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Structure and Properties of U(IV) and Np(IV) Selenium Bis(phenolate) Complexes and Their Reaction with p-Benzquinone

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The synthesis and characterization of U(IV) and Np(IV) selenium bis(phenolate) complexes are reported. The reaction of two equivalents of the U(IV) complex with p-benzoquinone results in the formation of a U(V)-U(V) species with a bridging reduced quinone. This represents rare examples of high-valent uranium chemistry as well as one of the first examples of a neptunium aryloxide complex.

The coordination chemistry and reactivity of the actinides provides insight into their structure and bonding, which in turn improves our understanding of the behaviour of these elements especially with regard to the nuclear fuel cycle. Transuranic actinides are particularly understudied even compared with lighter actinides due to the difficulty in obtaining these elements and the infrastructure required to handle these elements safely.

We recently examined the structure of diamagnetic complexes with the selenium bis(phenolate) ligand. This dianionic, chelating ligand effectively stabilizes tetravalent metal complexes, and we endeavoured to extend this study to uranium and neptunium. Herein, we report the synthesis of the U(IV) and Np(IV) complexes. The reactivity of these complexes with p-benzoquinone has been explored. With U(IV), this reaction affords a dinuclear U(V)-U(V) compound bridged by p-hydroquinone dianion. However, the interaction between the Np(IV) species and Np-benzoquinone seems to produce an equilibrium between the Np(IV) and the binuclear Np(V)-Np(V) complex. The magnetic, spectroscopic, and structural properties of these complexes are detailed.

The salt metathesis reaction of UCl₄ with two equivalents of K₄[SeO₄] (Ar = 4,6-di-tert-butylphenol) in THF resulted in an emerald green solution, eqn (1). The ¹H NMR spectrum showed paramagnetically shifted resonances between 15.2 and -10.3 ppm. X-ray quality crystals were grown from a saturated toluene solution at -20 °C. Analysis of a single crystal revealed the U(IV) complex, U₄[SeO₄]₂(THF)₂, 1, Figure S11. The THF molecules in complex 1 are labile, and when exposed to vacuum for extended periods of time, the unsolvated complex is observed by ¹H NMR spectroscopy.

Similar to the previously reported thorium analogue, 1 displays a highly distorted octahedral geometry where the phenolic oxygen atoms are cis to one another. Additionally, one selenium atom is above the aromatic rings while the other is below. The U-Ophenoxide bond distances range from 2.185(4)-2.223(4) Å and compare well with other uranium aryloxide complexes. For example, U(1-2,6-tert-butylcyclohexane)² and U[benzenedithiolate]₃ have U-O bond distances of 2.135(4) Å and 2.219(2)-2.263(2) Å, respectively. The U-Se distances are 3.2606(6) and 3.1642(6) Å, which are longer than the sum of the covalent radii (Σ = 2.86 Å) suggesting no interaction exists between the selenium atom and the uranium centre.

The magnetic susceptibility of 1 is typical of U(IV). The magnetic moment of the ground state can be determined from the value of χT vs T extrapolated to 0 K. For 1, χT is zero at 0 K, so the ground state is a singlet and only displays temperature independent magnetism, which is typical for U(IV) in low symmetry. χT is linear in T to 20 K, which indicates that the first excited state is approximately 40 to 60 K (27 to 40 cm⁻¹) above the ground state.

The nominal ground state of U(IV) is Σ₄ in Russell-Saunders coupling. Bonding in U(IV) is expected to be largely ionic due to poor energy match between the metal and ligand orbitals. The Russell-Saunders ground state of U(IV), Σ₄, is split by the ligand field into 9 substates characterized by mₗ = 4, 3, 2...-4, which will be mixed by the crystal field due to the ligands. The free ion moment of Σ₄ when all the mₗ substates are equally thermally populated, is 3.6 μB which is considerably greater than that of 1 at room temperature, 2.5 μB. The low value of μB for 1 indicates that the total splitting of Σ₄ ground state by the crystal field is greater than kT at room temperature (200 cm⁻¹).

The synthesis of Np₄[SeO₄]₂(THF)₂, 2, as a yellow powder, was achieved using a similar route as for 1, eqn (1). Crystallization from a concentrated toluene solution at -35 °C gave X-ray quality crystals, Figure 1. The structural characterization of 2 revealed a six-coordinate, highly distorted octahedral Np⁴⁺ metal centre nearly isostructural with 1. Like 1, the selenium bis(phenolate) ligands are arranged with the phenolic oxygen atoms cis to one another. The Np-Ophenoxide bonds range from 2.168(9) to 2.228(11) Å and are shorter than the Np-O bonds found in the β-diketonate Np(FOD)₄ (FOD = 6,6,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione), 2.290(7)-2.347(5) Å and slightly longer than the Np-O bond distance in (C₆H₅)₃Np(OPh), 2.136(7) Å. The Np-Se distances of 3.1289(15) and 3.2287(17) Å are larger than the sum of the covalent radii of 2.87 Å as observed for 1. Despite the prevalence of actinide aryloxide complexes,⁷ the only other neptunium alkoxide or aryloxide is (C₆H₅)₃Np(OPh).
The thermal ellipsoid plot of 2 shown at the 50% probability level. The tert-butyl groups and hydrogen atoms have been omitted for clarity. Note: O2 and O4 are cis.

The magnetization of 2 decreases sharply at low temperatures, as illustrated in Figure 2. However, the field dependent at low temperature indicates that the decrease is due to saturation rather than coupling. The data of 2 from 25 K to 150K at magnetic fields 0.1 T, 0.5 T, 1 T and 2 T were used to determine the magnetic susceptibility of 1.67 $\mu_B$ at 0 K. The Russell-Saunders coupling ground state of Np(IV), $4I_9/2$, is split by the ligand field into 10 substates characterized by $m_J = 9/2, 7/2, 5/2...-9/2$, which will be mixed by the crystal field due to the ligands. Once the ligand field is considered, the $4I_9/2$ state will split into 5 Kramers doublets. In 2, the first energy of the first excited doublet is approximately 200 - 300 cm$^{-1}$ above the ground state as determined from the temperature at which the plot of $\chi_T$ vs. $T$ deviates from linearity. Interestingly, the first excited state in the Np(IV) compound is much higher in energy than the first excited state in U(IV). Although Np(IV) complexes have the potential to exhibit single molecule magnet behaviour,$^{8,9}$ 2 does not display a hysteresis in the magnetization vs. field measurements at 2K, Figure S5.

The EPR spectrum of 2 is shown in Figure 3 along with spectrum simulated using EasySpin$^{10}$ and the parameters given in Table S4. The sharp feature at 300 mT is due to a minor contribution from organic radical impurities. The simulated spectrum is in general agreement with the experimental spectrum. The largest discrepancy is the position of the two peaks at $\sim$175 mT and $\sim$190 mT. In addition, the linewidths of the features above 400 mT are too narrow in the simulation. Given these differences, it is possible that the simulation represents a local minimum rather than the best fit; however, the largest g and A values, 2.85 and 5134 MHz must be close to the correct values due to the position of the low field peaks. The g-values are related to $\mu_{eff}$ of the ground state by $4\mu_{eff}^2 = g_1^2 + g_2^2 + g_3^2$ for effective spin = 1/2. In 2, the EPR spectrum is consistent with a ground state magnetic moment of 1.65 $\mu_B$, which is in excellent agreement with the value determined by magnetic susceptibility, 1.67 $\mu_B$. 

Figure 1. Thermal ellipsoid plot of 2 shown at the 50% probability level. The tert-butyl groups and hydrogen atoms have been omitted for clarity. Note: O2 and O4 are cis.
While Np(IV) is generally EPR active, EPR studies of Np(IV) compounds are rare. The paucity of EPR studies is due in part to the very strong hyperfine coupling between the unpaired electron and the large nuclear moment of Np. Accurate determination of the spin Hamiltonian parameters $g$ and $A$ from the fields of spin transitions requires use of the Breit-Rabi formula. For simulation of the spectrum, diagonalization of the full spin Hamiltonian is required, which was accomplished here using EasySpin. As noted by Poirot et al., the values of $A/g$ are relatively constant for Np(IV) and vary from 1807 MHz to 1869 MHz. In 2, these values are 1779 MHz, 1955 MHz, and 1805 MHz. The first and last are in the range expected for Np(IV) although the value of 1955 MHz is slightly greater than expected. The discrepancy likely indicates the uncertainty in the $g$ and $A$ values for this component, 1.632 and 3256.5 MHz, respectively. Attempting to change either $g$ or $A$ for this component resulted in a much poorer simulation of the experimental spectrum. While the $g$-values can reveal details of the electronic structures of Np complexes, this typically requires at least axial symmetry for meaningful discussion. The low symmetry of the Np(IV) site in 2 precludes such an analysis.

Inspired by the use of $p$-benzoquinone to oxidize Ce(III) to Ce(IV), the reaction of 1 with 0.5 equivalents of $p$-benzoquinone was examined. It resulted in a colour change from green to black. The $^1H$ NMR spectrum showed four resonances ranging from 9.73-1.25 ppm. Black, X-ray quality crystals were grown from a concentrated solution of toluene to reveal the structure as \( \text{[U\((\text{OSeO})_2(\text{THF})_2\)(\text{O}_2\text{C}_6\text{H}_4\text{O})]} \), Figure 4. The structure of 3 has the same coordination as 1 except for the addition of the bridging benzochinone and loss of one THF molecule. To confirm the uranium oxidation state, electronic absorption spectroscopy was employed. A weak, sharp f-f transition was observed at 1488 nm ($\varepsilon = 136.6 \text{ M}^{-1} \text{ cm}^{-1}$) indicative of U(V), Figure S10.
The U-O\textsubscript{(phenoxide)} bond distances of 1, 2.185(4)-2.223(4) Å, contract upon oxidation to 3, 2.163(3)-2.140(3) Å. The U-O\textsubscript{(phenoxide)} distances in 3 are longer than the 2.02-2.03 Å found for the terminal U-O\textsubscript{Pr} distances in the U(V)/V dimer; U\textsubscript{2}(O\textsubscript{Pr})\textsubscript{16}, and shorter than the 2.28-2.29 Å of the bridging U-O\textsubscript{Pr} bonds.\textsuperscript{25} These distances are similar to those of U(V) aryloxide, [U(O\textsubscript{Bu})\textsubscript{3}]+, 2.05(1)-2.24(1) Å.\textsuperscript{26}

The magnetic susceptibility of 3 is surprising. As illustrated in Figure S8, \( x_T \) is linear from 10 K to 300 K, which indicates that only a single state is occupied or that multiple states are occupied, but their splitting is very small, < 2 K (1.2 cm\(^{-1}\)). Bonding in U(V) is expected to be more covalent than in U(V) due to a better energy match between the metal and ligand orbitals; consequently, the ligand field in 3 expected to be strong relative to 1. The ground state of U(V) is \( ^2\Sigma_{\text{g}} \), which consists of 6 substates with \( m_J = -5/2, -3/2, ..., 5/2 \). The ligand field will mix these substates based on the site symmetry of the U ion. In this case, the uranium centre has low symmetry, and the \( ^2\Sigma_{\text{g}} \) state will split into 3 Kramers doublets. The magnetic moment of each Kramers doublet is directly related to \( m_J \) as shown in Table S2. The measured ground state moment of 3 is ~0.85 µB per U center, which is not in agreement with any of the “pure” \( m_J \) states. Given the low symmetry at the U centre and the fact that the relatively strong crystal field of U(V) will strongly mix the \( m_J \) states, this result is not particularly surprising.

The most interesting aspect of the magnetic susceptibility of 3 is that only a single crystal field state is significantly occupied below 300 K, which is unusual for an actinide or lanthanide complex. In addition, the unpaired electrons on the two uranium centres are weakly exchange-coupled with \( J = -0.9 \text{ K/ks} (~0.6 \text{ cm}^{-1}) \).\textsuperscript{27,29} The U1-05-C57(quad) bond angle is 151.3(2)° deviates greatly from linearity, so this weak coupling is not surprising.

When the reaction of 2 with p-benzoquinone was attempted, a colour change from yellow to black was observed, but only when the reaction was attempted in toluene. No change was observed when the reaction was conducted in THF. Attempts to recrystallize the dark-coloured solution were unsuccessful. The standard reduction potentials of p-benzoquinone, UO\textsubscript{2}\textsuperscript{+} and NpO\textsubscript{2}\textsuperscript{+} are 0.7 V, 0.45 V and 0.60 V, respectively.\textsuperscript{30} Since Np(V) is more difficult to oxidize than is U(V) and since the potentials of p-benzoquinone and Np(V) are similar, this reaction between 2 and p-benzoquinone is most likely an equilibrium that favours the Np(IV) product. Similar chemistry has been observed previously with Np(III).\textsuperscript{31}

The synthesis and spectroscopic characterization of U(IV) and Np(IV) arylloxides as well as their magnetism has been accomplished. This is the first Np(IV) EPR spectrum reported since 2004, and only the second Np(IV) aryloxide complex structure published to date. The reactivity of these complexes with p-benzoquinone has been studied. The U(IV) complex affords a rare dinuclear U(IV)-U(V) compound, while the Np(IV) complex seems to be in equilibrium with p-benzoquinone with the Np(IV) being favoured. Overall, this represents a rare comparison of the reactivity of uranium and an element to the right of it in the periodic table.

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**Conflicts of interest**

The authors declare no competing financial interests.

**Notes and references**