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Actinides

Remarkably High Stability of Late Actinide Dioxide Cations: Extending Chemistry to Pentavalent Berkelium and Californium


Abstract: Actinyl chemistry is extended beyond Cm to BkO$_2^-$ and CfO$_2^-$ through transfer of an O atom from NO$_2$ to BkO$^-$ or CfO$^-$, establishing a surprisingly high lower limit of 73 kcal mol$^{-1}$ for the dissociation energies, D[O-(BkO$^-$)] and D[O-(CfO$^-$)]. CCSD(T) computations are in accord with the observed reactions, and characterize the newly observed dioxide ions as linear pentavalent actinyls; these being the first Bk and Cf species with oxidation states above IV. Computations of actinide dioxide cations AnO$_2^+$ for An = Pa to Lr reveal an unexpected minimum for D[O-(CmO$^-$)]. For CmO$_2^+$, and AnO$_2^+$ beyond EsO$_2^+$, the most stable structure has side-on bonded $\eta^2$-(O$_2$) as An$^\delta$ peroxides for An = Cm and Lr, and as An$^\delta$ superoxides for An = Fm, Md, and No. It is predicted that the most stable structure of EsO$_2^+$ is linear [O=Es$^{\delta^\prime}$=O]$^+$, einsteinyl, and that FmO$_2^+$ and MdO$_2^+$, like CmO$_2^+$, also have actinyl(V) structures as local energy minima. The results expand actinide oxidation state chemistry, the realm of the distinctive actinyl moiety, and the non-periodic character towards the end of the periodic table.

Introduction

Among the most central aspects of metal ion chemistry is the accessibility of oxidation states. This attribute, for example, clearly distinguishes the strictly monovalent alkali metals from the divalent alkaline earth metals. In contrast, the valence-state metals, a core aspect of the fertile chemistry of the late actinides, distinctly differs from the relatively inert and localized 4f electrons of the homologous lanthanide (Ln) series, for which the dominant oxidation state is Ln$^{III}$. Whereas several Ln$^{IV}$ compounds have been reported,[2,3] only recently was the first Ln$^{V}$ molecule, PrO$_2^+$, identified.[6] In contrast, the pentavalent oxidation state is known to be stable for several members of the actinide series, beginning with Pa$^{IV}$ and continuing through at least Am$^{IV}$. The aqueous actinyl(V) cations, NpO$_2^+$, PuO$_2^+$, and AmO$_2^+$, are particularly important in actinide chemistry.[7,8] Although aqueous ceryl(V) and californyl(V) have been claimed, the evidence for them is dubious; berkelyl(V) has not been reported as a stable species.[5,6,8] There are no claims of oxidation states above An$^{IV}$ beyond Cf.

The recent discoveries of Pr$^{IV}$ in PrO$_2^+$[6] and Ir$^{IV}$ in IrO$_2^+$[7] illustrate the ability to create new high oxidation states in isolated gas-phase molecules, particularly in oxide cations. Intrinsically stable high oxidation states can occur in isolated gas-phase molecules because reduction of chemically fragile species by solvents or other interacting moieties is avoided. A central goal of the present work is to evaluate the intrinsic stabilities of the actinyl(V) cations in the gas phase, absent potentially destructive effects in aqueous solution and other condensed phase environments. Gas-phase actinide dioxide cations, AnO$_2^+$, have been reported for An = Pa$^{VI}$[9] U$^{V}$[9] Np$^{V}$[9] Pu$^{V}$[9] Am$^{V}$[10], and Cm.$^{[11]}$ Each of these An$^{V}$ ions was produced by the sequential gas-phase reactions of the bare An$^{+}$ ions with neutral O-atom donor molecules, to first yield AnO$^{+}$ and then AnO$_2^+$. An aim of the present work is to extend this chemistry further into the actinide series, to BkO$_2^+$ and CfO$_2^+$. Although neither berkelyl(V) nor californyl(V) are stable in the condensed phase, it is feasible that they are stable as isolated gas-phase species, in analogy with the PrO$_2^+$ molecular ion, a moiety that...
is not known in condensed phase chemistry. In parallel with the synthesis of new AnO$_2^+$ molecular ions, electronic structure calculations were performed at the correlated molecular orbital theory coupled cluster CCSD(T) level to assess the structures, including formal actinide oxidation states, for known, new, and predicted AnO$_2^+$ gas-phase ions for all of the actinides from Pa through Lr. The combined experiment and computational results provide evidence for the synthesis of two new prototypical actinyl(V) molecules, BkO$_2^+$ and Cfo$_2^+$, and furthermore present an evaluation of the variations in stability of actinyl(V) ions, [O-An=O]$^-$, across the series and the prospects for producing EsO$_2^+$ and actinyls of even heavier members of the series. The relative energies of alternative AnO$_2^+$ and An$^+$O$_2^+$ structures having side-on bonded $\eta^1$($O_2$) superoxide or peroxide moieties are also assessed.

Results and Discussion

Synthesis of MO$_2^+$ cations

The ESI mass spectra, obtained with NO$_2$ in the quadrupole ion trap (QIT), for the five studied metal ions, shown in Figure S1 of the Supporting Information, revealed substantial abundances of MO$^+$ (M = Ce, Pr, Am, Cf, Bk). The monoxide cation was dominant, except for the case of Bk for which the BkO$_2^+$ was most abundant. Each of the MO$^+$ was isolated by ejection of all other ions from the QIT and then exposed to an indeterminate but constant pressure of NO$_2$ for reaction times ranging from 0.05 to 0.55 s. The results are shown in Figure 1 where it is apparent that each of the five studied monoxide cations abstracted an oxygen atom to yield MO$_2^+$. The formation of the dioxides occurs by O-atom abstraction from some neutral species RO in the ion trap under thermal conditions: MO$^+$ + RO $\rightarrow$ MO$_2^+$ + R. As noted below, and expected based on the presence of H$_2$O in the ion trap, abstraction of NO$_2$ yielded HNO$_2$, as demonstrated by its addition [14] to PuO(NO)$_2$ to yield PuO(ONO)$_2$(NO$_3$). It can be inferred that HNO$_2$ was also produced, and it is known that O$_3$ is also present in the trap.[12]

The bond dissociation energies (D) for abstraction of an O-atom from the various neutral RO molecules (potentially) present in the ion trap are as follows (in kcal mol$^{-1}$):[15] D[O-(NO)] = 73.2; D[O-(HNO)$_2$] = 73.3; D[O-(HNO)] = 101.7; D[O-(H$_2$)] = 117.3; and D[O-O] = 119.1. Notably, the energies for O-atom abstraction from NO$_2$ and HNO$_2$ are essentially the same, which is a manifestation of reaction (1) being nearly thermoneutral.

HNO$_3$ + NO $\rightarrow$ HNO$_2$ + NO$_2$ + O$_3$  
(1)

The results for the reactions of CeO$^+$ and PrO$^+$ to yield CeO$_2^+$ and PrO$_2^+$ can be compared with previous experimental studies of the gas-phase reactivity of these monoxide cations by Bohme and co-workers.[16, 17] It was found that neither CeO$^+$ nor PrO$^+$ react with O$_2$ or H$_2$O to yield the dioxide cations, whereas both react with NO$_2$ to yield CeO$_2^+$ and PrO$_2^+$ according to reaction (2) when M = Ce or Pr.[18]

MO$^+$ + NO$_2$ $\rightarrow$ MO$_2^+$ + NO + O$_3$  
(2)

Reaction (2) was reported to occur at 56% of the collisional efficiency for M = Ce but at only 3.7% efficiency for M = Pr. Despite complications introduced by the formation of the hydroxides identified in Figure 1, it is apparent there that CeO$_2^+$ was similarly produced here with a substantially higher efficiency than PrO$_2^+$ (note the different reaction times). Schwarz and co-workers also reported reaction (2) for M = Ce and furthermore found that CeO$^+$ does not react with N$_2$O, O$_2$, or NO.[16] The inability of N$_2$O, a thermodynamically good O-atom donor (D[O-(N$_2$O)] = 39.9 kcal mol$^{-1}$), to yield CeO$_2^+$ suggests that NO$_2$ distinctively exhibits both the thermodynamic and kinetic attributes necessary to achieve O-atom donation to CeO$^+$. Also apparent in Figure 1 are products at 1 and 2 m/z higher than the MO$_2^+$ of primary interest. The MO$_2$H$_2^+$ products likely
correspond to addition of H$_2$O to MO$^+$. These MO$_2$H$_2^+$ could be physisorption hydrates, MO(H$_2$O)$_n^+$, or chemisorption hydrides, M(OH)$_n^+$, in both of which the oxidation state remains M$. The observed MO$_2$H$_2^+$ are likely hydrides, MO(OH)$_n^+$ having oxidation state M$, possibly produced by (OH)-donation to MO$^+$ from H$_2$O and/or HNO$_2$. The values for D[(O)H-(NO)$_2$] = 49.2 kcal mol$^{-1}$ and D[(OH)-(NO)$_2$] = 49.3 kcal mol$^{-1}$ are much lower than D[(OH)-H] = 119.2 kcal mol$^{-1}$.[18] It is known that H$_2$O is unreactive with both Ce$^{IV}$ and PrO$^{IV}$.[17] The origins and nature of the MO$_2$H$_2^+$ and MO$_2$H$^+$, which are likely M$^+$ and M$^{IV}$ species, respectively, are not directly pertinent to the synthesis of the MO$_2^+$ cations that offer the possibility of higher oxidation states.

A detailed description of the structure and energetics of the AnO$_2^+$ cations is presented below, whereas the computed reaction energetics are described here. We predict the energy for reaction (1) to be nearly thermoneutral at the CCSD(T)/cc-pwCVTZ-DK/aug-cc-pwCVTZ-DK level of theory at the CCSD(T)/cc-pwCVTZ-DK/aug-cc-pwCVTZ-DK equilibrium geometries. We also predict the reaction energies for (2) as well as for reactions (3), (4), and (5) as shown in Table 1.

$$\text{HNO}_2 + \text{AnO}^+ \rightarrow \text{HNO}_2 + \text{AnO}_2^+ \quad (3)$$

$$\text{AnO}^+ + \text{O}_2 \rightarrow \text{AnO}_2^+ + \text{O} \quad (4)$$

$$\text{AnO}^+ + \text{HNO}_2 \rightarrow \text{AnO}_2^+ + \text{HNO}_2 \quad (5)$$

Reactions (2) and (3) are exothermic for all An except Cm and Bk; they are nearly thermoneutral for Cf. The endothermic value for reaction (4) for Cm is consistent with the fact that hyperthermal conditions are needed to induce this reaction.[31] Reactions (2) and/or (3) are observed for Bk but we predict them to be endothermic by $\approx 10$ kcal mol$^{-1}$. This arises because of the aug-cc-pwCVTZ-DK basis set is giving too small bond dissociation energies (i.e., D) for the An–O bond in AnO$^+$ (see below). We note that the values for Cf are near thermoneutral, consistent with experiment. The reaction energetics are for the formation of the most stable product.

**Synthesis of dioxide cations including BkO$_2^+$ and CfO$_2^+$**

It is apparent in Figure 1 that AmO$^+$ reacts with NO$_2^-$ (and/or HNO$_2$) to yield AmO$_2^+$, which is presumed to be the linear ameryl(V) ion, [O$-\text{Am}=\text{O}$]$^+$, that is well known in condensed phase chemistry.[20] The computational structural and energetic results discussed below support this hypothesis. The AmO$_2^+$ cation was previously produced by the reaction of AmO$^+$ with C$_2$H$_2$O$_2$, ethylene oxide, establishing D[(O)-Am(O$^+$)] > D[(O)-(C$_2$H$_2$O$_2$)] = 84.7 kcal mol$^{-1}$.[10] The observed reaction of AmO$^+$ with NO$_2^-$ or HNO$_2$ is thus thermodynamically favorable. In contrast, oxidation of AmO$_2^+$ by O$_2$ or H$_2$O is not exothermic and is not observed under thermal conditions.[16]

The key results for the reactions of BkO$^+$ and CfO$^+$ are shown in Figure 1. They react with NO$_2^-$ and/or HNO$_2$ to yield BkO$_2^+$ and CfO$_2^+$. Although absolute reaction efficiencies cannot be derived because the constant pressure of NO$_2^-$ is not accurately known, it is apparent from Figure 1 that the reaction efficiency for CfO$^+$ is somewhat lower than for BkO$^+$; the reaction efficiency is significantly lower for AmO$^+$. As noted above, the 248BkO$^+$ reactant included 7.6% of nearly isobaric 249CfO$^+$ when the experiments were performed. The observed different reaction rates and product distributions for BkO$^+$ versus CfO$^+$ cannot be attributed to the 249CfO$^+$ impurity” in the former.

The occurrence of reaction (2), or the corresponding reaction (3) with HNO$_2$ rather than NO$_2^-$ establishes a lower limit of D[(O)-M(O$^+$)] $\geq$ 73 kcal mol$^{-1}$ for M = Bk and Cf. Previous attempts to synthesize CfO$_2^+$ under thermal conditions were unsuccessful.[11] The CfO$_2^+$ cation was however produced in a hyperthermal reaction of CfO$^+$ with O$_2$, demonstrating that CfO$_2^+$ is an inherently stable species.[11] Based on systematic trends across the actinide series, D[(O)-Cf(O$^+$)] has been estimated as 48 $\pm$ 14 kcal mol$^{-1}$, a value that is substantially lower than for the earlier AnO$_2^+$.[21] The authors of that work did not extrapolate these thermodynamic trends beyond CfO$_2^+$; the present results indicate that D[(O)-An(O$^+$)] does not continue to decrease beyond CfO$_2^+$ but instead increases for both BkO$_2^+$ and CfO$_2^+$. This result is computationally assessed below.

The synthesis of an MO$_2^+$ cation does not directly reveal its structure or the metal oxidation state. The two plausible geometric structures are shown in Figure 2. In highly bent struc-

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**Table 1. Computed reaction energies in kcal mol$^{-1}$.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
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<td>$-170.0$</td>
<td>$-63.4$</td>
</tr>
<tr>
<td>U</td>
<td>$-95.6$</td>
<td>$-94.4$</td>
<td>$-50.8$</td>
</tr>
<tr>
<td>Np</td>
<td>$-69.3$</td>
<td>$-68.1$</td>
<td>$-24.5$</td>
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<tr>
<td>Pu</td>
<td>$-44.8$</td>
<td>$-43.6$</td>
<td>$0.0$</td>
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<td>Am</td>
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<tr>
<td>Cm</td>
<td>$12.1$</td>
<td>$30.1$</td>
<td>$56.8$</td>
</tr>
<tr>
<td>Bk</td>
<td>$9.1$</td>
<td>$10.2$</td>
<td>$53.8$</td>
</tr>
<tr>
<td>Cf</td>
<td>$0.9$</td>
<td>$0.9$</td>
<td>$44.5$</td>
</tr>
<tr>
<td>Es</td>
<td>$-5.5$</td>
<td>$-4.3$</td>
<td>$39.3$</td>
</tr>
<tr>
<td>Fm</td>
<td>$-12.5$</td>
<td>$-11.3$</td>
<td>$32.3$</td>
</tr>
<tr>
<td>Md</td>
<td>$-34.8$</td>
<td>$-33.7$</td>
<td>$9.9$</td>
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<tr>
<td>No</td>
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<td>$-22.3$</td>
<td>$21.3$</td>
</tr>
<tr>
<td>Lr</td>
<td>$-11.9$</td>
<td>$10.7$</td>
<td>$47.3$</td>
</tr>
<tr>
<td>Pr</td>
<td>$-30.3$</td>
<td>$-29.1$</td>
<td>$14.4$</td>
</tr>
</tbody>
</table>

[a] Values in brackets are for the linear structure (oxidation state V) if it is higher in energy than the highly bent $\eta^1$-O$_2$ structure 1 in Figure 2. [b] Values in brackets are for the $\eta^1$-O$_2$ structure of LuO$^+$ with a bond angle of 106.6$^\circ$. The corresponding values for the linear structure are 28.6, 29.8, 87.8, and 61.0 kcal mol$^{-1}$ in the order of the columns.

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**Figure 2. Schematic representations of two plausible structures of the MO$_2^+$ cations.** For the $\eta^1$-O$_2$ highly bent side-on bonded structure 1 the formal oxidation state is M$^+$ for a superoxide (O$^-$) and M$^+$ for a peroxide (O$_2$$^-$). In the “actinyl” structure 2, which is typically nearly linear, the oxidation state is generally An$^+$ with two double An=O bonds. Exceptions are discussed in the text.
ture 1, an O₂ moiety is side-on bonded with η² coordination. In the case of a peroxide, formally O₂⁺, the formal oxidation state is M²⁺, which is the probable situation for a species such as BaO₂⁺. In the case of a peroxide, formally O₂⁺, the formal oxidation state is M²⁺, which is a stable and feasible oxidation state for all the MO₂⁺ synthesized in this work. In structure 2, which may not be linear as shown in Figure 2, the formal oxidation state ranges from M⁴⁺ for two single M–O bonds to M⁶⁺ for two double M–O bonds; the intermediate M⁴⁺ oxidation state (or a non-integer oxidation state) would result from bonds of single/double character. It should be noted that structures resulting from other atomic connectivities, specifically M–O–O, are feasible but are almost certainly high-energy (and may not be minima) given the strong binding of O atoms to these metals, and were not studied further computationally.

Previous results for PrO₂⁺ indicated structure 2 with a Pr²⁺ oxidation state.[6] The structure of CeO₂⁺ was also assigned as 2 but with a formal oxidation state intermediate between Ce⁴⁺ and Ce⁷⁺,[26] a Ce oxidation state above Ce⁵⁺ is remarkable because it implies chemical engagement of electrons from the closed-shell (Xe) core. The linear AmO₂⁺ moiety, structure 2 with Am³⁺, is common in condensed phase chemistry, and is also likely the structure of the bare cation, as is confirmed with the AnO₂⁺ beyond AmO₂⁺, predicting the structures based on known chemistry is dubious. Consideration of established and estimated reduction potentials[5] suggests that it might be feasible to prepare pentavalent CmO₂⁺ and CfO₂⁺; unsubstantiated claims have been made for both as unstable (unpaired) d⁸ electrons. The relatively high reduction potential for BK²⁺ and the similar stabilities of Ce⁴⁺ and BK³⁺ suggest the possibility of BK²⁺ in BK₂O₅. However, the identification of Pr²⁺ in PrO₂⁺, an oxidation state that is unknown in the condensed phase, provides a lucid illustration of the limitations of inferring structures and bonding in isolated gas-phase species based on known condensed phase chemistry. Accordingly, high-level electronic structure computations at the coupled cluster CCSD(T) level were employed to assess the nature of the AnO₂⁺ molecular ions. The computational results presented below compare favorably with the thermodynamic constraints imposed by the experimental observations.

### Computed structures and energetics of AnO₂⁺ cations

The key computational results are compiled in Table 2, for the AnO₂⁺ from An = Pa through Lr; the first two actinides are not included because their highest practically attainable oxidation states are Ac⁴⁺ and Th⁴⁺ such that the formation of actinyl(V) species for these two An would require the ionization of inner shell electrons. Both of the types of structures shown in Figure 2 were examined. When the lowest energy structure is 2 for the actinides up to Es, the oxidation state is found to be An²⁺. For structure 1, up to Cf, the oxidation state is An⁴⁺. We base this assignment of oxidation state on the An–O and O–O bond lengths, as well as the electronic population analysis discussed below. The bond length in the prototypical closed shell V species is 1.785 Å for Pa and the bond lengths decrease from Pa to Pu to a minimum value of 1.732 Å for PuO₂⁺. The actinyl(V) An–O bond lengths then increase to 1.812 Å for MdO₂⁺, with a small decrease at Cf. Thus, the AnO₂⁺ from PaO₂⁺ through MdO₂⁺ exhibit linear structures and An–O bond distances that are characteristic of actinyl(V) ions, with a slight elongation for Md. The bond distance then increases substantially, by 0.05 Å, to 1.870 Å for NO₂⁺; it is thus unlikely that NO₂⁺ is in the V oxidation state, and the actinyl character is apparently disrupted. Because the computed spin on both O atoms is 0.5 we assign the oxidation state as NO⁴⁺. Notably, the

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**Table 2.** Computed CCSD(T) relative energies (kcalmol⁻¹), geometries and oxidation states (OS) for the linear and bent AnO₂⁺.¹⁴

<table>
<thead>
<tr>
<th>An</th>
<th>ΔE/AnO₂⁺</th>
<th>D(O=AnO₂⁺)</th>
<th>AnO₂⁺ Structure 2</th>
<th>ΔE/AnO₂⁺</th>
<th>AnO₂⁺ Structure 1</th>
<th>ΔE/AnO₂⁺</th>
<th>AnO₂⁺ Structure 1</th>
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<th>ΔE/AnO₂⁺</th>
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<th>AnO₂⁺ Structure 1</th>
<th>ΔE/AnO₂⁺</th>
<th>AnO₂⁺ Structure 1</th>
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<td>Pa</td>
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<td>2 (2)</td>
<td>2.041/1.539/44.3</td>
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<td>V/III</td>
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<tr>
<td>U</td>
<td>1 (1)</td>
<td>166 (177 ± 3)</td>
<td>1.771</td>
<td>3 (3)</td>
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<td>110/110</td>
<td>1.816</td>
<td>V/III</td>
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<td>Pu</td>
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<td>115 (122 ± 9)</td>
<td>1.732</td>
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<td>Cm</td>
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<tr>
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<tr>
<td>Cf</td>
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<td>70 (≥73)</td>
<td>1.763</td>
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<tr>
<td>Md</td>
<td>10 (2)</td>
<td>105 (62)</td>
<td>1.812</td>
<td>12 (2)</td>
<td>2.212/1.362/45.9</td>
<td>43/37</td>
<td>1.834</td>
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<td>No</td>
<td>11 (1)</td>
<td>93 (8)</td>
<td>1.870</td>
<td>13 (1)</td>
<td>2.228/1.372/45.9</td>
<td>86/76</td>
<td>1.978</td>
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<td>Lr</td>
<td>12 (2)</td>
<td>67 (46)</td>
<td>2.048</td>
<td>14 (0)</td>
<td>1.989/1.626/48.2</td>
<td>21/20</td>
<td>1.865</td>
<td>III/III</td>
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[a] Relative energies calculated with cc-pwCVTZ-DK/aug-cc-pwCVTZ-DK basis sets at CCSD(T)/cc-pwCVDZ-DK/aug-cc-pwCVDZ-DK equilibrium geometries. [b] Values in parentheses from experiment, Ref. [21]. [c] Values in brackets for the V linear OS; IV for No and III for Lr. [d] See Figure 2 for structures. [e] R(Ο–Ο): (T₁L₁) = 1.365 Å, O₂⁺: (O₁O₂⁺) = 1.631 Å, in H₂O₂: 1.478 Å. [f] CeO₂⁺: ‘ground-state is best described as “non-actinyl” (OMO 106.6), linear singlet for LuO₂⁺ (in parenthesis) is 4.5 kcalmol⁻¹ above the bent actinyl structure. [f] AnO₂⁺ OS is III for all except No, which is assigned II.
stability of this No\(^{2+}\) “actinyl” is much lower, by 86 kcal mol\(^{-1}\), than the \(\eta^1\) No\(^{2+}\) structure. LrO\(^{2+}\) has a much longer bond length, 2.05 Å, and is bent with a bond angle of 107°. The corresponding linear structure for LrO\(^{2+}\) is only 4.5 kcal mol\(^{-1}\) higher in energy. Thus it is probably best to describe ground-state highly bent \(\eta^1\) LrO\(^{2+}\), as a \(\text{La}^\text{II}\) peroxyde and the higher-energy less bent structure as a non-actinyl, also having the oxidation state III with a closed shell Lr and two O atoms with an open-shell electron on each.

The dominant electronic configurations of the linear AnO\(^{2+}\) are given in Table 3 as determined in the current work. Denny et al. has given a description of the orbital ordering in the actinyls built on experimental data for the earlier actinyls. The two lowest lying orbitals for the f electrons are the 1\(\delta_u\) and the 1\(\psi_u\) which are very close in energy and have no contribution from the oxygen 2\(p\) orbitals. These are followed energetically by the 3\(\pi_u^*\) and then by the 4\(\alpha_u^*\), both of which contain some contribution from the O electrons. Electronic structure CASSCF/CASPT2 calculations\(^{[23]}\) have been reported for PaO\(^{2+}\) to CmO\(^{2+}\) and the results are in agreement with our values in Table 3. The f electrons want to remain high spin so the 1\(\delta_u\) and the 1\(\psi_u\) take the first 4f electrons. At Cm, the 3\(\pi_u^*\) becomes occupied and a second f electron is added to the 3\(\pi_u^*\) for Bk. Rather than occupying the 4\(\alpha_u^*\) and staying high spin, the f electrons go back to filling the 1\(\delta_u\) and the 1\(\psi_u\) with 2 electrons in the 3\(\pi_u^*\) for Cf to Md. For No and Lr, the f electrons are added to the 3\(\pi_u^*\). We note that filling the 3\(\pi_u^*\) leads to a change in the oxidation state and No and Lr are no longer in the V oxidation state for the AnO\(^{2+}\). Notably “actinyl” NoO\(^{2+}\) is linear whereas LrO\(^{2+}\) is bent to 107° with the linear structure 4.5 kcal mol\(^{-1}\) higher in energy. The prior work\(^{[23]}\) on linear AnO\(^{2+}\) up to An=Cm showed that the these ions are dominated by a single configuration with at least the wavefunction being dominated by >80% of a single configuration. In fact, all of the AnO\(^{2+}\) \(\delta_u^\text{VI}\) were shown to be dominated by a single configuration in the CASPT2 calculations for Pa to Cm.

The \(\eta^1\)-structure is very bent with a bond angle up through CF of 43–46° and an O–O bond distance of 1.52 to 1.56 Å, which is very similar to the O\(^2–\) distance of 1.63 Å at this level of theory. The An–O bond distance is much longer, 2.01 to 2.05 Å. Thus, in this case, the An is clearly in the III oxidation state. For Es to No, the \(\eta^1\)-structure is more like a superoxide with a smaller bond angle near 36°, a shorter O–O bond of 1.36–1.37 Å comparable to that of O\(^2–\) (1.365 Å), and a very long An–O bond of 2.21 to 2.23 Å. These structures are best described as being in the II oxidation state. For LrO\(^{2+}\), the strongly bent structure is again in the III oxidation state, with a larger O–O bond and a larger angle to accommodate the O\(^2–\). Due to the low symmetry, there is substantial mixing of the orbitals on the An and it is not possible to make a simple assignment of the electronic configuration as for the linear structure.

The bond distances show that there is a crossover from the III to the II oxidation state for the \(\eta^1\)-structures as the O\(^{2–}\) goes from a peroxyde (O\(^2–\)\(^{2+}\)) to a superoxide (O\(^2–\)). This occurs between Cfu and Es with a reversion back to III at Lr. It is clear that the II formal oxidation state occurs for the bent structure of Es as one of the open-shell electrons switches from a 5\(\ell\) \(\delta\) as found for Cf to an O 2\(p\) for Es. The only real change in the linear actinyl-type structures is for No and Lr where the Lr is in the III oxidation state and the No is assigned as IV based on the spin 0.5 on both O atoms.

How do the relative energetics of the two structures change as one goes across the actinide row? The comparative energies of the AnO\(^{2+}\) and An\(^{11+}\)O\(^{2–}\) (or AnO\(^{2+}\)) dissociation energies, are given in Table 2 and plotted in Figure 3. For Pa to Am, the \(\eta^1\)-structure with the An in the III oxidation state is much higher in energy than the linear V oxida-
vation state structure. At Cm, the energy difference switches so that the III η1-structure is favored because the III oxidation state has the quite stable 5f6 electron configuration, whereas the V oxidation state has 5 unpaired electrons. The energy difference between the two AnO2+ isomers is very small for Bk with the linear V only favored by 10 kcal mol−1. The linear V structure for Cf is stable by 23 kcal mol−1 as compared to the III η1-structure. The V structure for Es is only 6 kcal mol−1 more stable than the II η1-structure. A crossover occurs between Es and Fm, and the lowest energy structure for Fm is predicted to be the η1-structure. The η1-structure becomes more stable as one continues across the row to No. At Lr, the η1-structure is still the most stable, but the energy difference has significantly decreased from that for No.

The maximum effect of spin orbit interactions for the energy difference between the two structures is <10 kcal mol−1. Except for Pa and Np, the spin orbit effects are always positive for the energy difference as written. This leads to an increase in the positive energy differences and will lead to a less negative value for the negative energy differences. None of the signs change when the effect of spin orbit is included. The effect for Cm is to change the energy difference from −18 to −14 kcal mol−1, for Bk, it increases the energy difference from 5 to 10 kcal mol−1, and for Es, it increases the energy difference from 4 to 6 kcal mol−1. The largest effect is to change the energy difference for Fm from −13 to −3 kcal mol−1. Except for Es and Fm, it is unlikely that higher level multi-reference configuration interaction calculations and spin orbit calculations will impact the sign of the energy difference between structure 1 and structure 2.

The computational results for PrO4− are included in Table 2. The results confirm the previous report that PrO4− is linear “praseodymyl(V)”. The stability of PrO4− is comparable to that of AmO4−, as indicated by both their similar bond dissociation energies and their energies relative to the trivalent peroxides. The experimental results establish a lower limit for D[O-(PrO4−)] of 73 kcal mol−1, revealing a remarkably high stability of this Pr6+ molecule.

The value for D[O-(AnO4−)] is the energy for reaction (6) where the oxidation states are designated as X and Y for the dioxo and monoxo cations, respectively. The oxidation states X were discussed above, those for the monoxides, that is, Y, are considered here.

\[
\text{An}(X)O_2^+ \rightarrow \text{An}(Y)O^+ + O \quad \Delta E = D[O-(\text{AnO}^4-)]
\]  

(6)

We note that the computed An−O bond distances for the AnO− fall within the range of 1.79 to 1.86 Å except for No, where the bond distance is much longer at 1.98 Å (Table 1). We can thus assign the An oxidation state Y in reaction (6) as III in AnO− for all of the An except for No, where it is better assigned as II. The computed values for D[O-(AnO4−)] are given in Table 2 together with estimates based on experimental results; the computed values are plotted in Figure 3. The agreement between the experimental and computed values is very good, and both indicate a monotonic decrease in bond dissociation energy from PaO2− to CmO2−. We note that the value for

linear CmO2− is quite low, 40 kcal mol−1, consistent with a high spin f occupation for the III oxidation state in CmO+ that increases the stability of the monoxide. The actual bond energy for the most stable CmO2− is 58 kcal mol−1 for the η1-structure with Cm. A simplistic extrapolation of this trend for the linear AnO2+ would predict even lower D(O-(AnO4−)) for An = Bk and Cf, whereas the computational results in Table 2 indicate that the dissociation energy for BkO2+ is about 21 kcal mol−1 higher than the value for linear CmO2−. The value for Cf is about 30 kcal mol−1 higher in energy and that for Es is about 36 kcal mol−1 higher, both with respect to linear CmO2−. The validity of the computed D(O-(BkO2+)) and D(O-(CfO2+)) is established by the new experimental lower limit of 73 kcal mol−1 for both. Although the computed values are below the new experimental lower limit, the CCSD(T) values with this basis set are found to be somewhat lower as compared to experiment as evidenced by the comparison between theory and experiment for the earlier AnO4− species in Table 2.

The D(O-(AnO4−)) starting at FmO2− (and for CmO2−) are for the η1-structures. The value for η1-FmO2− is comparable to that for linear AmO2− and that for η1-MdO2− is comparable to that for PuO2−. The D(O-(AnO4−)) then decrease for η1-NoO2− and η1-LrO2− with the value for LrO2− similar to those for BkO2− to EsO2−. The D(O-(AnO4−)) for the linear isomer for the later actinides decrease from Fm to No, where a small value of 8 kcal mol−1 is predicted, and then increases to 46 kcal mol−1 for Lr. The D(O-(PrO4−)) falls between those of AmO2− and PuO2−, consistent with the above discussion.

Up to Es, excluding Cm, reaction (6) corresponds to reduction of AnV to AnIII, so one can correlate the trends in bond dissociation energies with estimated reduction potentials $E^{0}$. The $E^{0}$(IV/III) are similarly high (≈ 3.1 V) for Cm and Cf, neither of which exhibit particularly stable AnV oxidation states in the condensed phase. $E^{0}$(IV/III) for Bk is much lower, 1.67 V, and BkV is stable in solutions and solids. The $E^{0}$(V/IV) for Cf is only ≈ 1.0 V, which reflects the stability of the half-filled 5f valence orbital shell in CfV. In contrast, $E^{0}$(V/IV) for Cm is ≈ 1.6 V, and $E^{0}$(V/IV) for Bk is much higher at ≈ 3.1 V. Based on the (estimated) reduction potentials, it is expected that CfV should be more stable than CmV. This is in line with what has been predicted, and the favored oxidation state for CmO2− is actually III with the η1-structure.

A particularly remarkable result is that BkV is comparably stable to CfV, with the predicted relatively high stability of the latter expected due to its 5f configuration. Based on the solution reduction potentials, it is expected that BkV should be more much susceptible towards reduction to BkVI, though not towards further reduction to BkVII. The latter prediction is in accord with the higher stability of BkO2− versus BkIVO−. The result that the oxidation state is BkV rather than BkVI in BkO2− is a manifestation of the very different chemistry in the gas phase versus solution and solid. $E^{0}$(V/IV) reflects the (free) energy for reduction of BkO2− (aq) to BkIII (aq), which is clearly a very different process from conversion of BkO2− (g) to BkVI (g). The results here indicate that it is more favorable for the BkO2− cation to have two Bk=O double bonds rather than intermediate bond orders to yield BkVII. Solution reduction
entirely excludes from consideration the non-ionic character of the bonding in BkO$_2$$^+$, and specifically significant bond covalency. In this regard, it should be emphasized that the synthesis of the BkO$_2$$^+$ molecular ion does not suggest that aqueous beryllyl(V) is expected to be a stable solution species. Similarly, neither “praseodymyl(V)” nor Ir$^+$ are likely to be stable in condensed phase; substantial effort was made to produce the latter but to no avail. The AnO$_2$$^+$ oxidation states assigned here are shown in Table 4 along with the known (and proposed) actinide oxidation states.

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[a] States with question marks are unsubstantiated. The most stable OS is in bold (see text for references). The computed AnO$_2$$^+$ OS are in red. The ground state is in bold. Underlined values correspond to [O=An=O]$^+$ actinyls.Italicized values correspond to highly bent η$^1$(O)$_2$ An$^{5+}$ peroxides or An$^{5+}$ superoxides.

Natural population analysis (NPA)

The Natural Population Analysis based on the Natural Bond Orbitals (NBO)$_{2,3,3}$ using NBO$^{2,4,3}$ was performed with densities and Kohn–Sham orbitals calculated with the B3LYP functional and the basis sets given above using Gaussian 09. The charges are given in the Supporting Information. For the AnO$_2$$^+$ actinyl type structures, the An charges range from +1.88 (Md) to +2.31 (U). Except for Md, most of the values fall in the range of +2.10 to +2.31 with Am being the outlier at +2.00. For Pa, there are 1.85 e in the 5f and ≈0.9 e in the 6d. These are in doubly occupied orbitals and are due to backbonding from the O atoms to the An. Proceeding from U to Fm, the 6d orbitals are approximately doubly occupied (backbonding) and have a population of 0.75 to 0.9 e. The doubly occupied 6d orbitals are not important for the determination of the electronic states given in Table 3 which arise from how the 5f orbitals are occupied. Except for Lr, the 7s occupancy is very small. For UO$_2$$^+$, there is one unpaired 5f electron and two paired 5f electrons representing backbonding from the O. There is only a small spin polarization on the O atoms. The two 5f electrons involved in backbonding persist through Cm and there is an increase in the spin polarization with ≈0.25 e excess β electron spin on each O. At Bk, there is no longer any negative spin polarization and there is ≈0.25 e of α spin on each O. For Cf, which is a sextet, there is ≈0.25 e of α spin on each O and there are 4.5 paired 5f electrons showing an increase in the backbonding or additional pairing on the Cf. From Bk to Lr, excluding Md, there are ≈6.8 to 7 e α electrons on the An in the 5f and the amount of spin pairing increases. In addition, the excess α spin on O increases as well. We note that the crossover from the An$^4$ actinyl to the An$^{5+}$ η$^1$-structure occurs between Es and Fm in terms of the energetics. For Md, the electronic structure dramatically changes with significant α spin on each O (1.4 e) and a large β spin on the Md for the 5f electrons. The charge on the Md is clearly decreased and the 6d population (mostly doubly occupied) is also decreased to < 0.2 e.

For the AnO$_2$$^+$ η$^1$-structures, there is a charge of ≈+2.1 on the An for Pa to Bk excluding Am, which is ≈+1.9. The charges for Es to No are ≈+1.8 and this increases to +2.2 for Lr. Except for Am, there is very little spin on the O up to Bk. For Am, there is a substantial β spin of −0.27 e on the O. From Es to Lr, there is about 0.5 e α spin on each O, consistent with an O$_2$$^-$ species. For Pa to Cm, there is very little backbonding in the 5f in terms of the amount of β spin except for Am where there is 1.1 e of β spin. There is always excess α spin in the 6d orbitals with only about 0.5 e α spin paired backbonding and the 6d population decreases from Pa to a low value of 0.40 e for Am. It then increases to Cm with small decreases to Bk and Cf. At Es, the 6d population is only ≈0.2 e and is essentially all spin paired due to backbonding. Except for Pa and Lr at the ends of the period, there is very little 7s character. For Bk and Cf, there are 2.7 and 2.8 spin paired 5f electrons and then the number of spin paired 5f electrons is 8, 10, 12, and 14 for Es, Fm, Md, No, and Lr, respectively.

The energy differences between the AnO$_2$$^+$ actinyl and An$^{5+}$ η$^1$-structures are less than ±20 kcal mol$^{-1}$ for Cm to Fm. It is in this region that spin pairing of the 5f β electrons begins to occur and there is a slight decrease in the 6d population from Bk to Fm for AnO$_2$$^+$. For Cm$^{5+}$, the amount of backbonding into the 5f is sufficiently small that Cm can attain a 5f$^7$ configuration and the η$^1$-structure is more stable than the actinyl, as noted above. For the AnO$_2$$^+$ from Bk to Fm, there are always 7 5f electrons with α spin and spin pairing of the 5f electrons begins to occur. For BkO$_2$$^+$ and CFO$_2$$^+$, there is 0.2 to 0.3 e excess α spin on the O atoms so there is some spin polarization on the An. At Es, the η$^1$-structure changes to O$_2$$^-$ from O$_2$$^+$ for An$^{5+}$O$_2$$^+$ and the energy differences between the actinyl and peroxide structures are small. For Es, the actinyl is slightly favored and for Fm, the η$^1$-structure is favored. For Es and Fm, there is very little backbonding into the 6d for AnO$_2$$^+$ η$^1$-structure in contrast to the actinyl structures where significant 6d backbonding is still present. The AnO$_2$$^+$ have small amounts of spin polarization on the O up to Cm and the amounts are very similar to the values for the AnO$_2$$^+$ η$^1$-structure. The values of the α spin on the O increase from 0.03 e for Cm to 1.00 e for No. Except for No and Lr, there are essentially no contributions from the 7s electrons. The amount of 6d orbital participation decreases from 1.12 e for Pa to 0.16 e for No and then increases to 0.66 e for Lr. There is always excess α spin in the 6d with approximately 0.5 to 0.6 e spin paired on the An up to Es; this excess spin decreases to 0.16 e for No. Up to Cm, there is only a modest...
amount of spin pairing for the 5f on the An of 0.4 to 0.6 e due to backbonding. For Cm to Lr, there are approximately 7 5f α electrons and the 5f electrons pair up. Due to the positive spin on O for the heavier actinides, there is always somewhat less spin than expected on the An.

Summary and Conclusions

The two new actinide dioxide molecular ions, BK2O2+ and CF2O2+, were synthesized in the gas phase by oxygen atom transfer from NO2 or HNO3 to BK to and CF+ under thermal conditions (≈ 300 K) in an ion trap. The AnO2+ molecular ion had previously been synthesized for An = Pa through Cm; the experimental (or estimated) dissociation energies, D(0-AnO2+), monotonically decrease from Pa to Cm such that it was anticipated that AnO2+ beyond CmO2+ would be decreasingly stable and synthetically inaccessible. However, CCSD(T) computations predict an increase in D(0-AnO2+) beyond CmO2+; these values, plotted in Figure 3, follow the same trend as the experimental values but are generally lower by ≈ 10 kcal mol−1. The observed, but not empirically expected, syntheses of BK2O2+ and CF2O2+ are thus consistent with computations and provide substantiation of theory, which is further validated by the result here that PrO2+ is a lanthanide(V) species. The computed lowest-energy structures of the two new AnO2+ molecules are linear pentavalent actinyls, [O- An=O]+, with the energies of alternative structures too low to be synthesized by the employed approach. The actinyl(V) series has thus been extended to “berkelyl” and “californyl”, these being the first Bk+ and Cf+ species.

The CCSD(T) computations were extended to all AnO2+ from PaO2+ through LrO2+. The D(0-AnO2+) are sufficiently high (> 50 kcal mol−1) that all of these AnO2+ should be synthetically accessible by oxygen atom transfer to the corresponding AnO2+. The two viable considered structures of the AnO2+ are: linear, or sufficiently close to linear, such that there is no O−O bonding interaction, referred to as actinyl-like; and highly bent with a side-on bonded Ω−(O2)+ moiety that may be either a superoxide (O2−) or peroxide (O22−). For PaO2+ through AnO2+, linear actinyl structures with two short An=O bonds are clearly the most stable. In contrast, the lowest energy structure of CmO2+ is a highly bent peroxide Ω−structure in which the oxidation state is 5f7+24m. For BK2O2+ and CF2O2+, the actinyl(V) structures are somewhat more stable than the An8 peroxides, and for EsO2+, the Es8 structure is slightly more stable than the Es8 superoxide. Beginning with FMnO2+, the An8 superoxides become more stable, with the trivalent peroxide the most stable in the case of Lr due to the stability of closed-shell 5f44Lr+.

In addition to the first synthesis of Bk+ and Cf+ species, a particularly significant result of this work is the revelation that the AnO2+ actinyl(V) structure are the most stable dioxo cations for all of the An from Pa through Es (except Cm), and that the linear actinyl(V) ions are local energy minima through MD2O2+. These results extend the knowledge of actinide oxidation states to Bk+ and Cf+ and extend the distinctive actinyl motif towards the end of the series.

Methods

Experimental Section

Caution: The 242Pu, 241Am, 249Bk, and 249Cf employed in these experiments are highly radioactive isotopes that can be safely handled only using rigorous radiological control procedures in an approved facility.

The following stock solutions were used to prepare electrospray ionization (ESI) solutions: 235AmO2(NO3)3 at pH 1; 10 mM CeBr2 in water; 10 mM PrBr2 in water. For Cf, a solution of 0.40 mM 249Cf in 100 mM HCl was slowly evaporated to yield a solid californium chloride that was dissolved to produce the ESI solution. The 249Bk supplied by Oak Ridge National Laboratory as solid BkCl3 was dissolved to a concentration of 10 mM in ethanol/water. At the time of the experiments the 249Bk, which has a 320 day half-life, had partially beta-decayed to yield ≈ 7.6% of progeny 248Cf impurity, which is practically isobaric and indistinguishable except by high-resolution mass spectrometry. For all the metals, dilution yielded an ESI solution of ≈ 100 µM metal ion in ≈ 80% ethanol and ≈ 20% water. A 248Pu nitrate solution was prepared as described previously to monitor the presence of HNO2 in the quadrupole ion trap mass spectrometer (QIT/MS).14

The ESI mass spectrometry experiments were performed using an Agilent 6340 QIT/MS. The containment of the ESI source in a radioactive glove box enables handling of highly radioactive isotopes such as 242Pu, 241Am, 249Bk and 249Cf. Additionally, ions in the trap can undergo ion-molecule reactions for a fixed time at ≈ 300 K. In high resolution mode, the instrument has a detection range of 50–2200 m/z and a resolution M/ΔM of ≈ 3000. Mass spectra were acquired using the following instrumental parameters: solution flow rate, 60 µl min−1; nebulizer gas pressure, 12 psi; capillary voltage and current, 4350 V, 50.0 nA; end plate voltage offset and current, −500 V, 275 nA; dry gas flow rate, 3 ml min−1; dry gas temperature, 325 °C; capillary exit, 300.0 V; skimmer, 40.5 V; octopole 1 and 2 DC, 16.5 V and 0.0 V; octopole RF amplitude, 104 Vp-p, lens 1 and 2, −100.0 V and −10.5 V; trap drive, 52. The parameters for the PuO2(NO3)3 calibration experiments were described previously.14 High-purity nitrogen gas for nebulization and drying in the ion trap capillary was supplied from the boil-off of a liquid nitrogen Dewar. The helium buffer gas pressure in the trap is constant at ≈ 10−4 torr.

The ion trap has been modified to allow for the introduction of reagent gases, NO2 (≥ 99.5%, Sigma Aldrich) for the present study, through a vacuum manifold a leak valve.16 The NO2 pressure was not known but was essentially constant for all of the experiments. As has been discussed elsewhere, the background water pressure in the ion trap is estimated as ≈ 10−8 torr; reproducibility of hydride rates of UO3(OH)+ confirms that the background water pressure in the trap varies by less than ± 10%,12 A manifestation of the presence of water in the trap is surface-catalyzed hydrolysis of NO2 to yield HNO2 and HNO3.13 The presence of HNO2 was confirmed by its addition to Pu(NO3)4, produced as described previously14 to yield Pu(OH)(NO3)(NO3)2−. Although the presence of HNO3 was not similarly demonstrated by the appearance of Pu(OH)(NO3)2−, this negative result does not exclude HNO3 as a possible reactant gas in the ion trap.

Computational

The geometries were initially optimized and vibrational frequencies were calculated at the density functional theory (DFT) level with
the hybrid B3LYP exchange correlation functional.[39,40] The aug-cc-pVQZ basis set[41,42] was used for O and the aug-cc-pVQZ-PP basis set[43,44] with effective core potentials were used for An—U and Pa, and the Stuttgart large core effective core potential[45] and associated basis sets[46,47] for the remaining An. The DFT calculations provided starting geometries for subsequent CCSD(T) calculations. The DFT calculations were done with the Gaussian 09 program system.[48]

Starting from the DFT optimized geometries, CCSD(T)[51–54] (coupled cluster theory with single and double excitations and a perturbative triples correction) geometry optimizations using the 3rd-order Douglas–Kroll–Hess Hamiltonian[55–57] were carried out using the aug-cc-pwCVTZ-DK for C[42,58,59] and cc-pwCVVDZ-DK3 for An[43,60] basis sets. This is denoted in the text as CCSD(T)/cc-pwCVVDZ-DK3/aug-cc-pwCVTZ-DK. Single-point CCSD(T) calculations were then carried out at these geometries using the analogous TZ basis sets. The calculations did not correlate the electrons up through n = 4 on the anidite (60 electrons in the core) and correlated the remaining anidite electrons and all of the electrons on O. The open-shell calculations were done with the R/UCCSD(T) approach where a restricted open shell Hartree–Fock (ROHF) calculation was initially performed and the spin constraint was then relaxed in the coupled cluster calculation.[51,61–63] Only the geometries were optimized at the CCSD(T) level. The CCSD(T) method with the chosen basis set combination was chosen as a compromise between reliable predictions and computational efficiency. As noted above, the available multi-reference calculations[64] show that the electronic state of the AnO2− is dominated by a single reference so the CCSD(T) method is an acceptable computational approach. Because of the change in electron configurations between the “linear” and highly bent structures, a very large multi-reference calculation would be required including the anidite 5f electrons and the O 2p electrons in an orbital space including the An 5f and 6d and O 2p orbitals.

The CCSD(T) calculations were performed with the MOLPRO 2012 program package.[54,55] The spin-orbit calculations were performed with the ADF code[66,67] at the ZORA-spin orbit level[68–71] with the BLYP functional[72] and the TZ2P basis set. The calculations were performed on our local (UA and WSU) Opteron-based and Xeon-based Linux clusters.

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Conflict of interest

The authors declare no conflict of interest.

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