Subtle interactions and electron transfer between U(III), Np(III) or Pu(III) and uranyl mediated by the oxo group

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Abstract: A dramatic difference in the ability of the reducing An(III) center in AnCp₂ (An = U, Np, Pu; Cp = C₅H₅) to o xo-b ind and reduce the uranyl(VI) dication in the complex [(UO₂)(THF)(H₂L)] (L = ‘Pacman’ Schiff-base poly pyrrolic macrocycle), is found and explained. These are the first selective functionalizations of the uranyl oxo by another actinide cation. At first contradictory electronic structural data are explained by combining theory and experiment. Complete one-electron transfer from Cp₂U forms the U(IV)-uranyl(V) compound that behaves as a U⁴⁺-localized single molecule magnet below 4 K. The extent of reduction by the Cp₂Np group upon oxo-coordination is much less, with a Np(III)-uranyl(VI) dative bond assigned. Solution NMR and nIR spectroscopics suggest Np³⁺-U⁴⁺ but single crystal X-ray diffraction and SQUID magnetometry suggest a Np³⁺-U⁵⁺ assignment. DFT calculated Hirshfeld charge and spin density analyses suggest half an electron has transferred, and explain the strongly shifted NMR spectra by spin density contributions at the hydrogen nuclei. The Pu(III) - U(IV) interaction is too weak to be observed in THF solvent, in agreement with calculated predictions.

The uranyl(VI) dication UO₂²⁺ is the most common form of uranium in the environment, and is reduced by minerals and microbes to the less stable uranyl(V) monocation UO₂⁺.¹ One of the notable features of the 5f⁵ uranyl(V) ion is its tendency to coordinate to other metal cations through the oxo group, behaviour more reminiscent of the heavier f¹ and f² neptunyl and plutonyl cations which form a variety of oxo-bridged cation-cation interactions (CCIs) that interfere with nuclear waste manipulations.² Reduction of U⁴⁺ to uranyl to the more Lewis basic U⁵⁺ uranyl ion dramatically increases CCI interactions, providing good models for the behaviour of the Np and Pu ions, which are significantly more radiactive than the uranyl ion. In addition to the actinyl ions, civil nuclear waste also contains a large number of 5f metal cations from fuel additives and cladding bombardment.³ Thus, understanding the interaction of uranyl, which represents ca 98 % of spent fuel, with other 5f metal ions is important.

Simple U(III) complexes can reduce and activate inert small molecules,⁴ but no such reactivity has been reported for transuranic An⁵⁺ complexes in which the An⁵⁺ formal oxidation state is less thermodynamically favoured compared to U⁴⁺. However, the reduction of U⁵⁺ to U⁴⁺ in the uranyl ion is thermodynamically accessible,⁵ and recent work by us and others has shown that reduction can be accompanied by oxo-group functionalization with either main group⁶ or magnetically more interesting 3d- and 4f- metal cations.⁷ The strong anisotropy of the f-block ions has enabled recent breakthroughs in the design of molecular magnets with slow relaxation times that could have applications in spintronic devices, for example.⁸ Actinides have been favored over lanthanides in this area due to the relatively greater proportion of covalency (and therefore potential for magnetic communication) in their bonding interactions. Furthermore, the axial symmetry of the uranyl ion offers a design element to control the orientation of the magnetic vector of the single 5f electron in U⁵⁺ uranyl complexes and has been used to construct mixed, oxo-bridged uranyl-transition metal single molecule magnets (SMMs).⁹

The difference in preferred coordination geometries of actinyl and actinide cations has been used successfully to make coordination network materials that combine uranium as U⁴⁺ uranyl and the transuranic neptunium(IV) cation in a phosphate structure,¹⁰ but to the best of our knowledge no reaction to form a heterobimetallic actinide complex through an inner-sphere redox reaction has been reported. We envisaged that the binding and redox-reaction of the uranyl oxo group with potentially reducing f-block metal cations could provide fundamental information on the behaviour of actinyl cations in solution, and a versatile and powerful design principle for the synthesis of electronically coupled, redox-active, 5f elements. Here, we report synthetic routes to the first actinide-functionalized uranyl(V) complexes and a study of their 5f-5f magnetic coupling.

The reaction between THF solutions of [(UO₂)(THF)(H₂L)] A and Cp₂An (An = U, Np, Pu, Cp = C₅H₅) results in a color change of the greenish solution of A to brown or red-brown for U and Np, but no observable reaction for the Pu analogue; presumably the Pu cation is insufficiently Lewis acidic and the THF donor solvent thus becomes competitive with Pu-oxo coordination (Scheme 1). For U and Np crystals of [Cp₂AnOUO(THF)(H₂L)] (An = U, 1a dark orange; 1b golden-brown; An = Np, 2a dark red, 2b dark red-brown), are isolated in yields of around 30 %. All the complexes are highly air-sensitive, but in general, the octamethyl ligand derivatives (b) are much easier to isolate as they crystallize as

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large blocks that are readily separable from powdery impurities. Complexes 2 are the first molecular heterobimetallic uranium-neptunium complexes.

![Diagram of complexes](image)

The new An-OU complexes are exclusively exo-oxo metalated, as characterised by $^1$H NMR, NMR, and IR spectroscopy, and single-crystal X-ray diffraction, and are readily oxidised by trace impurities to form the known An$^{IV}$ complexes [Cp$_2$An]$_2$(µ-O)$_2$($^{5a,11}$) and the U$^{VI}$ uranyl starting material A. The solution stability of 2b is greater than that of 2a, enabling a full NMR spectroscopic assignment (see SI).

In the $^1$H NMR spectrum of 1a the two ligand pyrrolic NH protons in the endo-cavity resonate at 51.4 ppm (51.1 ppm in 1b, 55.5 in 2a, 54.8 ppm in 2b). These highly paramagnetically shifted resonances, along with other macrocyclic ligand resonances strongly suggest that both Cp$_2$An$^{IV}$ fragments have reduced the uranyl to U$^{IV}$ uranyl forming An$^{IV}$-U$^{IV}$ uranyl complexes with strong NH-endo hydrogen bonding interactions.$^{[5a,11]}$ The resonances for the Cp-ring protons are not similarly diagnostic, however, appearing at 3.17 ppm in 1a and 3.30 ppm in 1b. For the pseudo-tetrahedral [Cp$_2$U] containing complexes reported, the corresponding value for the Cp H is -15.41 ppm in Cp$_2$U($^{IV}$(THF), with U$^{IV}$ values ranging from -3.48 ppm in Cp$_2$UCl to -8.8 ppm for Cp$_2$U$^{IV}$(OPh) and -18.4 for Cp$_2$U$^{IV}$(Q(E))$^{[12]}$.

The chemical shift of the Cp protons of -12.1 ppm in 2a and -11.8 in 2b are very similar to the Cp ring resonances in the THF-solvated Cp$_2$NP$^{IV}$(THF) (5.5 = -9.65 ppm) and around 10 ppm higher in frequency than the value of -21.49 ppm in the Np$^{IV}$ complex Cp$_2$NpCl.$^{[13]}$ Although there is only scant data for comparison, it suggests the Np center is closer in character to Np$^{IV}$, with the uranyl oxo behaving as a donor atom to Np.

The absorption for the uranyl asymmetric stretch is best assigned to uranyl(V) in all four Cp$_2$U and Cp$_2$Np complexes in the FTIR spectra with absorptions at 893 cm$^{-1}$ (1a), 837 cm$^{-1}$ (1b), 892 cm$^{-1}$ (2a), and 891 cm$^{-1}$ (2b). In each case the value is shifted from that in the parent U$^{IV}$ complex (907 cm$^{-1}$) in accordance with a weakening of the U=O multiple bonding in uranyl(V). Additionally, UV-Vis-NIR spectroscopic characterization of 2 shows several bands characteristic of the Cp$_5$-symmetric Cp$_2$NP$^{IV}$ group (in particular around 1066 and 987 nm$^{[14]}$) and no evidence of the strong absorption at 1260 nm of Cp$_2$Np(THF).

Comparison of the solid state structures of 1a and 2a (Figure 1), and of 1b and 2b (SI) confirm their isostucturality and all of the metrics argue for formal U$^{IV}$ and U$^{VI}$ uranyl assignment as a result of complete single electron transfer, but are less conclusive for the choice of Np$^{IV}$ or Np$^{VI}$ in 2.

![Solid-state structures of 1a and 2a](image)

In each case, the uranyl remains linear (O$_{\text{exo}}$U-O$_{\text{endo}}$ = 178.05(12)$^\circ$ in 1a, 176.9(3)$^\circ$ in 2a), and the bimetallic bridge is also close to linear (An-O$_{\text{exo}}$U$_1$ = 170.70(15)$^\circ$ in 1a, 170.5(4)$^\circ$ in 2a). The uranyl ions are equatorially bound by four macrocyclic N donors, with a coordinated THF molecule in the fifth site. The elongated U=O$_{\text{exo}}$ bond lengths in all four imply singly reduced U$^{IV}$ uranyl, with a significant lengthening in particular to the metalated exo-oxo (in 1a U-O$_{\text{exo}}$ is 1.976(3) but U-O$_{\text{endo}}$ is only 1.840(3) Å). The geometry around the An cation which is coordinated to the exo-oxo is unremarkable with approximate C$_{5v}$ symmetry rather than tetrahedral An geometry due to centroid-An-O angles that are smaller than the tetrahedral angle. The average An-C(Cp) distance is 2.733 Å in 1a and 2.709 Å in 2a. These data are consistent with a formal oxidation state of U$^{IV}$ as the average U-C distance in Cp$_2$U$^{IV}$(OPh) is 2.74 Å$^{[16]}$ and in Cp$_2$U$^{IV}$(THF) is 2.79 Å.$^{[12]}$ The average Np-C distance in Cp$_2$Np$^{IV}$(OPh) (2.73(3) Å) is somewhat greater than found in 2a but there are no structurally characterised Np$^{IV}$ cyclopentadienyl complexes for comparison. The Cp$_2$An-O distance in 1a is
2.245(3) Å and in 2a is 2.497(7) Å. In 1a this is consistent with a covalent single bond to U(V) although there is a wide range, for example 2.119(7) Å in Cp₃UIV(OPh)₁[15] and 2.551(10) Å in Cp₃U(V)(THF).[12] However, in 2a, this is more consistent with a long single bond or dative bond; the covalent single Np-O bond is 2.136(7) Å in Cp₃Np(V)(OPh)₁[16] whereas the dative Np-O bond in CpNp(OP(OPh)₂)₂ is in the range 2.265(12) - 2.283(12) Å.[17]

In the anticipation that this synthetic approach could generate actinyl-actinide complexes with magnetic coupling through the bridging oxo group, we have studied the variable temperature magnetic behaviour of 1b and 2b by SQUID magnetometry. The dc susceptibility (χ) curves (Fig. 2) show that both complexes have an effective magnetic moment around 2.4 µₜₜ at low temperature, but upon increasing the temperature their behaviour differs. While the χT product for 1b rapidly increases well above the upper theoretical limit expected for a U(IV)-U(V) pair, and at room temperature approaches the expected value for a U(IV)-U(V) pair, the effective moment for 2b slowly reaches the value corresponding to a Np(III)-U(V) pair and tends to saturate without increasing further. This indicates that the electron transfer in the Np-U 2b adduct is extremely poor, whereas reduction of the uranyl group has taken place in the U-U analogue 1b.

Because of this, we have investigated the dynamic magnetic properties of 1b by ac magnetic susceptibility measurements (Fig. 3). Clear peaks in the out-of-phase component of the ac susceptibility indicate that slow magnetic relaxation takes place and that 1b behaves as a single-molecule magnet below 4 K. The temperature dependence of the relaxation time τ can be fitted equally well to a Raman or an Orbach relaxation pathway, in addition to a direct process; however, we note that both the characteristic time τ₀ = 3.26×10⁹ s and the thermal activation barrier Δ = 26.9 K are very similar to previously reported U(V) based single-ion magnets.[18] This, together with the consideration that U(V) is often non-magnetic in low-symmetry geometries, and with the absence of any clear sign of magnetic interaction between the two uranium sites in the susceptibility curves, allows us to attribute the slow magnetic relaxation to the uranyl(V) group. We note that a more symmetrical heterodimetallic uranyl(V)-Mn(II) complex has the highest reported relaxation barrier for a mono-U(V) system, of 81±0.5 K, presumably due to the high Ising anisotropy.[19]

It is therefore clear that not all of the experimental characterisation data agree on the extent of electron transfer from the organometallic actinide to the uranyl group:

- NMR: the paramagnetic shifting of the resonances in the macrocyclic ligand in both 1 and 2 is suggestive of singly reduced uranyl(V) in both. The paramagnetic chemical shifts of the Cp protons are less diagnostic; in the U-U complexes 1 the chemical shift of the Cp protons is similar to most U(V) complexes whereas those in the Np-U complexes 2 are comparable with those of Np(III) cyclopentadienyl complexes.

- NIR-UV-Vis-IR: The vibrational data support a U(IV)-U(V) oxidation states for 1 and Np(III)-U(V) oxidation states for 2.

- XRD: The crystal structures of both the Cp₃An(=OOPh) systems are fully isostructural, and present convincing evidence for single electron transfer in 1 but less so in 2. The data show characteristic elongation of the U(=O)-An distances and to smaller extent also U-O(endo), suggestive of the uranyl(V) ion in both but the An-Oexo uranyl distances are more in line with U(V) and Np(III) formal oxidation state assignments.

- SQUID magnetometry: For 1b the data are consistent with full electron transfer to form a U(IV)-U(V) complex. However, for 2b the magnetic ground state saturation values closely match those of the isolated Np(III) ion, suggesting a donor-acceptor oxo bridged Np(III)-U(V) product.

DFT calculations on models of 1b to 3b help with the bond type assignments and support the proposed decreasing level of...
electron transfer from Cp₃U through Cp₃Pu. The Gibbs Free Energies for each reaction in Scheme 1 were calculated (Table S3) and the positive gas phase value (2.81 kcal/mol) for Cp₃Pu gas-phase, Cp₃AnIV/V/AnIII reduction potentials vs ferrocene (Table S4) are −1.21 eV for U, −0.81 eV for Np, and −0.41 eV for Pu and follow the same trend as the experimental data, i.e., the reduction of Cp₃AnCl is −1.80 V for U⁴⁺ and −1.29 V for Np⁴⁺ in THF vs ferrocene.[20] We previously measured the relatively facile reduction of the uranyl complex A⁶⁺ as −1.18 V vs. ferrocene in THF solution[21] and so comparison of these reduction potentials predicts that it will be more difficult to transfer an electron from Cp₃Np⁴⁺ than Cp₃U⁴⁺.

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[12] Re-recorded by us in d₄-benzene on a modern spectrometer. ¹H NMR (CD₃OD, 293.1 K, 400.33 MHz): δ 21.49 (s, 15H) ppm.
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