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Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding

This article presents a new benchmark in organometallic neptunium chemistry: up to now there were only three known structurally characterised organometallic neptunium complexes. In this work the structures of overall five organometallic complexes are supported by modern NMR and single crystal XRD analyses, enabling for the first time a comparison via more detailed insight into the structural features of these complexes. JRC-KA is one of the research sites of the European Commission. The research in Karlsruhe is aimed to the fulfilment of the Euratom treaty, dedicated to nuclear safety and security.
Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding†

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Neptunium complexes in the formal oxidation states II, III, and IV supported by cyclopentadienyl ligands are explored, and significant differences between Np and U highlighted as a result. A series of neptunium(III) cyclopentadienyl (Cp) complexes [Np(Cp)3], its bis-acetonitrile adduct [Np(Cp)3(NCMe)2], and its KCp adduct K[Np(Cp)3] and [Np(Cp)3] (Cp′ = C5H4SiMe3) have been made and characterised providing the first single crystal X-ray analyses of NpIII Cp complexes. In all NpCp2 derivatives there are three Cp rings in η5-coordination around the NpIII centre; additionally in [Np(Cp)3] and K[Np(Cp)3] one Cp ring establishes a μ-η1-interaction to one C atom of a neighbouring Np(Cp)3 unit. The solid state structure of K[Np(Cp)3] is unique in containing two different types of metal–Cp coordination geometries in the same crystal. Np(III) Cp4 units are found exhibiting four units of η5-coordinated Cp rings like in the known complex [Np(IV)Cp4], the structure of which is now reported. A detailed comparison of the structures gives evidence for the change of ionic radii of ca. −8 pm associated with change in oxidation state between NpIII and NpIV. The rich redox chemistry associated with the syntheses is augmented by the reduction of [Np(Cp)3] by KC8 in the presence of 2,2,2-cryptand to afford a neptunium(II) complex that is thermally unstable above −10 °C like the UII and ThII complexes K(2,2,2-cryptand)[Th(U)4]. Together, these spontaneous and controlled redox reactions of organoneptunium complexes, along with information from structural characterisation, show the relevance of organometallic Np chemistry to understanding fundamental structure and bonding in the minor actinides.

Introduction

Fifty years have passed since the foundation of organometallic neptunium chemistry in the form of cyclopentadienyl 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 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.§ Understanding the subtleties are key to the safe handling and separations of the highly radioactive nuclei.** For example, recent quantitative carbon K-edge X-ray absorption spectroscopy (XAS) analyses on the organometallic [An(COT)2] (An = Th, U), “actinocenes” provided the first experimental evidence for extensive φ-orbital interactions in thorocene, and remarkably little in the U analogue, with contrasting trends in orbital mixing.† Furthermore, a combination of experimental and QTAIM computational comparisons of [M(LH)X] (M = Sm, U, Np; X = Cl, I; L = dianionic arenedrugged trans-calix[2]benzene[2]pyrrole*†) showed significant differences (up to 17%) in orbital contributions to M–L bonds between the Ln and An analogues, and that the covalency in the Np–ligand bonding arises from spatial orbital overlap rather than a coincidental energy degeneracy.‡ The work also demonstrated differences between U and Np in their reaction chemistry, such as the stability of the NpIII formal oxidation state or the reduction of NpIV to NpIII upon complexation.

Organoneptunium chemistry has relied heavily on the ubiquitous cyclopentadienyl ligand, Cp = (C5H5)−, as a strongly binding, sterically demanding yet flexible, monooanion, and focused almost exclusively on NpIV complexes. The first evidence for the formation of [Np(Cp)3] (X = Cl, F) came from a radiochemical synthesis, i.e. the irradiation of a 238U complex with thermal neutrons,§ and [Np(Cp)X] (X = Cl, F) were

† Electronic supplementary information (ESI) available: General procedures, synthetic details, spectroscopic data, X-ray crystallographic data, CCDC 1524162–1524166. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc00034k

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Chem. Sci., 2017, 8, 2553–2561 | 2553
subsequently reported from standard chemical routes as thermally robust, volatile complexes.11,12 Baumgärtner et al. reported the first homoleptic organoneptunium complex, tetraakis(η⁵-cyclopentadienyl)neptunium(v), [Np(Cp)₄], from treatment of NpCl₄ with excess KCP in benzene.13 Many of the earliest studies on neptunium cyclopentadienyl complexes also had the aim of exploring covalency in the bonding, using the fact that Np is a Mössbauer active nucleus. However, not all the studies agreed. The first Mössbauer studies on [Np(Cp)₃] and [Np(COT)₃] suggested less interaction between the central ion and the Cp ligands but appreciable covalency in the Np–COT bonding.14 On the other hand, Bohlander15 reported the isomer shift of the Np nucleus in [Np(Cp)₃] closely approaches that of the record-breaking, covalent [Np(COT)₃], thus being the most covalent Np–Cp derivative. Finally, from analysis of the isomer shifts Karraker16,17 stated that there were smaller covalent bonding contributions in [Np(Cp)₃] than [Np(Cp)Cl], whereas Adrian18,19 concluded the opposite.

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 +7.16 Recently, we reported that a formally Np⁵⁺ complex NpL₄(dme) supported by L₄, the trans-calix[2]benzene[2]pyrrole is accessible; black solutions were sufficiently stable (up to 90 minutes) for spectroscopic analyses but crystals were too small for single crystal diffraction analyses.4 Somewhat surprisingly, given the increased stability of the Np⁶⁺ oxidation state compared to t⁵⁺, this work was also the first to report single crystal structural studies on organometallic Np⁴⁺ complexes. To date, the only organometallic Np⁴⁺ complexes characterised by single crystal X-ray diffraction are neptunocene [Np(C₅H₅SiMe₃)₃]²⁻,²⁰ [Np(Cp)Cl]₂(OPPh₃Me)₂,²⁰ [Np(Cp)₃(0Ph)]²⁻ and two examples of the Cp₂Np-functionalised adduct [(UO₂)(THF)(H₂L)] (L = ‘Pacman’ Schiff-base polypryrole macrocycle),³ in which we studied the Cp₂Np coordination to one oxo group of the uranyl dication to compare the degree of electron transfer via the oxo-bridge between U, Np, and Pu cations. Structurally characterised Np⁴⁺ organometalllics are still limited to the [M(L⁴)X] complexes reported.⁴ Modern characterising data including ¹H NMR spectroscopic data have been reported for just a couple of complexes.

Many routes to solvated and base-free U⁵⁺(Cp)₃ complexes exist, but only the THF solvate of [Np⁵⁺(Cp)₃] has been reported to date, and was made from treating [Np(Cp)₃]Cl with potassium metal and catalytic naphthalene in refluxing THF for a few days. The product was first assigned as the tris THF solvate [Np(Cp)₃(THF)]³⁻ but subsequent IR, FIR and UV-vis-NIR spectroscopic analyses suggested the constitution of an 1:1 Lewis base adduct [Np(Cp)₃(THF)] analogously to that of uranium.¹² Attempts to desolvate it by heating samples in vacuo led to significant decomposition.¹⁴,¹²

Herein, we report the synthesis and structural characterisation of a series of Np³⁺ cyclopentadienyl complexes, and their reduction chemistry, both spontaneous and directed. Structural changes are discussed in relation to the neptunium formal oxidation state and nature of the ligands, as the majority of the complexes have been structurally characterised by single crystal X-ray diffraction.

## Results

### Syntheses

All the syntheses start from NpCl₄. This can be directly transformed into [Np(Cp)₃], NpCp₄ by the reaction of NpCl₄ with an excess of KCP in toluene.¹₃ Single crystals of NpCp₂ grow in the supernatant during a prolonged extraction of the crude product with pentane. The spectroscopic data agree with the literature reports.¹₁,¹₂ NpCp₄ itself can be – from a reaction with NH₄Cl¹¹,¹₂ – converted to [Np(Cp)₃Cl], NpCp₃Cl which is an ideal starting material for the synthesis of [Np(Cp)₃], NpCp₃. The reduction of NpCp₂Cl by Na/Hg in Et₂O affords NpCp₃ as its diethyl ether solvate [Np(Cp)₃(ET₂O)], Scheme 1. This solvent molecule is labile and can be easily removed in vacuum to afford the solvent free NpCp₃ which is only sparingly soluble in non-coordinating solvents due to the polymeric nature of the molecular structure (see below) but dissolves slowly in Et₂O, THF, or MeCN, again forming solvates [Np(Cp)₃(ET₂O)], [Np(Cp)₃(THF)], or [Np(Cp)₃(NCMe)₂], NpCp₃(NCMe)₂, respectively.

Crystals of [Np(Cp₃)(ET₂O)] could not be analysed via X-ray diffraction as during the crystal mounting procedure they lose coordinated Et₂O solvent molecule readily. Similarly, no stable adducts of a lanthanide analogue [Ln(Cp₃)(OET₂)] have been yet reported. However, single crystals of the bis-acetonitrile adduct NpCp₃(NCMe)₂ have been grown from acetonitrile solution at RT and studied by X-ray diffraction.

The reaction of NpCp₃Cl with 1.1 equiv. of KCp in THF does not lead to the simple Cl substitution product NpCp₄. After 4 d reflux and evaporation of the solvent, n-pentane extraction recovered half of the starting material NpCp₃Cl (49%), and a subsequent extraction with Et₂O afforded maroon single crystals of the new, reduced, Np³⁺ complex K[Np(Cp)₃], K[NpCp₃] in 37% yield. When the reaction is repeated without heating the mixture, no soluble, molecular product can be isolated.

For the synthesis of [Np(C₅H₅SiMe₃)₃], NpCp₃, another reaction pathway was followed as no starting material [Np(C₅H₅SiMe₃)₃] was available: NpCl₄ is generated in situ from the reaction between NpCl₄ and excess Na(Hg) in diethyl ether at room temperature. The reaction between this NpCl₃ and three equivalents of K(C₅H₅SiMe₃) in diethyl ether at room temperature afforded the target NpCp₃. Green, crystalline NpCp₃ is deliquescent under 1 atm of n-pentane vapour at room temp.
temperature but single crystals can be isolated reproducibly by evaporation and cooling of pentane solutions.

The reduction of a solution of NpCp₃ with KC₈ was carried out similarly to the method originally described for the synthesis of the thermally unstable [K(2.2.2-cryptand)][U(C₅H₄SiMe₃)₃] by Evans et al., but the crystallization temperature maintained lower, at −78 °C. A trial reduction of NpCp₃ confirmed that no compound could be isolated even at the coldest achievable reaction temperatures. In THF/Et₂O the mixture immediately turns very intense dark brown on contact with the solid reducing agent, and small, shiny black crystallites with the assumed composition K[2.2.2-cryptand][Np(C₅H₄Me)₃] appear in the filtrate after approx. 1 h of storage at −78 °C. Several potentially single crystals of suitable size for an X-ray diffraction study were analysed but only very weak diffraction was observed as the crystals had degraded during the radiologically protective mounting procedure. Due to the high sensitivity of the compound we were not able to determine the structure of the reduced product from this reaction or to measure any spectra.

**Spectroscopy**

The $^1$H and $^{13}$C gHMOC NMR spectra of NpCp₃ in THF-$d_8$ show only one resonance for the Cp ring protons at $\delta_H = -9.65$ ppm and the respective $^{13}$C shift of $\delta_C = 150.4$ ppm. The $^1$H NMR spectrum of NpCp₃ in toluene-$d_8$ solution contains three paramagnetically contact-shifted resonances between −1.38 ppm (the SiMe₃ protons) and −9.51 ppm in a 9 : 2 : 2 ratio, implying the identical bonding mode of the three ligands. The spectrum acquired in THF-$d_8$ solution appears similar, the resonances are slightly shifted downfield (by −0.6 to −9 ppm) suggesting an interaction with the THF solvent. The $^1$H NMR spectrum of the sparingly soluble K[NpCp₄] in THF-$d_8$ contains one broad resonance at −11.9 ppm, again showing the identical coordination behaviour of the Cp rings in solution. The solubility of K[NpCp₄] in THF is however too low to observe measurable absorptions in the UV-vis-NIR spectra.

For the NpIII complexes, all the Cp ring proton resonances are observed at ca. −10 ppm suggesting an electronically similar environment in each complex. Where no correlated spectra are reported here then the complex decomposes in the fluoropolymer NMR-tube liners before the spectra could be recorded.

The ATR spectrum of NpCp₄ features several characteristic vibrations of the Cp rings, which correlate well with the previously reported IR data of the complexes [M(Cp)₃] (M = U, Pu, Am, and Tm). Indeed, the similarity of the values of the entire series shows the very comparable constitution of the complexes. The most characteristic bands are the set of four absorptions at 666, 611, 581 and 519 cm$^{-1}$. ATR-FTIR spectra of K[NpCp₄] show similar Cp ring vibrations to those previously described for NpCp₃ with a slight shift to lower energy of the vibrations in K[NpCp₄] vs. NpCp₃, agreeing with the higher overall negative charge in the complex K[NpCp₄].

**Molecular structures**

The molecular structure of NpCp₄ is here reported for the first time. Dark red single crystals were obtained by extraction with pentane over several days. The compound is kinetically stable. X-ray diffraction analyses revealed an ideal tetrahedral environment of the Np centre, shielded with the four Cp rings in an isostructural complex to its Th²⁺ or U²⁺ analogue (Fig. 1).

Across the row of the isostructural [Ln(Cp)₃] (Ln: Th, U, Np), in line with the actinide contraction the cell volume decreases from 802 Å³ (Th) to 786 Å³ (U) to 775 Å³ (Np). Furthermore, a shrinking of the entire molecule is expressed by a decreasing An–Cp ring centroid distances. These are found to be 2.606 Å for Th, whereas in the U analogue they are determined to 2.588 Å and for the here presented Np complex they are 2.551 Å, again shorter. The shrinking parallels the decrease of the ionic radii; 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.

Dark-brown, almost black single crystals of NpCp₄ suitable for X-ray crystal structure determination were obtained from a 3.5% v/v diethyl ether in $n$-pentane solution stored at room temperature for 7 d.

The solid-state structure of NpCp₄ shows a polymeric structure motif. All the three Cp rings are bound towards the central NpIII atom. Due to its Lewis acidity coordinative saturation is achieved by additional $\eta^1$-coordination to one of the Cp rings of another NpCp₄ unit resulting in one $\mu-\eta^1$,$\eta^1$-coordinated bridging cyclopentadienyl group, Fig. 2a, establishing an overall polymeric zig–zag structure with a Np1–C1–Np1A angle close to 170, Fig. 2b. This is in agreement with the structures of isostructural [Ln(Cp)₃] complexes. In this coordination environment a distorted tetrahedral geometry around the NpIII centre is established with a strong Np–C interaction to the C-atoms to which the $\eta^1$ coordination is established (Np–C1 2.815(11) Å whereas the bond distance between the Np1 atom and the carbon atoms C3 (3.266(9) Å) and C5 (3.552(10) Å) may be considered as non-bonding. The geometry around the cation in NpCp₄ is more closely aligned with the larger rare earth analogues that have more electron-rich Cp rings, [Ln(C₅H₅Me)₃]₃ (Ln = La, Ce, Nd). These all show $\mu-\eta^1$,$\eta^1$-binding for each cyclopentadienyl ligand. However, some of the published data were recorded at room temperature and are less well resolved. In order to discuss fully the differences between the isostructural complexes of the type...
Red-brown crystals of K[NpCp₄] suitable for single crystal X-ray diffraction analysis were grown from a diethyl ether solution stored at room temperature for ca. 100 h. The asymmetric unit consists of 1.5 molecules of K[NpCp₄] and 0.5 molecule of a heavily disordered diethyl ether molecule residing on the crystallographic C₂ axis. K[NpCp₄] is also polymeric in the solid-state, with all Cp ligands forming bridging interactions of either \(\eta^1\) to another Np atom or \(\eta^5\) to a K or Np cation. This results in two different types of Np coordination geometries arising from the bridging modes, Fig. 3. The coordination environment around the first Np\(^{III}\) cation, labelled A, is \(\eta^5\)-Cp\(_3\)(\(\eta^1\)-Cp), which closely mirrors that of the parent complex NpCp\(_4\); that around the second Np\(^{III}\) cation, labelled B, is \(\eta^1\)-Cp\(_4\) comparable to the coordination observed for the four Cp rings in NpCp\(_4\). To our knowledge, this is the first instance of a Cp complex showing two different types of metal coordination geometries in the same crystal. This behaviour might be explained by the high coordinative flexibility of the relatively large An cations. Very few f-block complexes have comparable solid state structures. The complex [Ce\(_4\)C₂H₈Me\(_3\)]\(_4\) forms a tetramer in the solid state with \(\eta^1,\eta^1\)-Cp anions bridging,\(^{15}\) and one uranium complex was published very recently.\(^{[5-Cp]\_4} \) is also polymeric in the solid-state structures of the corresponding Ln complexes.

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recently, \([\text{K}[\text{2.2.2-cryptand}]\text{U(Cp')}_3]\)\textsuperscript{\textsuperscript{2+}} also shows an \((\eta^5-\text{Cp})_3(\eta^1-\text{Cp})\) geometry. The \(\text{An}^{3+}(\eta^1-\text{Cp})\) \(\text{M}–\text{C}\) distance is 2.752(7) Å for \(\text{NP}\) and 2.776(2) for \(\text{U}\), consistent with the ionic radius difference (six-coordinate \(\text{NP}^{3+} = 1.01\ \text{Å}; \ \text{U}^{3+} = 1.025\ \text{Å}\)).\textsuperscript{28}

The \(\text{NP}A\) and \(B\) type cations both form polymeric chain structures, which connect to each other, and into a 3D network via further \(K\) cation interactions. For \(\text{NP}A\), Fig. 3a, there are three distinct \(\text{Cp}\) binding modes for the four \(\text{Cp}\) ligands: one \(K(\eta^5-\text{NP})(\eta^5-\text{NP})(\eta^5-\text{NP})\) (for \(\text{Ct1}\) and \(\text{Ct3}\)); and two \(K(\eta^5-\text{NP})(\eta^5-\text{NP})(\eta^5-\text{NP})\) (for \(\text{Ct1}\) and \(\text{Ct3}\)). The second type of \(\text{NP}\), type \(B\), Fig. 3b, displays \(\eta^3\) binding of all the \(\text{Cp}\) ligands arranged in an irregular tetrahedral fashion around the \(\text{NP}^\text{III}\) centre. The average separation between the \(\text{NP}\) atoms and the \(\eta^3-\text{Cp}\) ring centroids in these molecules is slightly longer in accordance with the greater steric encumbrance at the \(\text{NP}\) centre (2.635(1) Å in \(\text{B}\) vs. 2.507(5) Å in \(\text{A}\)-type). Accordingly, the \(\text{C}\)-atoms for the fourfold \(\eta^1\)-coordinated \(\text{NP}\) centres show larger \(\text{NP}–\text{C}\) distances between 2.835(12) to 2.955(9) Å. The range of \(\text{NP}–\text{C}\) distances to like in \(\text{NP}_{\text{Cp}}^3\), coordinated \(\text{NP}\) centre \(\text{NP}(A)\) for the \(\eta^5\)-bound carbon atom is with 2.732(13) to 2.842(9) Å comparable.

There are also two different types of potassium coordination. Cation \(K1\) shows only \(\eta^1-\text{Cp}\) binding, with long \(\text{K}–\text{Cp}\) (centroid) distances of 3.013(5) and 3.067(6) Å. Cation \(K2\) shows both \(\eta^1-\text{Cp}\) binding (to \(\text{C}\) with a distance of 3.197(10) Å) and much closer \(\eta^3-\text{Cp}\) binding than \(K1\), with \(\text{K}–\text{Cp}\) (centroid) distances of 2.884(7) and 3.003(5) Å. These latter are more typical \(\text{K}–\text{Cp}\) distances. There are also molecules of diethyl ether present in the lattice, but no close contacts to metal centres are evident, Fig. 3c.

\(\text{NP}(A)\) in \([\text{KNpCp}_4]\) exhibit very similar coordination behaviour to \([\text{NP}_{\text{Cp}}^3]\). The zig-zag chains formed by the \(\text{A}\)-type \(\text{NP}^\text{III}\) units are only slightly more bent in \([\text{KNpCp}_4]\) \(\text{NP}–\text{NP}(149.8(3)°)\) than in \([\text{NP}_{\text{Cp}}^3]\) \(156.9(5)°\). The mean distance between the \(\text{NP}(A)\) atoms and the centre of the \(\eta^3\)-coordinated \(\text{Cp}\) rings is in average 2.51(1) Å and absolutely comparable to the one in \([\text{NP}_{\text{Cp}}^3]\) with 2.52(1) Å. A bigger difference is observed for the bond length \(\text{C}–\text{NP}\) of \(\eta^1\)-coordinated \(\text{C}\)-atoms: in \([\text{NP}_{\text{Cp}}^3]\) at 2.815(11) Å it is significantly larger than for \(\text{NP}(A)\) in \([\text{KNpCp}_4]\) with 2.752(7) Å. The different coordination behaviour of the \(\text{Cp}\) rings (binding \(\eta^3\) to the \(\text{NP}\) atoms but \(\eta^5\)-coordination to a \(\text{K}\) cation in \([\text{KNpCp}_4]\) and to a \(\text{NP}\) in \([\text{NP}_{\text{Cp}}^3]\)) is attributed to poorer competition by \(\text{K}\) for coordination than \(\text{NP}\), allowing the \(\text{Cp}\) ring to enable a stronger interaction towards the metal on the opposite site.

\(\text{NP}(B)\) in \([\text{KNpCp}_4]\) with its four \(\eta^5\)-coordinated \(\text{Cp}\) rings placed in an identical coordination environment to \([\text{NP}_{\text{Cp}}^3]\) with the difference of the charge on central \(\text{NP}\) atoms. According to the higher charge the mean centre of \(\text{Cp}\) ring to \(\text{NP}\) distance in \([\text{NP}_{\text{Cp}}^3]\) is with 2.551(1) Å about 0.08 Å shorter than for \(\text{NP}(B)\) in \([\text{KNpCp}_4]\) where it is determined to 2.635(1) Å. This effect can be attributed mainly to the change of the ionic radii from \(\text{NP}^\text{III}\) to \(\text{NP}^\text{IV}\) in an otherwise identical coordination environment; in this case four \(\text{Cp}\) ligands.

Single crystals of \([\text{NP}_{\text{Cp}}^3(\text{NMe})_2]\) grow from a \(\text{MeCN}\) solution of \([\text{NP}_{\text{Cp}}^3]\) as a solution is concentrated under reduced pressure. They are stable enough that they can be transferred on the goniometer and the single crystal solid state structure measured (Fig. 4).
Although the neutral complex [Np(Cp)₃] has been reported several times to be formed in the reaction between NpCl₃ and excess KCp in THF, benzene, toluene solution, the reaction reported here between [Np(Cp)₂Cl] and KCp affords the Np³⁺ ate product K[Np(Cp)₃] giving evidence that in this case Cp⁻ acts in two roles: as reducing agent plus as stabilising ligand for the coordinatively unsaturated Np³⁺ ion, dependent on the reaction conditions.

These observations could provide an explanation for the disagreements in the Mössbauer studies on covalency. Adrian observed that Mössbauer spectra of the [Np(Cp)₃] targets provided by Bohlander contained two low intensity bands arising from the unidentified impurities, which may provide an argument for this study. The utility of the Cp anion as a reductant is well documented in preparative inorganic chemistry, and an additional equivalent(s) of either NaCp or MgBr(Cp) can be conveniently employed to reduce in situ the higher oxidation state transition metal and lanthanide precursors and produce metalloccenes of the MIV centres i.e. Cr, V, Ru, Os or Eu. In actinide chemistry this reactivity is rarer, and the only reported synthesis to date is of the homoleptic complex [²³⁹Pu(Cp)₃] from treatment of [Cs₂[²³⁹PuCl₆]] with excess Mg(Cp). However, it is pertinent to note that the salt metathesis reactions between [Np(Cp)₂Cl], and group 1 alkyl- or aryl-anions formed only low yields of [Np(Cp)₃(ν-Bu)] and [Np(Cp)₂Ph] (40–60%) alongside undefined Np³⁺ by-products, presumably due to the homolysis of the NpIV-alkyl bond.

The reported formal potentials summarized in Table 1 show the Np⁴⁺/Np³⁺ couple is intermediate in value between U and Pu in the triad, as would be expected. Cyclic voltammetry experiments have demonstrated that [An(Cp)₂Cl] (An = U, Np) complexes show reversible one-electron reduction processes at $E_{1/2} = −1.80 \text{V (U⁴⁺/U³⁺)}$ and $−1.29 \text{V (Np⁴⁺/Np³⁺)}$ in THF (vs. Fe⁺⁺/Fe). Early actinide elements (An = Th–U) demonstrate a clearer thermodynamic preference for the +4 over +3 oxidation state and in its organometallic chemistry, for Np⁴⁺/³⁺, the preference is more finely balanced. The electrochemical properties of actinide centres in organoactinides are usually considerably affected by ligand environments.

The disproportionation of U⁴⁺ into 0.75 eq. of An⁴⁺ and 0.25 eq. of An⁵⁺ is well-known, and has been reported for Np⁴⁺. We used a variety of techniques to confirm the formal U⁴⁺ oxidation state in the inverse sandwich complexes $[X₂U(\mu-\eta^6-n^6-C₆R₆)₂]$, (in which the arene carries a dianionic charge) (X = bulky aryloxide or amido monoanion, C₆R₆ = benzene, toluene, naphthalene).

| Table 1 | Formal potentials (V, vs. SHE) of An⁴⁺/An³⁺ couples in aqueous solutions⁵⁹ |
| Couple | Formal potential, $E^{\circ}$, in V vs. SHE | 1 M HClO₄ | pH 8 | 1 M NaOH |
| U⁴⁺/U³⁺ | $−0.631$ | $−1.95 \pm 0.17$ | $−2.78 \pm 0.35$ |
| Np⁴⁺/Np³⁺ | $0.155 \pm 0.010$ | $−1.13 \pm 0.14$ | $−1.88 \pm 0.24$ |
| Pu⁴⁺/Pu³⁺ | $0.9821 \pm 0.0005$ | $−0.39 \pm 0.15$ | $−1.04 \pm 0.24$ |
naphthalene, and silylated or borylated arene derivatives) that were formed from the disproportionation of U^{III}X_{3} molecules into U^{IV}X_{4} and the formal intermediate U^{IV}X_{2}.\textsuperscript{72} More recently, Meyer used computational analyses to confirm the formal U^{III} oxidation state in the aren-supported tris(aryl oxide) ate complex [K[2,2,2-crypt]]\{[(Ad,MeArO)mes]U\}.\textsuperscript{73} Following the report of the +2 oxidation state for uranium in a molecular complex [K[2,2,2-cryptand]]U(Cp\')\textsubscript{3} by Evans et al.,\textsuperscript{44-47} and our report of the relatively stable, formally Np(II) complex Np(L\textsubscript{Ar})(dme),\textsuperscript{4} which survives up to 90 minutes in solution and as a solvent, the synthesis of the neptunium homologue K[NpCp\textsubscript{4}] of the U\textsuperscript{2+}ate\textsuperscript{1} complex seemed a reasonable target. While a conventional low-temperature route with radiological protection was devised to afford solutions and crystals of a Np(u) complex it was insufficiently thermally stable to enable characterisation of the solutions or X-ray data collection on single crystals.

This situation should be even easier moving from Np to Pu which already shows a much more stable M\textsuperscript{III} oxidation state in its complexes.

**Solid state structures**

All the complexes presented here, three Np\textsuperscript{III} and one Np\textsuperscript{IV}Cp\textsubscript{4}, contain at least three Cp ligands in the coordination sphere of the Np, so that a structural comparison can be performed. In the structures of the Np\textsuperscript{III} complexes NpCp\textsubscript{4}(NCMe)\textsubscript{2}, K[NpCp\textsubscript{4}], NpCp\textsubscript{3}, the Np centres are surrounded by three Cp rings in \eta\textsuperscript{5}-coordination mode. In all these complexes the centre of the Cp ring is placed between 2.51 Å and 2.54 Å distant from the Np atom. However, in K[NpCp\textsubscript{4}] there is a second coordination mode of the Np\textsuperscript{III} atoms: besides the coordination known from the NpCp\textsubscript{4} (and from the complexes LnCp\textsubscript{3}) consisting of the three already mentioned \eta\textsuperscript{5}-coordinated Cp rings plus one bridging Cp ring establishing an additional \mu-\eta-coordination in K[NpCp\textsubscript{4}] there is a NpCp\textsubscript{4} unit with the Np atom surrounded by four Cp rings all in \eta\textsuperscript{5}-coordination. This situation is comparable to the coordination found in complexes [An\textsuperscript{IV}Cp\textsubscript{4}], where in the row from Th over U to Np to Me at centre of ring distances are found of 2.606 Å, 2.588 Å, and 2.551 Å (Np), respectively. These values compare to the one of 2.635 Å for the four times \eta\textsuperscript{5}-coordinated Np centres in K[NpCp\textsubscript{4}]. Thus one can consider the difference in the ionic radii between Np	extsuperscript{III} and Np	extsuperscript{IV} in an equivalent coordination environment built by in this case four \eta\textsuperscript{3}-coordinated Cp rings to be equal to (2.635 – 2.551 =) 0.08 Å.

We note that the CN stretch in the IR spectrum of NpCp\textsubscript{4}(NCMe)\textsubscript{2} is observed at 2262 cm\textsuperscript{-1}, lower than in the corresponding U cationic complexes which have a stronger M-N interaction.

The trigonal planar arrangement of the three Cp' ligands [Np(Cp\')\textsubscript{3}] around the Np	extsuperscript{III} centre, analogous to the corresponding U complex raises the possibility that this complex should be able to show comparable redox chemistry to that of U and Th, where the geometry provides suitable orbitals for an additional valence electron to reside. Therefore, it was used as the starting material for the organometallic Np(u) complex for reduction with KC\textsubscript{6}.

**Conclusions**

As could be anticipated, the synthetic chemistry of cyclopentadienyl-supported Np\textsuperscript{III} and Np\textsuperscript{IV} complexes is comparable to that of uranium, with the differences mainly being caused by the less negative reduction potential of the Np\textsuperscript{4+} ion. For the first time a solution-based method for the quantitative formation of green, poorly soluble, but high-surface area, and therefore reactive NpCl\textsubscript{4} has been demonstrated from reduction of NpCl\textsubscript{4}, and shown to be synthetically useful in anaerobic reactions, even in the absence of strongly coordinating solvents. Complexes NpCp\textsubscript{3} and NpCp\textsubscript{4} were synthesized reproducibly in high yields via salt metathesis routes from this or from more traditional reduction of the known complex NpCp\textsubscript{4}Cl.

One notable example of the greater stability of the Np\textsuperscript{III} ion with respect to U\textsuperscript{III} in these complexes is the overlooked reactivity of NpCp\textsubscript{4}Cl with excess KCP, which results in the isolation of the first actinide(u) tetrakis-cyclopentadienyl complex, K[NpCp\textsubscript{4}] under the synthetic conditions previously assumed to afford only the neutral complex NpCp\textsubscript{4}. Remarkably, the solid-state structure of K[NpCp\textsubscript{4}] exhibits intra-crystal dimorphism; two different types of NpCp\textsubscript{4} coordination geometries, half of the Np\textsuperscript{III} cations are (\eta\textsuperscript{1}-Cp)(\eta\textsuperscript{5}-Cp), and half are (\eta\textsuperscript{2}-Cp), with the two different types of Np\textsuperscript{III} forming separate polymeric chains that are bridged by potassium counter-cations to form the extended polymeric structure. Unexpectedly, this structure may answer the concerns expressed by Adrian et al. who reported two similar, but unidentified impurities in samples of NpCp\textsubscript{4} that they studied by Mössbauer spectroscopy. Comparison of the structures of K[NpCp\textsubscript{4}] and NpCp\textsubscript{4} enables a differentiation of the ionic radii of Np\textsuperscript{III} and Np\textsuperscript{IV} in this organometallic environment of 0.08 Å. Complex NpCp\textsubscript{4} shows an even closer contact around the Np atom establishing a trigonal planar coordination environment which is again 0.03 Å smaller but offering further redox chemistry opportunities.

Indeed, potassium reduction at low temperatures of NpCp\textsubscript{4} leads to the formation of very dark-brown crystals of a complex assigned as [K[2,2,2-cryptand]][Np(Cp\')\textsubscript{3}] K[NpCp\textsubscript{4}]; these can be isolated but are less thermally stable than the formally Np(u) complex [Np(L\textsubscript{Ar})(dme)] previously reported by us;\textsuperscript{4} single crystals of the putative Np\textsuperscript{III} complex K[NpCp\textsubscript{4}] do not survive for long enough to be encapsulated for radiological protection prior to the collection of diffraction data.

The results presented show that neptunium cyclopentadienyl chemistry can show significant deviations from its uranium congeners, in sharp contrast to previous assertions, and the resulting spectroscopic, redox, and structural investigations provide a significant and deeper understanding of minor actinide chemistry.

**Acknowledgements**

The experiments were supported by Talisman Joint Research Project under contract with the European Commission. M. S. D. acknowledges the European Commission for support in the frame of the Training and Mobility of Researchers programme. P. L. A. also thanks the UK EPSRC (grants EP/N022122/1 and EP/M010554/1).
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