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Trapping of a Highly Bent and Reduced Form of 2-Phosphaenolate in a Mixed-Valence Diuranium-Triamidoamine Complex


Abstract: The chemistry of 2-phosphaenolate is burgeoning, but there remains much to learn about this ligand, for example its reduction chemistry is scarce as this promotes P-C-O fragmentations or couplings. Here, we report that reduction of [U(Tren)²⁺(OCP)]⁻ (Tren²⁺ = N(CH₃CH₂NSiPr₂)₃) with KC₂/2,2,2-cryptand gives [[U(Tren)²⁺]₂(μ-η¹(TP):η²(CP)-OCP)]⁻[K(2,2,2-cryptand)]. The coordination mode of this trapped 2-phosphaenolate is unique, and derives from an unprecedented highly-reduced and -bent form of this ligand with the most acute P-C-O angle in any complex to date (P-C-O ≤ ~127°). The characterisation data support a mixed-valence diuranium(III/IV) formulation, where backbonding from uranium gives a highly reduced form of the P-C-O unit that is perhaps best described as a uranium-stabilised OCP⁺ radical dianion. Quantum chemical calculations reveal that this gives unprecedented carbene character to the P-C-O unit, which engages in a weak donor-acceptor interaction with one of the uranium ions.

The 2-phosphaenolate anion, OCP⁻, is a valence isoelectronic, heavy-analogue of the ubiquitous cyanate anion, OCN⁻, and therefore its chemistry is of fundamental interest.[1] However, even though the inception of the OCP anion may date back to 1894,[2] and it certainly moved to a firmer footing in 1992,[3] it has not been until now in the past decade that reliable, accessible routes to OCP have become widely available.[4] Consequently, despite the increasingly burgeoning nature of the area there are still many unanswered questions about the intrinsic properties and coordination chemistry of the OCP anion.[11]

Although the oxidation chemistry of the OCP anion is now quite established,[12] reports of its formal reduction chemistry are exceedingly scarce.[13] This is perhaps unsurprising since as a closed-shell anion OCP would be expected to inherently resist reduction as this would populate anti-bonding orbitals, and indeed where examples of reduction have been reported fragmentation of the OCP unit is usually the decisive, inevitable result. For example, strongly reducing [U[N(OC)(AsMe₂)₃]₂(DME)] [OAs(AsMe₂)₃] = triamido(tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)amine] cleaves the C-O bond of OCP to give an oxo-bridged dinuclear product containing cyphate, CP⁺,[6]

whereas the more weakly reducing [Ti(OCP)(HCMeCNAr)₂][OAr] (Ar = 2,6-disopropylphenyl) cleaves the C-P bond to release CO and give a P₂ derivative.[5] However, in contrast reduction of [Sc(OCP)(HCMeCNAr)₂][OAr][THF] results in P-P coupling to give (OCPPCO)²⁺ rather than fragmentation, which implies dimerisation of a transient, unstable OCP⁺ radical dianion.[14] Notably, in the unique case of [Th(μ-η¹(1O):η²(1P)-OCP)(PC(O)CNiCOD)]; [PhC(NSiMe₂)₂] (1)[9] the P-C-O angle is 148.1°(3°). This suggests a reduced form of OCP by Ni→P=C backboning, but the extent of OCP reduction remains an open question since instability of this complex hampered its characterisation.

In recent years, we have been investigating the coordination chemistry of triamidoamine complexes of uranium and thorium,[10] and in particular complexes of the type [U(Tren)²⁺X]⁻ or [[U(Tren)²⁺]₂(μ-X))][Tren]⁻ = N(CH₃CH₂NSiPr₂)₃; X = formally charged ligand; n = 0 or -1]. The list of main group X-ligands is extensive and growing, and includes: -NH₃, =NH, =N, -PH₃, =P, -µ(PH₃), -µ-cyclop-P, -µ-AsH₃, -AsH₃, -µ-As, -µ-AsK, -µ-η¹ -As, -µ-η¹-AsH₃, -µ-η¹-As₅, -E(SiMe₃); (E = P, As, Sb); =O, -µ-S, -µ-η¹ -S, -µ-Sc, and -µ-Te.[15] It is clear, therefore, that uranium-Tren in mono- or bi-metallic formations is highly effective at trapping otherwise elusive, reactive main group fragments, and this can involve unusual, highly reduced formal charge states that are stabilised by U-X π-or δ-bonding.[11],[16] We therefore sought to determine if a highly reduced form of the OCP anion could be prepared and trapped in a uranium-Tren coordination environment.

Here, we report that a highly-reduced form of 2-phosphaenolate can indeed be trapped in a diuranium-Tren⁻¹⁰ complex. The combined characterisation data suggest a mixed-valence diuranium(III/IV) formulation, and the highly-bent P-C-O unit, with the most acute P-C-O angle to date, suggests extensive charge transfer to the P-C-O unit. Furthermore, the P-C-O unit is so bent and reduced that it gains some carbene character at the central C-atom, and quantum chemical orbital and electron topology descriptions of the chemical bonding suggest the presence of a weak U-C donor-acceptor interaction that is reminiscent of the classical bonding model of Fischer carbenes and uranium mesionic/N-heterocyclic carbene complexes.[17]
Noting the prior incompatibility of uranium(III) with OCP,[1] but that less reducing uranium(IV) congeners afford isolable OCP derivatives,[6,9] we first sought to introduce the OCP anion to a uranium(IV)-Tren[4] fragment. Treatment of \[\text{[U(Tren)}^{18}\text{(THF)][BPh}_4^-\text{]} \text{(1)}\] with [Na(OCP)(1,4-diox)\textsubscript{2}]\textsuperscript{4+} in THF straightforwardly afforded, after work-up, \[\text{[U(Tren)}^{18}\text{OCP)] (2)}\] isolated as green crystals from pentane in 51% isolated yield (Scheme 1).\textsuperscript{13} The crystal structure of 2 (Figure 1) reveals U-O, O-C, and C-P distances of 2.2942(14), 1.241(2), and 1.557(2) Å, and U-O-C and O-C-P angles of 173.36(14) and 179.3(2)', respectively. The U-N\textsubscript{amide} and U-N\textsubscript{amine} distances are unexceptional. The \(^1\)H NMR spectrum of 2 spans the range from ~35 to +11 ppm and the \(^{31}\)P NMR spectrum reveals a resonance at ~320 ppm. The ATR-IR spectrum of 2 exhibits a clear, strong absorption at 1677 cm\(^{-1}\), which corresponds to the POC\(_2\) stretch, but the \(v_1\) stretch, residing in a complex fingerprint region, could not be assigned. The UV/Vis/NIR spectrum of 2 is dominated by charge transfer bands in the UV/Vis regions, and weak \(f-f\) absorptions are observed in the NIR region. Variable-temperature SQUID magnetometry on a powdered sample of 2 (Figure 2) returns a magnetic moment of 3.04 \(\mu_B\) at 298 K consistent with its \(\text{H}_2\) formulation, and this falls smoothly to 0.46 \(\mu_B\) at 2 K reflecting that at low temperature uranium(IV) is a magnetic singlet subject to temperature independent paramagnetism (TIP)\textsuperscript{14}. When considered together, these data are consistent with other \(\text{T}^\text{II}-\text{OCP}\) complexes\textsuperscript{6,9} and are indicative of the presence of uranium(IV) and the dominance of \(\text{P}^\text{IV}-\text{C}=\text{O}\), rather than \(\text{P}^\text{III}-\text{C}=\text{O}\), resonance forms as is common when this anion is coordinated to electropositive metal ions\textsuperscript{11}.

With complex 2 in-hand, we examined its reduction chemistry. Addition of 2 to a preformed mixture of K\(_2\) and 2,2'-cryptand in THF in a 1:1:1 ratio resulted in a dark green solution, from which, after work-up, dark brown \[\text{[U(Tren)}^{18}\text{]}_2[\mu-\eta^2(\text{OP})\eta^2(\text{CP})-\text{OCP]}][\text{K(2,2,2-cryptand)}] (3)\] was isolated from toluene in 43% crystalline yield (based on uranium content, Scheme 1).\textsuperscript{13} The presumed by-product of this reaction for mass-balance is \[\text{[K(OC)(2,2,2-cryptand)}],\] though this was not confirmed despite several attempts since no other compound could be cleanly isolated from reaction attempts that afforded 3.

To confirm the formulation of 3, its crystal structure was determined (Figure 3). The salient feature of this structure is that a highly-bent P-C-O moiety resides between two \[\text{[U(Tren)}^{18}\text{]}\] units in the anion component. The \(\mu-\eta^2\text{I}(\text{OP})\eta^2\text{I}(\text{CP})\)-OCP coordination mode is unique for 2-phosphaethynolate. The P-C and O-C distances are 1.734(11) and 1.172(16) Å, respectively, and so the C-O distance in 3 is slightly shortened compared to that of 2 and other U-OCP linkages\textsuperscript{6,9} The P-C distance is elongated in 3 by almost 0.2 Å compared to 2 and other U-OCP linkages\textsuperscript{6,9} indeed, the P-C distance in 3 is ~0.1 Å longer than that in 1\textsuperscript{9} indicating substantial charge transfer from the uranium ions to the PCO’ ligand. Further reinforcing the notion of a highly-reduced form of the PCO’ anion by extensive uranium charge donation, the P-C-O angle in 3 is 126.6(9)\(^\circ\), which is an unprecedented divergence from linearity for the PCO unit, and it is ~52° more acute than in 2 and ~21° more acute than the P-C-O angle in 1\textsuperscript{6} The U1-O1, U1-P1, U2-P1 bond distances are 2.226(8), 2.845(4), and 2.866(3) Å, respectively, and are unexceptional. The U1-C1 distance of 2.478(15) Å, is shorter than distances of 2.576(12)-2.598(11) and 2.672(5) Å in the mesionic and N-heterocyclic carbene complexes \[\text{[U(CN(Me)C(Me)N(Me)CH(N)}^\text{\textsubscript{1}},\text{]}\] and \[\text{[U(CNMe(Me)C,N(Me)CH(N)}^\text{\textsubscript{1}},\text{]}\textsuperscript{12} [\text{N}^\text{\textsubscript{N} = N(SiMe)}_3]}\textsuperscript{12} which together with the acute P-C-O angle suggests the C-atom in 3 possesses some carbene character when highly reduced by backbonding, analogously to some reduced CO\(_2\) and CS\(_2\) complexes\textsuperscript{12,13} The U-N\textsubscript{amide} (av. 2.324(11) Å) and U-N\textsubscript{amine} (av. 2.790(9) Å) distances are averaged by the disorder, and towards the high end of such distances. This most likely reflects the overall anionic charge state of the diuranium component of 3, but may also reflect the presence of uranium(III) character since the anion portion of 3 can be formulated as a ‘high spin’ diuranium(III)/PCO-monoanion or a mixed-valence diuranium(III/IV)/PCO-highly-reduced ‘low spin’ form. Which of these is the most appropriate electronic structure description is addressed below.

The ATR-IR spectrum of 3 exhibits a complex band structure in the range 1797-1750 cm\(^{-1}\), with at least four discernable absorptions attributed to \(\nu_1\)-derived stretching modes of the P-C-O unit\textsuperscript{11} and this is consistent with charge accumulation on the P-C-O linkage and a lowering of the C-P bond order. IR data for 3 are not available for comparison, but the data for 3 fall in the range of side-on \(\eta^2\) and \(\mu-\eta^2\) coordination modes of the PCO’ anion (1890-1688 cm\(^{-1}\))\textsuperscript{10}
The UV/Vis/NIR spectrum of 3 reveals significant ($\varepsilon \sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$) absorptions in the region 23,000-13,000 cm$^{-1}$, suggestive of Laporte-allowed 5f-6d transitions of uranium(III)$^{14c,17}$ along with multiple weak ($\varepsilon \sim 50 \text{ M}^{-1} \text{ cm}^{-1}$) f-f absorptions in the NIR region. These data are distinct to 2 and suggest that at least one of the uranium ions in 3 has Kramers uranium(III) character.

Given the likely Kramers nature of 3, we investigated this complex using EPR spectroscopy. The low temperature (5 K) X-band spectrum of 3 exhibits g-values of g = 3.6, 1.4, and 0.55 arising from the ground-Kramers doublet of uranium(III), and this compares well to g-values of 3.9, 1.8, and 0.6 for [U(Tren)$_{125}$]$_{11}$. The non-Kramers uranium(IV) would be expected to be silent under these experimental conditions, but a sharp EPR signal with g = 2.0028 is also observed that is indicative of unpaired spin-density on the P-C-O unit. However, we note that the EPR spectrum of 3 is extremely weak, and is only observed due to the high sensitivity of EPR spectroscopy, which hints at the presence of U-OCP magnetic coupling that could diminish the magnetism of 3. The computed frontier orbital region of the linear PCO$^-$ anion, and the PCO$^-$ anion bent to an angle of 130°. The energy scale is arbitrarily set such that 14A and 15A of linear PCO$^-$ are 0 eV.

As a benchmark, we geometry optimised the septet ‘high spin’ formulation of the anion of 3 (sept3). However, the computed core U(PCO)U bond distances and P-C-O angle (141.4°) do not agree well with the solid state structure of 3, and so this model does not represent an appropriate description of 3. This diuranium(III) formulation is also inconsistent with the experimental characterisation data. Nevertheless, a quintet ‘low spin’ formulation (quin3), in which there are four unpaired electrons overall in the α-spin manifold, is found to lie ~20 kcal/mol lower than the septet form. This results in occupancy of the α- and β-spin MOs at 1448 (Figure 5a) which derives from the mixing of a uranium 5f orbital and orbital 16A of free PCO. The computed core U(PCO)U bond lengths and P-C-O angle (125.1°) of quin3 are in agreement with the solid state data for 3. Inspection of 448a and 448b of quin3 reveals that they are each composed of ~50:50 U-5f:2p character, thus equating to one 5f-electron and one 2p-electron overall. These two electrons formally derive from backbonding, and thus represent population of orbital 16A of PCO$^-$ giving it some carbene character. Thus, combined with the four α-spin 5f-electrons the ‘low spin’ quintet form is equivalent to an antiferromagnetically coupled 5f-2p system, which accounts for the experimental data that suggest a mixed-valence diuranium(II/IV) formulation, the very weak nature of the EPR spectra, and the lower than anticipated magnetic moment data of 3. In addition, interestingly MO 449a does not possess pure 5f-character, being mixed weakly with a PCO orbital of 17A-parentage to constitute a weak backbond (Figure 5b) further supporting the notion of the P-C-O unit in 3 as having some carbene character.
The computed Mayer bond orders for the C-O, C-P, U1-P, U2-P, U2-C1, and U1-O1 bonds are 1.33, 1.80, 0.84, 0.84, 0.61, and 0.68, respectively. As would be expected, this shows that reduction of PCO results in lowering of the C-O and P-C bond orders. The computed MDC charges for quin3 are O (∼0.39), P (∼1.40), C (∼1.19), U1 (3.10), and U2 (3.11). Thus, the P-C-O unit in quin3 has a total computed charge of ∼2.98. For comparison, the Tren-amides have average relative computed charges of ∼1.6 and so since an amide is formally a -1 charge ligand the P-C-O unit in 3 is perhaps best described as approximating to the OCP⁻ radical diion form. Lastly, analysis of the bonding topology with QTAIM shows polar U-C and -C bonds with 3-1 bond critical point (BCP) p values of 0.09, 0.05 (av.), and 0.08, respectively. Most of these bonding interations present roughly spherical charge ellipticity (ε) distributions around the inter-nuclear axes at their respective BCPs (ε = 0.05-0.14), but the U-C bond exhibits an ε value of 0.42 confirming the weak π-backbond and thus a two-fold U-C bonding interaction.

To conclude, by using uranium-Tren we have been able to trap a highly reduced form of 2-phosphaethynolate with a unique coordination mode, thus defying and avoiding the usual fragmentation or coupling reactions of this ligand when it is strongly reduced. The P-C-O unit in 3 is bent to an unprecedented degree due to extensive backbonding from uranium to this ligand. The combined experimental and computational characterisation data suggest a mixed-valence uranium(III)-uranium(IV) form with a P-C-O unit most likely best described as a uranium-stabilised OCP⁻ radical diion form. Whilst U→CP backbonding is clear, this charge transfer to PCO generates some carbene character that is unknown for 2-phosphaethynolate, such that it binds to uranium in a donor-acceptor manner that is reminiscent of Fischer carbenes and uranium mesoionic/N-heterocyclic carbene complexes.

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Keywords: uranium • 2-phosphaethynolate • mixed-valence • carbene • density functional theory

[13] See the Supporting Information for full details.


[19] CCDC 1909770 and 1909771 (2 and 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. All other data are available from the corresponding authors on request.
We report trapping of an unprecedented highly reduced form of 2-phosphaethynolate in a mixed-valence diuranium(III/IV) complex that is best formulated as a uranium-stabilised OCP$^2^-$ radical dianion and which imparts some carbene character to the P-C-O linkage as evidenced by its highly bent geometry and a weak U-C donor-acceptor interaction.