

(97) Karraker, D. G. In *Organometallics of the f-Elements. Proceedings of the NATO Advanced Study Institute held at Sogesta, Urbino, Italy, September 11–22, 1978*; Marks, T. J.;Fischer, R. D., Eds.; Springer Netherlands: Dordrecht, 1979.

(98) Adrian, G. A model for describing paramagnetic Mössbauer relaxation spectra of organometallic ^{237}Np compounds. *Inorg. Chim. Acta* **1987,** *139*, 323-325.

(99) Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. Identification of the formal +2 oxidation state of plutonium: Synthesis and characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^-$. *J.Am. Chem. Soc.* **2017,** *139*, 3970-3973.

(100) Karraker, D. G. Cyclopentadienyl bonding in bis(cyclopentadienyl)neptunium(IV) compounds from neptunium-237 Moessbauer spectra. *Inorg. Chem.* **1983,** *22*, 503-506.

(101) Sonnenberger, D. C.; Gaudiello, J. Synthesis and cyclic voltammetric study of bis(pentamethylcyclopentadienyl)neptunium dichloride. *J. Less Common Metals* **1986,** *126*, 411-414.

(102) Bagnall, K. W.; Payne, G. F.; Alcock, N. W.; Flanders, D. J.; Brown, D. Actinide structural studies. Part 8. Some new oxygen-donor complexes of trichloro(cyclopentadienyl)neptunium(IV); the crystal structure of trichloro(η^5-cyclopentadienyl)bis(methyldiphenylphosphine oxide)neptunium(IV). *J. Chem. Soc., Dalton Trans.* **1986**, 783-787.

(103) Zwick, B. D.,Organometallic elements: the next generation; in Transuranium elements: a half century; Morss, L. R.;Fuger, J., Eds.; ACS: Weinheim, 1992.

(104) Marks, T. J.; Seyam, A. M. Observations on the thermal decomposition of some uranium(IV) tetraalkyls. *J. Organomet. Chem.* **1974,** *67*, 61-66.

(105) Adrian, G.; Appel, H.; Bohlander, R.; Haffner, H.; Kanellakopulos, B. Mössbauer effect studies on organometallic ^{237}Np-compounds. *Hyperfine Interact.* **1988,** *40*, 275-278.

(106) Marks, T. J.; Wachter, W. A. Tris(η^5-cyclopentadienyl)alkyl and -alkenyl compounds of thorium(IV). *J.Am. Chem. Soc.* **1976,** *98*, 703-710.

(107) Marks, T. J.; Seyam, A. M. Stable uranium(IV) alkyl and aryl complexes. *J.Am. Chem. Soc.* **1972,** *94*, 6545-6546.

(108) Streitwieser, A.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. Preparation and properties of uranocene, di-.pi.-cyclooctatetraeneuranium(IV). *J.Am. Chem. Soc.* **1973,** *95*, 8644-8649.

(109) Streitwieser, A.; Yoshida, N. Di-.pi.-cyclooctatetraenethorium. *J.Am. Chem. Soc.* **1969,** *91*, 7528-7528.

(110) Seyferth, D. Uranocene. The First Member of a New Class of Organometallic Derivatives of the f Elements. *Organomet.* **2004,** *23*, 3562-3583.

(111) Raymond, K. N. The structure determination of uranocene and the first COT lanthanide complexes. *New J. Chem.* **2015,** *39*, 7540-7543.

(112) Karraker, D. G.; Stone, J. A.; Jones, E. R.; Edelstein, N. Bis(cyclooctatetraenyl)neptunium(IV) and bis(cyclooctatetraenyl)plutonium(IV). *J.Am. Chem. Soc.* **1970,** *92*, 4841-4845.

(113) Magnani, N.; Apostolidis, C.; Morgenstern, A.; Colineau, E.; Griveau, J. C.; Bolvin, H.; Walter, O.; Caciuffo, R. Magnetic memory effect in a transuranic mononuclear complex. *Angew. Chem. Int. Ed.* **2011,** *50*, 1696-1698.

(114) De Ridder, D. J. A.; Rebizant, J.; Apostolidis, C.; Kanellakopulos, B.; Dornberger, E. Bis(cyclooctatetraenyl)neptunium(IV). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996,** *52*, 597-600.

(115) Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. Two isostructural actinide π complexes. The crystal and molecular structure of bis(cyclooctatetraenyl)uranium(IV), $U(C_8H_8)_2$, and bis(cyclooctatetraenyl)thorium(IV), $Th(C_8H_8)_2$. *Inorg. Chem.* **1972,** *11*, 1083-1088.

(116) Porter, J. A. Production of Neptunium Dioxide. *Ind. Eng. Chem. Proc. Des. Dev.* **1964,** *3*, 289-292.

(117) Rausch, J.; Apostolidis, C.; Walter, O.; Lorenz, V.; Hrib, C. G.; Hilfert, L.; Kuhling, M.; Busse, S.; Edelmann, F. T. One ligand fits all: lanthanide and actinide sandwich complexes comprising the 1,4-bis(trimethylsilyl)cyclooctatetraenyl (=COT[prime or minute][prime or minute]) ligand. *New J. Chem.* **2015,** *39*, 7656-7666.

(118) Kerridge, A. f-Orbital covalency in the actinocenes (An = Th-Cm): multiconfigurational studies and topological analysis. *RSC Adv.* **2014,** *4*, 12078-12086.

(119) Kondo, J. Sticking to My Bush. *J. Phys. Soc. Jpn.* **2005,** *74*, 1-3.

(120) Savrasov, S. Y.; Kotliar, G.; Abrahams, E. Correlated electrons in [delta]-plutonium within a dynamical mean-field picture. *Nature* **2001,** *410*, 793-795.

(121) Karraker, D. G. Bis(alkylcyclooctatetraenyl)actinide(IV) compounds1,2. *Inorg. Chem.* **1973,** *12*, 1105-1108.

(122) Apostolidis, C.; Edelmann Frank, T.; Kanellakopulos, B.; Reißmann, U. Organoactinide Chemistry: Polysilylated Actinidocenes of Thorium, Uranium, and Neptunium. *Z. Naturforsch., B* **1999,** *54*, 960.

(123) Rinehart, J. D.; Long, J. R. Slow magnetic relaxation in a trigonal prismatic uranium(III) complex. *J.Am. Chem. Soc.* **2009,** *131*, 12558-12559.

(124) Karraker, D. G.; Stone, J. A. Bis(cyclooctatetraenyl)neptunium(III) and -plutonium(III) compounds. *J.Am. Chem. Soc.* **1974,** *96*, 6885-6888.

(125) Karraker, D. G.; Stone, J. A. Mössbauer study of $NpI_3.K_2C_8H_8$ reactions. *J. Inorg. Nucl. Chem.* **1977,** *39*, 2215-2217.

(126) Li, J.; Bursten, B. E. Electronic structure of cycloheptatrienyl sandwich compounds of actinides: $An(\eta^7\text{-}C_7H_7)_2$ (An = Th, Pa, U, Np, Pu, Am). *J.Am. Chem. Soc.* **1997,** *119*, 9021-9032.

(127) King, W. A.; Di Bella, S.; Lanza, G.; Khan, K.; Duncalf, D. J.; Cloke, F. G. N.; Fragala, I. L.; Marks, T. J. Metal−Ligand Bonding and Bonding Energetics in Zerovalent Lanthanide, Group 3, Group 4, and Group 6

Bis(arene) Sandwich Complexes. A Combined Solution Thermochemical and ab Initio Quantum Chemical Investigation. *J.Am. Chem. Soc.* **1996,** *118*, 627-635.

(128) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B. The first structurally authenticated zerovalent heteroarene complex of a lanthanide; Synthesis and x-ray structure of bis(2,4,6-tri-tert-butylphosphorin)holmium(o). *Chem. Comm.* **1997**, 481-482.

(129) Dolg, M. Combined pseudopotential and density functional study of bis-η^6-benzene d and f element complexes. *J. Chem. Inf. Comput. Sci.* **2001,** *41*, 18-21.

(130) Ilango, S.; Vidjayacoumar, B.; Gambarotta, S. Samarium complexes of a σ-/π-pyrrolide/arene based macrocyclic ligand. *Dalton Trans.* **2010,** *39*, 6853-6857.

(131) Arnold, P. L.; Farnaby, J. H.; White, R. C.; Kaltsoyannis, N.; Gardiner, M. G.; Love, J. B. Switchable π-coordination and C-H metallation in small-cavity macrocyclic uranium and thorium complexes. *Chem. Sci.* **2014,** *5*, 756-765.

(132) Arnold, P. L.; Farnaby, J. H.; Gardiner, M. G.; Love, J. B. Uranium(III) coordination chemistry and oxidation in a flexible small-cavity macrocycle. *Organomet.* **2015,** *34*, 2114-2117.

(133) Hong, G.; Schautz, F.; Dolg, M. Ab initio study of metal−ring bonding in the bis(η^6-benzene)lanthanide and -actinide complexes $M(C_6H_6)_2$ (M = La, Ce, Nd, Gd, Tb, Lu, Th, U). *J.Am. Chem. Soc.* **1999,** *121*, 1502-1512.

(134) Karraker, D. G.; Stone, J. A. Covalency of neptunium(IV) tris(cyclopentadienyl) compounds from Moessbauer spectra. *Inorg. Chem.* **1979,** *18*, 2205-2207.

(135) Stone, J. A.; Pillinger, W. L. Nuclear Moment Ratios in Np 237 from Mössbaur Spectra. *Physical Review* **1968,** *165*, 1319-1326.

(136) Cohen, R. L.; Kalvius, G. M. Proposed isomer shift standards for Mössbauer spectroscopy. *Nucl. Instrum. Methods* **1970,** *86*, 209-212.

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