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A Computational Assessment of Actinide Dioxide Cations AnO_2^{2+} for $\text{An} = \text{U}$ to Lr : The Limited Stability Range of the Hexavalent Actinyl Moiety, $[\text{O}=\text{An}=\text{O}]^{2+}$

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ABSTRACT: The isolated gas-phase actinide dioxide dications, AnO_2^{2+} , were evaluated by DFT and coupled cluster CCSD(T) calculations for 12 actinides, $\text{An} = \text{U} - \text{Lr}$. CASSCF calculations were used to define the orbitals for the CCSD(T) calculations. The characteristic linear $[\text{O}=\text{An}=\text{O}]^{2+}$ hexavalent actinyl(VI) was found to be the lowest energy structure for $\text{An} = \text{U}$, Np, and Pu, which also form stable actinyl(VI) species in solution and possibly for Am when spin-orbit effects are included. For Am, there is a divalent $[\text{An}^{\text{II}}(\text{O}_2)]^{2+}$ structure where the dioxygen is an end-on physisorbed $\eta^1\text{-}^3\text{O}_2$ 2 kcal/mol above the actinyl when spin-orbit effects are included which lower the energy of the actinyl structure. For $\text{An} = \text{Cm}$, Bk, and Lr, the lowest energy structure is trivalent $[\text{An}^{\text{III}}(\text{O}_2^-)]^{2+}$ where the dioxygen is a side-on superoxide, $\eta^2\text{-O}_2^-$. For Cm, the actinyl is close in energy to the ground state when spin-orbit effects are included. For $\text{An} = \text{Cf}$, Es, Fm, Md, and No, the lowest energy structure is divalent $[\text{An}^{\text{II}}(\text{O}_2)]^{2+}$ where the dioxygen is an end-on physisorbed $\eta^1\text{-}^3\text{O}_2$. The relative energies suggest that curyl(VI) and berkelyl(VI), like well-known americyl(VI), might be stabilized by coordinating ligands in condensed phases. The results further indicate that for californyl and beyond, the actinyl(VI) moieties will probably be elusive even using strong donor ligands. The prevalence of low oxidation states (OSs) An(II) and An(III) for transplutonium actinides reflects stabilization of the 5f orbitals and validates established trends, including the remarkably high stability of divalent No. Bond distances and other parameters suggest maximum bond covalency around plutonyl(VI), with a particularly substantial decrease in bond strength between americyl(VI) and curyl(VI).

INTRODUCTION

The actinyl dication, especially for $\text{An} = \text{U}$, has played a critical role in understanding binding in the actinides.^{1,2} Hexavalent actinyl cations (AnO_2^{2+}) for $\text{An} = \text{U} - \text{Am}$ are observed in solution and play an important role in the chemistry of the specific actinide.³⁻⁸ Studies of the actinyl(VI) dications as gas phase actinyl ions⁹ and actinyl cation-cation interactions¹⁰ were previously reported. The question exists as to how far across the actinide period does actinyl behavior hold, especially given the different oxidation states that are present in the actinides. In addition, what is the nature of the binding in the free actinyls without the presence of ligands in the equatorial shell such as would be found in aqueous solution?

To better understand the chemistry of the actinyls(VI), we studied the structures of the AnO_2^{2+} using computational chemistry approaches with a focus on predicting the ground states for AnO_2^{2+} to determine the effective oxidation state of the actinide. Thus, we studied the possible structures (Figure 1) for AnO_2^{2+} s ($\text{An} = \text{U} - \text{Lr}$) from the actinyl $[\text{O}=\text{An}=\text{O}]^{2+}$ with the An in the +VI formal oxidation state, to An binding to O_2 , O_2^- , or O_2^{2-} where the formal oxidation state on the An

varies from +II to +IV. For the AnO_2^{2+} structures, where An binds to diatomic oxygen, the O—O distance provides a key measure of the oxidation state of the An. One can examine the effective oxidation state at the level that we are using only by varying the spin of the AnO_2^{2+} and the geometry. As our focus is on the lowest energy structure for a given spin-geometry combination for a given AnO_2^{2+} , it may not be possible to access all possible oxidation states. An issue is that a lower spin state may lead to excess β spin on the O atoms, which we want to avoid. We also do not consider structures where an O atom dissociates as a triplet.

Figure 1. Possible AnO_2^{2+} minima. An is in blue and O is in red.

COMPUTATIONAL METHODS

The AnO_2^{2+} geometries were optimized and vibrational frequencies were calculated using density functional theory (DFT)¹¹ with the B3LYP exchange-correlation functional.^{12,13} The aug-cc-pVDZ basis sets^{14,15} were used for O and the Stuttgart small core effective core potential (ECP)s and associated basis sets for the actinides.^{16–18} This level has been shown to give reasonable geometries for UO_2^{2+} .¹⁹ Vibrational frequencies were calculated to show that the structures were minima. These calculations were performed using the Gaussian16 program system.²⁰

All-electron single point CCSD(T)^{21–24} calculations with the third-order Douglas–Kroll–Hess Hamiltonian^{25–27} were performed at the B3LYP/DFT optimized geometries with aug-cc-pVnZ-DK for O^{15,28} and cc-pVnZ-DK3 for An^{29–31} for $n = \text{D, T}$ as basis sets, noted as (a)VnZ-DK. We note that, below, when we compare the energies we refer to the highest level reported, CCSD(T)/(a)VTZ-DK. To obtain the starting orbital occupancies for the CCSD(T) calculations, we performed CASSCF^{32,33} calculations at the (a)VDZ-DK level because it was not possible to readily assign the correct starting occupations for the different spin-symmetry states based on the DFT calculations. The active space for the CAS calculations included the seven 5f orbitals on the metal for actinyls(VI) AnO_2^{2+} and the seven 5f orbitals on the metal and the three 2p orbitals on each of the oxygens for the An binding to O_2 , O_2^- , or O_2^{2-} . The number of electrons incorporated in CAS is based on the formal oxidation state of the An and the number of unpaired electrons on the O_2^x for $x = 0$ (two electrons) or -1 (one electron). Inclusion of more active electrons for a number of test cases did not change the occupancies. The single-point CCSD(T) calculations were done by changing the starting orbital^{29,34–36} for the CCSD(T) calculations from the Hartree–Fock orbitals to Kohn–Sham orbitals from DFT generated using the PW91-generalized gradient exchange-correlation functional.^{37–39} Previous calculations⁴⁰ show that PW91 orbitals resulted in much smaller values of the T_1 diagnostic.⁴¹ The reference energy in CCSD arises from diagonalizing the normal HF Hamiltonian with these Kohn–Sham orbitals. No additional correlation effects are included that are not normally in the CCSD calculation, and thus, these Kohn–Sham orbitals can be more optimal than HF for these systems. 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.^{42–45} The CCSD(T) calculations were performed with the MOLPRO 2018 program package.^{46,47} The natural population analysis (NPA) results based on the natural bond

orbitals (NBOs)^{48,49} using NBO6^{50,51} are calculated at the DFT/B3LYP level using Gaussian16. The calculations were done on our local UA Opteron- and Xeon-based Linux clusters.

RESULTS AND DISCUSSION

We discuss the energetics at the (a)VTZ-DK level. These energies are reported in Figure 2 and Figure S2. Figure 2 is a simplified version of Figure S2. Relative energies are given with respect to the lowest energy structure for a given An unless noted. The DFT/B3LYP energies are reported in the Supporting Information. As previously observed,²⁹ for these complicated electronic structure molecules with various numbers of occupied 5f orbitals, B3LYP is a good choice in terms of geometries. Although DFT/B3LYP does not provide quantitative energetics, the qualitative trends are the same as the higher level CCSD(T) calculations, especially for the lowest energy structures. The NBO population analysis is given in Table 1. We will refer to this table for our description of the 5f orbital occupancies, both the total and unpaired 5f electrons for An.

Relative Energies of AnO_2^{2+} Structures. UO_2^{2+} . For UO_2^{2+} , we were able to optimize most of the different types of structures shown in Figure 1, with U in formal oxidation states ranging from +II to +VI, except +V. Although we set up a spin-spatial structure that would correspond to U(V), it did not optimize to such a structure. As expected, the lowest energy structure for UO_2^{2+} is uranyl with U in +VI OS. The lowest higher energy structure is the triplet excited state of the uranyl(VI), which is 64.0 kcal/mol higher in energy. An O_2^{2-} structure could be optimized only for An = U in C_{2v} symmetry, and this $[\text{U}^{\text{IV}}(\text{O}_2^{2-})]^{2+}$ structure is 101.9 kcal/mol higher in energy than the ground state uranyl(VI). Two different $^2\text{O}_2^-$ structures were optimized for U(+III), one in C_{2v} symmetry, 126.3 kcal/mol higher in energy, where the spin is split between both oxygen atoms, and one linear, in $\text{C}_{\infty v}$ symmetry, which is 146.8 kcal/mol higher in energy with the unpaired electron localized on the O which does not form a direct bond with U. Two very high in energy structures were predicted for a diatomic neutral oxygen molecule binding to the U atom, $[\text{U}^{\text{II}}(\text{O}_2)]^{2+}$, a C_s symmetry structure 182.9 kcal/mol higher in energy and a linear, $\text{C}_{\infty v}$ symmetry structure 204.4 kcal/mol higher in energy.

NpO_2^{2+} . For NpO_2^{2+} and the next few AnO_2^{2+} s in the period up to An = Bk, the number of optimized (minima) symmetry structures is comparable to UO_2^{2+} with small differences. Thus, for Np we were able to optimize a Np(V) structure, although no structure could be optimized with Np(IV). Similar to UO_2^{2+} , the lowest energy structure for NpO_2^{2+} is the neptunyl with Np in the +VI formal oxidation state. The optimized quartet excited state of the neptunyl(VI) is 100.5 kcal/mol higher in energy. The quartet Np(V) C_s structure with one spin on the O is 82.6 kcal/mol higher in energy relative to the ground state neptunyl(VI). Similar to U, two different $^2\text{O}_2^-$ structures were optimized for $[\text{Np}(\text{O}_2^-)]^{2+}$ with Np in the +III OS. One has C_{2v} symmetry and is 86.2 kcal/mol higher in energy, where the spin is split between both oxygen atoms. There is also a linear $\text{C}_{\infty v}$ symmetry structure which is 104.5 kcal/mol higher in energy with the unpaired electron localized on the O which does not bond directly to the Np. A C_s structure with a triplet diatomic oxygen binding to Np(II), $[\text{Np}^{\text{II}}(\text{O}_2)]^{2+}$, is calculated to be 122.4 kcal/mol higher in energy relative to the neptunyl(VI) ground state.

Figure 2. ΔH_{0K} AnO_2^{2+} relative energies in kcal/mol at the CCSD(T)/(a)VTZ-DK level: (a) for An = U–Bk and (b) for An = Bk–Lr.

PuO_2^{2+} . The lowest energy PuO_2^{2+} structure is the plutonyl with the Pu in +VI OS. The quintet excited state plutonyl(VI) is 34.5 kcal/mol higher in energy. An asymmetric quintet Pu(V) C_s symmetry structure with one spin on the O is calculated to be 77.2 kcal/mol higher in energy relative to the

ground state plutonyl(VI). For $[\text{Pu}(\text{O}_2)]^{2+}$ with Pu in the +III OS, only the C_{2v} symmetry structure could be optimized, and it is 49.9 kcal/mol higher in energy. As observed for Np, for $[\text{Pu}^{\text{II}}(\text{O}_2)]^{2+}$, only a bent C_s symmetry structure could be optimized and it is 58.2 kcal/mol higher in energy. For

Table 1. An NBOs and Spins (Natural Spin Densities) at the B3LYP/aug-cc-pvdz(O)/Stuttgart(An) Level

compd	molecular spin ^a	type	OS ^b	sym	An spin	Sf total	Sf α	Sf($\alpha-\beta$) ^c	6d	6d α	6d($\alpha-\beta$) ^c
UO ₂ ²⁺	1	[O=U=O] ²⁺	VI	D _{∞h}	0	2.50	0	0	0.97	0	0
	3	[U(O ₂ ²⁻)] ²⁺	IV	C _{2v}	2.279	2.72	2.46	2.20	0.54	0.30	0.07
	5	[U(O ₂ ⁻)] ²⁺	III	C _{2v}	3.031	3.15	3.07	2.99	0.29	0.17	0.05
	5	[U(O ₂ ⁻)] ²⁺	III	C _{∞v}	3.111	3.16	3.08	3.00	0.34	0.22	0.10
	7	[U(O ₂)] ²⁺	II	C _s	4.018	3.97	3.96	3.96	0.03	0.02	0.01
	7	[U(O ₂)] ^{2+d}	II	C _{∞v}	4.022	3.74	3.73	3.73	0.09	0.08	0.07
NpO ₂ ²⁺	2	[O=Np=O] ²⁺	VI	D _{∞h}	1.136	3.69	2.39	1.09	0.95	0.49	0.03
	4	[(ONp)-O] ²⁺	V	C _s	2.280	3.56	2.91	2.26	0.91	0.47	0.03
	4	[Np(O ₂ ⁻)] ²⁺	III	C _{2v}	4.032	4.17	4.08	3.98	0.29	0.17	0.05
	6	[Np(O ₂ ⁻)] ²⁺	III	C _{∞v}	4.200	4.26	4.18	4.10	0.30	0.20	0.10
	8	[Np(O ₂)] ²⁺	II	C _s	5.017	5.00	4.99	4.99	0.03	0.02	0.01
PuO ₂ ²⁺	3	[O=Pu=O] ²⁺	VI	D _{∞h}	2.300	4.86	3.55	2.24	0.93	0.49	0.06
	5	[(OPu)-O] ²⁺	V	C _s	3.711	4.75	4.22	3.77	0.80	0.42	0.04
	7	[Pu(O ₂ ⁻)] ²⁺	III	C _{2v}	5.171	5.31	5.23	5.14	0.23	0.13	0.03
	9	[Pu(O ₂)] ²⁺	II	C _s	6.018	6.01	6.00	6.00	0.03	0.02	0.01
AmO ₂ ²⁺	4	[O=Am=O] ²⁺	VI	D _{∞h}	3.560	6.00	4.74	3.48	0.87	0.48	0.08
	6	[Am(O ₂ ⁻)] ²⁺	III	C _{2v}	3.854	6.19	5.00	3.81	0.29	0.17	0.05
	10	[Am(O ₂)] ²⁺	II	C _s	7.014	7.00	7.00	7.00	0.03	0.02	0.01
	8	[Am(O ₂)] ²⁺	III/II	C _{2v}	6.454	6.54	6.49	6.45	0.14	0.08	0.01
CmO ₂ ²⁺	5	[O=Cm=O] ²⁺	VI	D _{∞h}	5.052	7.16	6.04	4.93	0.79	0.46	0.13
	9	[Cm(O ₂ ⁻)] ²⁺	III	C _{2v}	6.874	7.17	6.99	6.81	0.30	0.18	0.07
	11	[Cm(O ₂)] ²⁺	II	C _s	8.022	7.00	7.00	6.99	0.21	0.20	0.19
	9	[Cm(O ₂)] ²⁺	III/II	C _{∞v}	6.599	7.45	6.99	6.53	0.22	0.14	0.07
BkO ₂ ²⁺	6	[O=Bk=O] ²⁺	VI	D _{∞h}	5.494	7.93	6.67	5.41	0.80	0.44	0.08
	8	[(OBk)-O] ²⁺	V	C _{∞v}	5.806	7.87	6.86	5.85	0.67	0.32	-0.04
	8	[Bk(O ₂ ⁻)] ²⁺	III	C _{2v}	5.729	8.29	6.99	5.69	0.24	0.14	0.04
	8	[Bk(O ₂)] ²⁺	II	C _{∞v}	5.070	8.94	6.99	5.04	0.04	0.03	0.02
CfO ₂ ²⁺	7	[O=Cf=O] ²⁺	V	D _{∞h}	4.825	8.76	6.83	4.90	0.83	0.37	-0.09
	7	[Cf(O ₂)] ²⁺	II	C _{∞v}	4.033	9.98	7.00	4.02	0.03	0.02	0.01
EsO ₂ ²⁺	6	[O=Es=O] ²⁺	IV/III	D _{∞h}	3.589	9.96	6.83	3.70	0.73	0.31	-0.11
	6	[Es(O ₂)] ²⁺	II	C _{∞v}	3.017	10.99	7.00	3.01	0.03	0.02	0.01
	8	⁸ [Es(O ₂)] ^{2+e}	II	C _s	5.012	10.00	7.00	3.99	0.14	0.13	0.12
FmO ₂ ²⁺	5	[O=Fm=O] ²⁺	III/II	D _{∞h}	2.450	11.09	6.83	2.57	0.68	0.28	-0.13
	5	[Fm(O ₂)] ²⁺	II	C _{∞v}	2.015	12.00	7.00	2.00	0.03	0.02	0.01
MdO ₂ ²⁺	4	[Md(O ₂)] ²⁺	II	C _{∞v}	1.016	12.99	7.00	1.00	0.03	0.02	0.01
NoO ₂ ²⁺	3	[O=No=O] ²⁺	II	D _{∞h}	-0.397	13.59	6.61	-0.36	0.17	0.07	-0.03
	3	[No(O ₂)] ²⁺	II	C _{∞v}	0.014	14.00	7.00	0.00	0.03	0.02	0.01
LrO ₂ ²⁺	2	[O=Lr=O] ²⁺	III	D _{∞h}	-0.098	14.00	7.00	0.00	0.56	0.23	-0.10
	2	[Lr(O ₂ ⁻)] ^{2+f}	III	C _{2v}	-0.027	14.00	7.00	0.00	0.34	0.16	-0.02
	4	[Lr(O ₂)] ^{2+g}	II	C _{∞v}	1.003	14.00	7.00	0.00	0.08	0.07	0.06

^a1 = singlet, 2 = doublet, 3 = triplet, 4 = quartet, etc. ^bAssigned oxidation state (OS) determined on the basis of the optimized geometries and spins. ^c($\alpha-\beta$) accounts for the unpaired spin, the difference between α spin and β spin. ^d7s = 0.22e α . ^e7s = 0.93e α . ^f7s = 0.08e paired. ^g7s = 0.99e α .

[Pu^{II}(O₂)]²⁺, a linear C_{∞v} symmetry structure was optimized and corresponds to an excited singlet diatomic oxygen.

AmO₂²⁺. The lowest energy AnO₂²⁺ structures for An = U–Pu are the actinyl with An in a high +VI formal oxidation state. Beginning with An = Am, the actinyl(VI) structures with the An in a +VI formal oxidation states are no longer the lowest energy structures. Thus, the lowest energy structure for AmO₂²⁺ is the bent dioxygen Am(II) C_s structure. Am(+II) has a 5f⁷ half occupied valence shell, which is an energetically stable electronic configuration. The quartet americyl(VI) structure is 15.5 kcal/mol higher in energy. For Am, according to the CCSD(T) energetics, the Am(II) with a 5f⁷ half occupied valence shell is more stable than the americyl(VI) with a 5f³ occupied valence shell. However, as noted below, spin–orbit effects may change the ordering. Similar to An = Pu, singlet excited state dioxygen structures are predicted for

Am; both a C_{2v} structure 17.4 kcal/mol higher in energy and a linear C_{∞v} structure 30.1 kcal/mol higher were optimized. The ⁶[Am^{III}(O₂⁻)]²⁺ in C_{2v} symmetry is 83.7 kcal/mol higher in energy. This Am(III) structure has four unpaired 5f electrons and one unpaired electron split between the two oxygen atoms. This Am(III) structure is almost at the same energy level as the corresponding Np(III) with both having overall 5 unpaired electrons. The sextet excited americyl(VI) state is 84.0 kcal/mol higher in energy than the ground dioxygen Am(+II) state and 68.5 kcal/mol higher in energy than the lowest energy americyl(VI). A structure with each oxygen having 0.27e with α spin and 6.45e α spin on the Am is 19.7 kcal/mol higher in energy relative to the ground state bent dioxygen Am(+II) C_s structure. The O–O distance is 1.282 Å, falling between an O₂ and O₂⁻ distance; thus, we assign the Am oxidation state to be between +II and +III. We describe this O₂ moiety as a

${}^2\text{O}_2^-/{}^1\text{O}_2$. This structure is probably the closest one can get to an actual Am(III), as we were unable to locate the expected low-energy octet ${}^8[\text{Am}^{\text{III}}(\text{O}_2^-)]^{2+}$ structure with a pure ${}^2\text{O}_2^-$ ligand. We use this octet, III/II OS structure in the discussion below when we describe the +3 oxidation states.

CmO_2^{2+} . The lowest energy structure for CmO_2^{2+} is the $[\text{Cm}^{\text{III}}(\text{O}_2^-)]^{2+}$ in C_{2v} symmetry. The Cm(III) has a $5f^7$ half full occupied valence shell, which enables the $[\text{Cm}^{\text{III}}(\text{O}_2^-)]^{2+}$ to be the lowest energy structure. Again, this Cm(III) with a $5f^7$ half full occupied valence shell is more stable than the actinyl Cm(VI) structure with a $5f^1$ occupancy on the Cm. As noted below, the spin–orbit corrections lower the energy of the actinyl Cm(VI) structure. The linear CmO_2^{2+} for Cm(VI) is 26.5 kcal/mol higher in energy. The bent dioxygen Cm(II) C_s symmetry structure is 38.0 kcal/mol higher in energy. As for Am, a ${}^2\text{O}_2^-/{}^3\text{O}_2$ structure could be optimized for Cm, although a linear $\text{C}_{\infty v}$ symmetry structure, and it is 27.5 kcal/mol higher in energy relative to $\text{Cm}(\text{III})\text{O}_2^-$ and 10.5 below $\text{Cm}(\text{II}){}^3\text{O}_2$. The O–O distance is 1.257 Å, falling between a ${}^3\text{O}_2$ and O_2^- distance. There is 6.60e α spin on Cm and a total of 1.40e α spin on the oxygen atoms, corresponding to an oxidation state between +II and +III for Cm. The septet excited state corresponding to the Cm(VI) state is 70.3 kcal/mol higher in energy relative to the lowest energy $[\text{Cm}^{\text{III}}(\text{O}_2^-)]^{2+}$ structure and 43.8 kcal/mol higher in energy than the lowest energy ${}^5[\text{Cm}^{\text{VI}}\text{O}_2]^{2+}$.

BkO_2^{2+} . As predicted for CmO_2^{2+} , the lowest energy structure for BkO_2^{2+} is the C_{2v} symmetry structure, $\text{Bk}(\text{III})\text{O}_2^-$. For this octet $[\text{Bk}^{\text{III}}(\text{O}_2^-)]^{2+}$ structure, Bk has a +III formal oxidation state, with a $5f^8$ occupancy. This electron configuration seems to impart some additional stability to the ground state. The dioxygen Bk(II) $\text{C}_{\infty v}$ symmetry structure is just 13.2 kcal/mol higher in energy. For Bk, a sextet linear $\text{D}_{\infty h}$ symmetry structure optimized to a structure with an oxidation of +VI, 17.3 kcal/mol higher in energy. The singlet dioxygen excited state Bk(II) $\text{C}_{\infty v}$ symmetry structure is calculated to be 38.1 kcal/mol higher in energy. The octet excited state with $\text{D}_{\infty h}$ symmetry for Bk is 60.4 kcal/mol higher in energy relative to the lowest energy $\text{Bk}(\text{III})\text{O}_2^-$ structure and 43.1 kcal/mol higher in energy than the ${}^6\text{Bk}(\text{VI})\text{O}_2^{2+}$. A linear asymmetric ${}^8[(\text{OBk})^3+(\text{O}^-)]^{2+}$ $\text{C}_{\infty v}$ symmetry structure with +V OS on Bk could be optimized and is calculated to be 107.8 kcal/mol higher in energy.

Beginning with An = Pu for a +VI OS on the actinide, spin polarization in the form of backbonding is predicted by the NPA (natural population analysis see below) at the DFT level and results in 0.24e excess α spin on Pu (Table 1) accompanied by 0.15e excess β spin on each of the plutonyl oxygen atoms (Supporting Information). This type of backbonding was previously predicted for An(V).^{29,40,62} The extra spin present on the actinide doubles from Pu to Am and is almost 1e for Cm; the β spin on the oxygens follow the same trend to balance the excess α spin on the An. For An = Bk, 0.41e excess α spin is on Bk and 0.25e excess β spin is on each oxygen. Thus, after An = Bk, we were unable to optimize a structure with a +VI OS on the An.

CfO_2^{2+} to LrO_2^{2+} . The lowest energy structures for AnO_2^{2+} for An = Cf–No are the linear dioxygen An(II). Linear $\text{D}_{\infty h}$ “actinyl-type” structures were optimized for most (except for Md) of these actinides and are very high in energy relative to the ground states. For the linear symmetric $\text{D}_{\infty h}$ structures, beginning with An = Cf, no backbonding is observed (Table 1). Thus, there is no β spin on the oxygens, but excess α spin is

present on the oxygens (SI), so the OS on the actinide will be lower as excess spin on the oxygen corresponds to less than a formal charge of –2. As an example, the $\text{D}_{\infty h}$ symmetry structure for An = Cf is a +V OS and is 65.1 kcal/mol higher in energy than the corresponding lowest dioxygen Cf(II) structure. The $\text{D}_{\infty h}$ symmetry structure for An = Cf optimized to a septet. From the DFT/NPA analysis, there are 4.90e unpaired α spins on Cf and 0.59e α spins on each oxygen, so we can assign this $\text{D}_{\infty h}$ symmetry structure as a Cf in the +V OS. For An = Cf, a singlet dioxygen excited state Cf(II) $\text{C}_{\infty v}$ symmetry structure was optimized and is calculated to be 28.6 kcal/mol higher in energy than the ground state.

The optimized $\text{D}_{\infty h}$ symmetry structures for these remaining actinides are over 100 kcal/mol higher in energy relative to the ground states. For An = Es, there is a bent $\text{Es}(\text{II}){}^3\text{O}_2$ structure that is 71.8 kcal/mol higher in energy. For An = Es, the optimized $\text{D}_{\infty h}$ symmetry structure is a sextet instead of an octet as expected if it were to be a high spin actinyl structure. This structure is assigned an OS of +IV/III. For An = Fm, a quintet $\text{D}_{\infty h}$ symmetry structure was optimized and the Fm is assigned to a +III/II OS. The $\text{D}_{\infty h}$ structure for An = No, optimized to a triplet, and is assigned a +II OS; the spin is localized on the oxygens, and there is 0.36e β spin on the No. The $\text{D}_{\infty h}$ symmetry structure for An = Lr is optimized to a doublet and is assigned to a +III OS with 0.55e α spin on each oxygen. The lowest energy structure for LrO_2^{2+} is the $\text{Lr}(\text{III})\text{O}_2^-$ with the dioxygen Lr(II) structure only 13.5 kcal/mol higher in energy.

Effects of Spin–Orbit Corrections. The spin–orbit corrections to various state splittings were calculated using the average-of-configuration (AOC) Dirac–Hartree–Fock (DHF) method as the difference between a calculation with the full 4-component (4c) Dirac–Coulomb Hamiltonian and one with Dyall’s spin-free Hamiltonian,⁵² both using a finite-nucleus model with the Dirac program.⁵³ These calculations used completely uncontracted VDZ-DK/aVDZ basis sets. These AOC calculations were resolved by complete open-shell configuration interaction calculations to yield the ground-state DHF/HF energies. The Gaunt (spin-other-orbit) correction was also calculated at the 4c AOC-DHF level of theory. Note that these spin–orbit calculations do not include coupling between the spin–orbit and dynamical correlation.

As shown in Table 2, the spin–orbit corrections to the state splittings for the two lowest states are negative for U, Am, Cm,

Table 2. Spin–Orbit Corrections to Splittings for the Two Lowest States in kcal/mol using DIRAC for Selected AnO_2^{2+}

molecule	ΔSO	ΔGaunt	$\Delta\text{SO}_{\text{total}}$
UO_2^{2+}	–11.54	–0.86	–12.4
NpO_2^{2+}	1.02	–0.06	1.0
PuO_2^{2+}	6.25	–1.16	5.1
AmO_2^{2+}	–24.88	6.95	–17.9
CmO_2^{2+}	–27.77	4.56	–23.2
BkO_2^{2+}	–0.81	–2.72	–3.5
CfO_2^{2+}	12.01	4.13	16.1
LrO_2^{2+}	0.57	0.11	0.7

and Bk and positive for Np, Pu, Cf, and Lr. The Gaunt correction can also be positive (Cm, Cf, and Lr) or negative (U, Pu, and Bk). For a number of these species, the Gaunt correction is not small, as much as 7 kcal/mol for Am, and can be larger in magnitude than the spin–orbit correction as found

for Bk. It is difficult to calculate the spin-orbit corrections for the state differences for these molecules as the electronic states can be quite different in terms of the numbers of 5f electrons and the presence or lack of spin on the oxygens. As an example of the difficulties in calculating the spin-orbit corrections, we also tried to calculate the values using the SO-DFT approaches in ADF^{54,55} and NWChem,^{56,57} and we did not find results consistent with the DIRAC results from relativistic molecular orbital theory.

The spin-orbit correction lowers the ${}^3\text{UO}_2^{2+}$ state by 12 kcal/mol relative to the ${}^1\text{UO}_2^{2+}$ ground state, but the triplet state is still much higher in energy. For Np, the spin-orbit correction is negligible, at 1 kcal/mol. For Pu, the energy of the ${}^5\text{PuO}_2^{2+}$ excited state is raised by 5 kcal/mol relative to the ${}^3\text{PuO}_2^{2+}$ ground state. For Am, inclusion of just the spin-orbit correction reverses the ordering of the two lowest states and makes the ${}^4\text{AmO}_2^{2+}$ state the ground state with the ${}^{10}[\text{Am}^{\text{II}}(\text{O}_2)]^{2+}$ state higher in energy by only 2.4 kcal/mol. Inclusion of the Gaunt correction is critical for the small energy difference. Given the combined errors in the CCSD(T) calculations coupled with the size of the spin-orbit corrections, the two states should be considered to be degenerate in energy with both likely being present. Note that these two states for Am are very different in terms of their electronic structure, so it is difficult to get a balanced spin-orbit correction without going to extremely high computational levels. For Cm, the total spin-orbit correction lowers the ${}^6\text{CmO}_2^{2+}$ state significantly, but it is still higher in energy than the ${}^9[\text{Cm}^{\text{III}}(\text{O}_2)]^{2+}$ ground state. Note that the positive contribution of the Gaunt correction is again important for the ordering of the states. Both states could be present for Cm as well. The spin-orbit correction for Bk is only -4 kcal/mol which does not change the ordering of the states. The spin-orbit correction for Cf is positive and raises the energy of the ${}^7\text{CfO}_2^{2+}$ even more. Because of the very large energy differences, we did not calculate spin-orbit corrections for the remaining actinides except for Lr, where the spin-orbit correction is negligible.

The excited states of the linear actinyl UO_2^{2+} have been reported at even higher levels.^{58,59} Without spin-orbit effects, Réal et al.,⁵⁸ reported values of 60–70 kcal/mol for the lowest energy vertical excitation to the triplet, consistent with our value of 64 kcal/mol. The spin-orbit correction reduces these excitation energies to 53–55 kcal/mol. The reduction of 10–15 kcal/mol is consistent with our decrease of 12 kcal/mol due to spin-orbit corrections in UO_2^{2+} . We note that use of a much larger set of active orbitals leads to a lower energy for the first excited state.⁵⁹

Additional Energetic Trends. As discussed above, it was not possible to optimize all +II to +VI oxidation states for a given actinide to a specific minimum without constraints. Initially, we tried to optimize all the possible structures for all the +II to +VI oxidation states, but many of these reverted to other structures. This relaxation is, in part, due to the fact that these are high energy structures. In order to provide additional chemical insights into periodic trends for the types of structures found for UO_2^{2+} , for example, we estimated the energetics of structures with different oxidation states where we were not able to optimize a structure to the minimum with the geometry needed to generate a qualitative picture. In order to provide insights into the qualitative trends, we used the optimized geometry of AnO_2^{2+} for a given structure with a

specific OS and then replaced the actinide and adjusted the spin state accordingly. For example, for +V OS we used the Np +V optimized structure to predict the energetics for U(V), which is $\Delta E = 88.4$ kcal/mol higher in energy relative to the uranyl (VI) structure. Using the optimized Pu(V) geometry, we predicted the energetics for an Am(V) which has a $\Delta E = 91.9$ kcal/mol higher in energy than the ground state Am(II) structure with significant spin contamination (SI). For An = Cm we were unable to obtain a +V structure either starting with Pu(V) or Bk(V) geometries.

Similarly, we obtained estimates for the energetics on An(IV) structures using the U(IV) geometry as a starting point (SI). For An = Np and Pu, the +IV structures are $\Delta E = 78.1$ and 52.3 kcal/mol, respectively, higher in energy than the corresponding actinyl ground states. For An = Am and Cm, the +IV structures have $\Delta E = 33.1$ and 36.4 kcal/mol, respectively, higher in energy than their ground states; however, there is significant spin contamination, and for Cm, the oxygens have a total of 0.5e.

Geometries of AnO_2^{2+} Structures. The optimized geometry parameters are reported in the [Supporting Information](#). The calculated O–O distances at the B3LYP/aD level are 1.209, 1.344, and 1.548 Å for ${}^3\text{O}_2$, ${}^2\text{O}_2^-$, and ${}^1\text{O}_2^{2-}$ respectively, as this aids in determining the oxidation state of the dioxygen moiety. These calculated distances are in good agreement with experiment.^{60,61} The An–O bond distances in the actinyl(VI) structures, for An = U–Bk, decrease from U to Pu and then increase from Pu to Bk. These An–O bond distances increase for the remaining $\text{D}_{\infty h}$ structures with a spike at Am = No (see the SI). Similar trends were previously observed for the calculated An–O bond distances in the actinyl(V) structures for monocationic AnO_2^+ .⁶²

A C_s symmetry structure for An(V) = Np and Pu was optimized with a short An=O bond of ~ 1.72 Å and a long An– ${}^2\text{O}^-$ bond of ~ 1.97 Å. The $\angle\text{OAnO}$ bond angles are 87° and 83° for Np and Pu, respectively. In analogy with complexes of actinyl(VI) with strong An=O_{axial} bonds and weaker bonds to equatorial ligands, these An(V) species can be considered to be a structure with one short “axial” An=O bond and one long “equatorial” An–O bond. For An(V) = Bk, a linear $C_{\infty v}$ symmetry structure was optimized with a short An=O bond of 1.78 Å and a long An– ${}^2\text{O}^-$ bond of 1.92 Å.

For the dicationic An(III) O_2^- structures in C_{2v} symmetry, the An–O and the O–O bond distances do not change much with the actinide, and they are about 2.20–2.22 Å and 1.30–1.32 Å, respectively, where the latter is slightly shorter than the 1.344 Å distance we obtain for bare ${}^2\text{O}_2^-$. The $\angle\text{OAnO}$ angles for the An(III) O_2^- structures are about 35° . The shortest An–O bond distance is calculated for An = Lr of 2.12 Å where the O–O distance is the longest at 1.35 Å and the $\angle\text{OLrO}$ is the largest of 37° .

For the dicationic An(II) ${}^3\text{O}_2$ structures, the early actinides (An = U to Cm) optimize to slightly bent structures with $\angle\text{AnOO}$ angles ranging from 156° for An = Pu to 173° for An = Np. For the late actinides (An = Bk–Lr) the structures are linear. The An–O bond distances decrease from U to Bk with the largest shortening observed from Am to Cm, and then they plateau. The O–O distance for these molecules does not change significantly across the actinide period and is about 1.21 Å, consistent with that for the neutral diatomic O_2 .

Population Analysis. The natural population analysis (NPA) results based on the natural bond orbitals (NBOs) are given in Table 1 for the An atoms and in the [Supporting](#)

Figure 3. The +VI to +II oxidation states trends for U–O distances (Å), NBO 5f (α – β), 6d populations, and NPA (q) charges for UO₂²⁺ molecules.

Figure 4. Trends observed for NBO 5f (α – β), 6d populations, and NPA (q) charges for actinyls, AnO₂²⁺, and An(VI) molecules with An = U–Bk.

Figure 5. AnO₂²⁺ NBO 5f (α – β) population for different OS on the An = +VI, +III, and +II. For Am(III), the octet Am(III/II) structure was used.

Information for the oxygen atoms. For An = U, different types of structures were optimized with a range of formal oxidation states on the U. For U, as the oxidation state decreases, the U–O bond distance increases, the 5f(α – β) (overall unpaired spin) population increases, and the 6d population decreases. For uranyl with U(VI), almost 1e is present in the 6d, resulting from backbonding from the oxygen atoms. For U(II), less than 0.1 e is present in the 6d. The oxygen atoms have a –0.5 e to –0.7 e total charge for all of the U oxidation states, except for U(II) where the total O total charge is approximately zero, which is consistent with the geometry. The charge on the U atoms slightly increases from +2.55 e for U(VI) to +2.70 e for U(IV), then slightly decreases for U(III) (~ +2.5 e) to about +2 e for U(II) (Figure 3).

For the actinyls with An(VI), the 5f(α – β) population (which represents the unpaired 5f electrons), there is almost a

linear increase in population with a deviation from linearity for An = Bk which has an OS of V–VI. (Figure 4). The backbonding 6d orbital population decreases from U to Cm, and then there is not much change for the remaining actinyls. The An charges become smaller from U to Cm and then increase from Cm to Cf with a slight decrease to Es. The charges on the oxygen atoms follow the reverse trend observed for the actinides, with the largest negative charge for the oxygen bonding to U (–0.27 e) and the smallest for the oxygen bonding Cm (–0.03 e). The amount of β spin density on each oxygen increases from 0.07 e for U to 0.28 for Am before almost doubling for Cm (0.53 e). The β spin density then drops to 0.25 e for Bk with positive spin of 0.59 and 0.71 on the oxygens bonding Cf and Es.

The trends observed for the dicationic An(III)O₂[–] and An(II)O₂ are reported in the Supporting Information. For the

Figure 6. AnO_2^{2+} NBO 6d population for $\text{An} = +\text{VI}$, $+\text{III}$, and $+\text{II}$. For $\text{Am}(\text{III})$, the octet $\text{Am}(\text{III}/\text{II})$ structure was used.

Figure 7. Selected parameters for the lowest energy structures of UO_2^{2+} with different U OS. Charges $q(\text{U})$ are NPA; orbital populations 6d and 5f Excess are NBO; distance in Å is the average U–O if the two are different. The parameter 5f Excess is the 5f orbital occupancy above that of the bare An^{N+} ion for oxidation state $\text{An}(\text{N})$ (the bare ion population is $5f^0$ for U^{6+} , $5f^1$ for Np^{6+} , etc.).

dicationic $\text{An}(\text{III})\text{O}_2^-$ molecules, the $5f(\alpha-\beta)$ population increases from U to Cm with a dip for Am where the lowest energy structure was optimized to be the $[\text{Am}^{\text{II}}\text{O}_2]^{2+}$. Then, the $5f(\alpha-\beta)$ population decreases to Bk. The 6d orbital contributions are 1/3 to 1/4 of what was predicted for the actinyls(VI). The 6d contribution does not change much with the actinide, with the highest 6d population for Lr (0.34 e) and the lowest for Pu (0.23 e). The charge on the actinide and on the oxygens does not significantly vary with the actinide. There is about -0.5 e on each oxygen in O_2^{2-} , with -0.42 e for each oxygen bonding Pu and -0.64 e for each oxygen bonding Bk.

For the dicationic $\text{An}(\text{II})\text{O}_2$ molecules, the $5f(\alpha-\beta)$ population increases from U to Cm with a plateau at 7 electrons for the half-filled 5f for Am and Cm. This half-filled $5f^7$ shell is consistent with the lowest energy $\text{Am}(\text{II})\text{O}_2$ structure. After $\text{An} = \text{Cm}$, the $5f(\alpha-\beta)$ population decreases reaching zero for $\text{An} = \text{No}$ and Lr. For the $\text{An}(\text{II})\text{O}_2$ molecules, there are about 0.03 e in the 6d orbitals, and the exceptions are Lr with 0.08 e in 6d and Cm with 0.21 e in 6d. For $\text{Lr}(\text{II})\text{O}_2$, there is one electron in the 7s orbital. The NPA charges of about 1.96–1.97 e on the actinides are pretty much constant through the actinide period. Smaller charges are calculated for Cm of 1.91 e and Lr of 1.93 e and highest of 2.00 e for Bk. These small charges on the Cm and Lr are balanced by ca. -0.08 e overall charge on the oxygen atoms. A higher charge on Bk is balanced by a larger overall negative charge on the oxygen atoms. For these three An's the lowest energy AnO_2^{2+} structures are the $\text{An}(\text{III})\text{O}_2^-$.

Figures 5 and 6 show $5f(\alpha-\beta)$ and 6d population trends for $\text{An} = +\text{VI}$, $+\text{III}$, and $+\text{II}$. For actinyls $\text{An}(\text{VI})$, the $5f(\alpha-\beta)$ increases to $\text{An} = \text{Bk}$ where it peaks and this increase is

accompanied by a decrease in the 6d population. For the $\text{An}(\text{III})$, the unpaired 5f ($\alpha-\beta$) and the 6d backbonding increase to a half-filled 5f to $\text{An} = \text{Cm}$, with a dip at Am. The 5f ($\alpha-\beta$) unpaired population for $\text{An}(\text{II})$ peaks at $\text{An} = \text{Am}$ and Cm with a half-filled 5f and mostly insignificant 6d backbonding. For the $\text{An}(\text{III})$, and $\text{An}(\text{II})$, less charge variations are observed.

QTAIM⁶³ charges were also calculated using AIMALL⁶⁴ and are reported in the Supporting Information. The QTAIM charges show very similar trends to the NPA charges with the actinyl(VI) charges being more positive for An and more negative for the oxygen atoms. The bond critical points (BCPs) between an An and an O were calculated using AIMALL and are reported in the Supporting Information. The variations in the BCP distances are only 2%. The BCPs are closer to the O ($\sim 45\%$) than to the actinide ($\sim 55\%$) independent of the type of bond between the An and O or formal oxidation state of the actinide. This has previously been predicted for the AnO_2^+ .⁶⁵

The spin density in the An shows similar trends to the 5f ($\alpha-\beta$) populations for each formal oxidation state of the actinide (Supporting Information). From the spin density on the oxygen bonded to the actinide, there are about two total unpaired spins on the oxygen atoms for $\text{An}(\text{II})\text{O}_2$ molecules consistent with $^3\text{O}_2$, and about one total unpaired spin on the oxygen atoms for $\text{An}(\text{III})\text{O}_2^-$ molecules. Again, for the actinyls(VI), the spin on the oxygen atoms varies as discussed above.

Analysis of Different Oxidation States (OS) of Uranium. The $\text{U}(\text{II})$ species $\text{U}^{\text{II}}(\text{O}_2)$ are the most ionic, i.e., electrostatic, as the charge transfer from O to U is minimal.

Figure 8. Selected charge parameters for An(VI)O_2^{2+} . Charges are NPA, orbital populations 6d and 5f Excess are NBO (all in e). An(VI)–O distances are in Å.

The result is $q(\text{U}) = 1.96$ e, and both 6d and 5f Excess are close to zero (0.03 e and -0.03 e, respectively), where we define the quantity 5f Excess as the amount of 5f population present relative to the 5f population of the free actinide ion An^{N+} in the idealized An(N) oxidation state. As the formal uranium OS increases, $q(\text{U})$ also increases, to 2.70 e for U(IV). The charge does not increase as dramatically as the OS due to increasing 6d and 5f Excess; these parameters, in essence, indicate the extent of covalency as charge transfer from O to U, which increases along with the OS. Increasing OS from U(IV) to U(VI) results in a decrease in $q(\text{U})$ that reflects large increases in 5f Excess, i.e., the extent of covalency, as indicated by donation from O to both 5f and 6d that increases with OS. The difference between the OS and $q(\text{U})$ monotonically increases from 0.04 for U(II) where $q \approx \text{OS}$ ($N = +2$), to 3.45 for U(VI) where $q \ll \text{OS}$ ($N = +6$). The results illustrate that only for low OS with minimal bonding interaction is there essentially no covalency such that the OS and charge states are nearly coincident. For higher OS, particularly U(VI), the bare ions become increasingly untenable in the presence of ligands (here O) such that there is significant charge transfer to the metal center with a reduction in the actual charge relative to the formal OS. For low OS, the 6d and 5f covalency contributions, indicated by 6d and 5f Excess, are roughly comparable; for high OS, U(V) and U(VI), the 5f contribution (i.e., 5f Excess) is much greater than the 6d (Figure 7). An analysis of a simple full Coulombic binding model using experimental data^{66,67} for ionization potentials and electron affinities is given in the SI.

Analysis of Different An(VI). The 6d population generally decreases across the An series, from 0.97 e for U to 0.80 e for Bk (Figure 8). A more striking effect is the substantial increase in 5f Excess, and resulting decrease in $q(\text{An})$, from U to Cm. It is also at Cm in the series of An(VI) that the configuration is closest to half-filled 5f⁷, which may be related to the enhanced 5f population there.

The variations in An–O distances reveal changes in bonding as well. The trend for An(III)–O is typical for a nearly constant (ionic and/or covalent) bond strength, with a gradual decrease in An(III)–O distance across the An series corresponding to the actinide contraction. In contrast, the entirely different trend for An(VI) is reminiscent of other actinide materials,^{3–8} including the actinide metallic elements, where the bonding increases across the series to ca. Pu and then decreases for Am and later An as the 5f orbitals become increasingly spatially contracted, lower in energy, and generally less amenable to participation in bond formation with ligands such as oxygen. From U to Np and from Np to Pu the An(VI)–O distance incrementally decreases by ~ 0.02 Å. In contrast, the An(VI) ionic radii from Shannon⁶⁸, i.e., 0.73 Å for U(VI), 0.72 Å for Np(VI), and 0.71 Å for Pu(VI), indicate an incremental decrease of ~ 0.01 Å due to the actinide contraction. The larger decrease found here may reflect slightly stronger An–O bonds from U to Np to Pu. It should be emphasized that An–O bond strength as revealed by such intrinsic parameters of an intact molecule as bond distance is not necessarily directly related to the bond dissociation energy (BDE) but more to the curvature near the energy minimum.⁶⁹ In contrast to intrinsic bond strength, variations in BDE may reflect differing properties of the separated constituent elements or fragments, such as differences in their electronic excitation energies to a prepared state for bond formation.⁷⁰ Beyond Pu, the An(VI)–O distance increases, indicating a decrease in bond strength. Because the minimum (least positive) $q(\text{An})$ and maximum (least negative) $q(\text{O})$ occur for Cm(VI), the minimum ionic contribution to An(VI)–O bonding should also occur there. The variation in An(VI)–O distances does not correspond to such a minimum at Cm(VI) but instead indicates a changing covalent contribution to bonding, which decreases after Pu(VI), particularly from Am(VI) to Cm(VI) and even more so from Cm(VI) to Bk(VI) (Figure 8). The increase in An(VI)–O distance after Pu indicates reduced covalent bonding.

Stability of An(VI) Relative to Lower OS. Perhaps the most remarkable aspect of the results in Figure 2 are the energies of the $[\text{O}=\text{An}^{\text{VI}}=\text{O}]^{2+}$ actinyl(VI) species relative to lower OS structures. Only for An = U, Np, and Pu are the actinyl(VI) the lowest energy structures. Not including the spin orbit corrections, Am(VI) is 15.5 kcal/mol higher energy than Am(II), the stability of which is enhanced by a $5f^7$ half-filled configuration. Not including the spin orbit corrections, Cm(VI) is 26.5 kcal/mol higher than Cm(III), which also has a $5f^7$ configuration, and Bk(VI) is 17.3 kcal/mol higher than Bk(III). Beyond Bk, the $5f$ orbital energy further decreases and we were unable to optimize structures with An(VI). The stabilization of the $5f$ electrons with increasing Z that inhibits higher OS is also revealed by the energies of atomic configurations. For example, the promotion energy from the ground state $\text{U}^{2+} 5f^4$ configuration to $5f^3 6d$ is only 1 kcal/mol, but this promotion energy increases to 57 kcal/mol for $\text{Es}^{2+} 5f^{11}$ to $5f^{10} 6d$.⁷¹ The inaccessibility of higher OS, specifically An(VI), for the later An is essentially a manifestation of decreasing $5f$ orbital energy as Z increases across the series. The reduced stability of higher OS reveals that the $5f$ electrons cannot directly participate in fully covalent bonding; as such, direct $5f$ bonding would not require promotion to higher energy $6d$ and/or $7s$ orbitals to achieve higher OS.

Absolute Stabilities of An(VI). The results in Figure 2 indicate the limited stability of the An(VI) relative to lower OS structures. Also of interest is the stability of the bare actinyl(VI) ions relative to dissociation reaction 1, which can be expressed as the sum of reactions 2 and 3: $\Delta H(1) = \Delta H(2) + \Delta H(3)$.

Reaction 2 corresponds to disruption of a simple ion-dipole interaction. We were able to calculate the energy of this reaction for Am, Cm, and Cf–Lr because the atomic An^{II} states can be calculated more readily as they are high-spin systems with only Cm having a d orbital occupied. The $\Delta H(2)$ are nearly constant for these An^{II} with a value of 19 ± 3 kcal/mol (see Supporting Information Table S1). In order to obtain enough points to get a good fit and to examine the interaction with a closed shell +II ion, we also calculated the interaction energies for Sr(II) and Ba(II) with ${}^3\text{O}_2$. The value of $\Delta H(2)$ can be evaluated using the calculated values for $\Delta H(1)$. The modest magnitudes of $\Delta H(2)$, ca. 19 kcal/mol, is consistent with an ion–molecule interaction, and with the minimal disruption of the O–O distance in $[\text{An}^{\text{II}}({}^3\text{O}_2)]^{2+}$ relative to free ${}^3\text{O}_2$. The values for $\Delta H(1)$ plotted in Figure 9 are obtained using $\Delta H(2)$ for each actinide as given in the SI, and the values for $\Delta H(3)$ reported in Figure 2. A previous assessment of experimental results suggested a regular decrease in the energy for reaction 3 from U(VI) to Am(VI), as is also predicted from the present results.⁷² The earlier estimates suggested a further decrease in the dissociation energy from Am(VI) to Cm(VI), but the uncertainties in these two particular dissociation energies, ± 30 and ± 36 kcal/mol, respectively, are too large to make a reliable comparison. The present results indicate that Cm(VI) exhibits a slightly lower absolute stability than Am(VI). Estimates were not previously provided for any An(VI) beyond Cm(VI); the

Figure 9. Estimated energies for dissociation of $[\text{An}^{\text{VI}}\text{O}_2]^{2+}$ to An^{II} and ${}^3\text{O}_2$, reaction 1. Bare U(VI), Np(VI), and Pu(VI) are substantially stable toward dissociation ($\Delta H > 50$ kcal/mol); Am(VI), Cm(VI), and Bk(VI) exhibit marginal stability/instability ($\Delta H \approx 0 \pm 20$ kcal/mol).

present results suggest a slight increase in stability from Cm(VI) to Bk(VI).

Although the energies for gas-phase dissociation reaction 1 do not capture differences that may be associated with decomposition of An(VI) to lower OS such as $\text{An}^{\text{V}}\text{O}_2^+$ in solution, rather than to An^{2+} and O_2 , they provide a general assessment of actinyl(VI) stability trends. The results summarized in Figure 9 predict that uranyl(VI), neptunyl(VI), and plutonyl(VI) should exhibit substantial thermodynamic stability. These three actinyls are indeed well established as stable species in solution and solid state, as well as in gas phase.^{3–8} The next three actinyls, americyl(VI), curyl(VI), and berkelyl(VI), are predicted to be marginally stable. Among these latter three, only Am(VI) has been definitively identified and it is metastable toward reduction in aqueous solution. The present results suggest that both Cm(VI) and Bk(VI) might also be obtained in favorable solution or coordination environments. Based on the present results, this is as far across the series of $[\text{AnO}_2]^{2+}$ as we would expect to find the +VI oxidation state. Our predictions suggest that quests for discovery of Cm(VI) and particularly Bk(VI) are sensible. The results provide an assessment of the limits of high OS across the An series; the $5f$ orbitals become too low energy beyond Bk to support the hexavalent OS.

CONCLUSIONS

The lowest energy structures for each actinide for AnO_2^{2+} are given in the summary in Table 3. For U to Pu, the AnO_2^{2+} structure is the standard actinyl, $[\text{O}=\text{An}=\text{O}]^{2+}$ with the An in the +VI oxidation state. For Am, the lowest energy structure is $[\text{Am}^{\text{II}}({}^3\text{O}_2)]^{2+}$ with the Am in the +II oxidation state complexed to an oxygen molecule. When the spin–orbit effects are included, the americyl(VI) becomes the lowest energy structure with the $[\text{Am}^{\text{II}}({}^3\text{O}_2)]^{2+}$ just 2 kcal/mol higher in energy. For Cm and Bk, the An are in the +III oxidation state, $[\text{An}^{\text{III}}({}^2\text{O}_2^-)]^{2+}$ with the actinide complexed to an ${}^2\text{O}_2^-$. For Cm, the actinyl is only 3 kcal/mol higher in energy after the inclusion of spin–orbit effects. The ground states for An = Cf to No are the $[\text{An}^{\text{II}}({}^3\text{O}_2)]^{2+}$ and the ground state for An = Lr is the ${}^2[\text{Lr}^{\text{III}}({}^2\text{O}_2^-)]^{2+}$. These particular results, and the overall results summarized in Figure 2, reflect known trends in actinide reduction potentials, particularly the decreasing stability beyond uranyl of An(VI) relative to lower oxidation states. The present results predict that the lowest energy structures of bare gas-phase AnO_2^{2+} are actinyl(VI) only for An = U, Np, Pu, and possibly Am when spin–orbit effects are

Table 3. Summary of Lowest Energy AnO₂²⁺ Structures

An	state/structure type	An OS	symmetry
U	¹ [O=U ^{VI} =O] ²⁺	VI	D _{∞h}
Np	² [O=Np ^{VI} =O] ²⁺	VI	D _{∞h}
Pu	³ [O=Pu ^{VI} =O] ²⁺	VI	D _{∞h}
Am ^a	¹⁰ [⁸ Am ^{II} (³ O ₂)] ²⁺ / ⁴ AmO ₂ ²⁺	II/VI	C _s /D _{∞h}
Cm	⁹ [⁸ Cm ^{III} (² O ₂ ⁻)] ²⁺	III	C _{2v}
Bk	⁸ [⁷ Bk ^{III} (² O ₂ ⁻)] ²⁺	III	C _{2v}
Cf	⁷ [⁵ Cf ^{II} (³ O ₂)] ²⁺	II	C _{∞v}
Es	⁶ [⁴ Es ^{II} (³ O ₂)] ²⁺	II	C _{∞v}
Fm	⁵ [³ Fm ^{II} (³ O ₂)] ²⁺	II	C _{∞v}
Md	⁴ [² Md ^{II} (³ O ₂)] ²⁺	II	C _{∞v}
No	³ [¹ No ^{II} (³ O ₂)] ²⁺	II	C _{∞v}
Lr	² [¹ Lr ^{III} (² O ₂ ⁻)] ²⁺	III	C _{2v}

^aFor Am, the two states are within 2 kcal/mol of each other.

included. Structures corresponding to An(II) and An(III) become more stable at Am and beyond. The observation of (metastable) americyl(VI) in aqueous solution reflects stabilization of high OS by electron-donating ligands, like neutral water or anionic hydroxide, and is consistent with our energetics when spin-orbit effects are included. As the relative energies of curyl(VI) and berkelyl(VI) are roughly comparable to that of americyl(VI), we expect that it might be feasible to prepare the two former in solution or solid state. Beyond Bk, the hexavalent OS is evidently of substantially lower stability and is unlikely to be made, except perhaps as transient metastable species. The results shown in Figure 2 and in the summary Table 3 provide a new perspective on chemical trends across the actinide series. Although generally diminished stability of high OS, specifically An(VI), has been previously well established, our results more clearly predict the absence of An(VI) beyond Bk, in favor of An(II) and An(III).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03690>.

Complete citations for references 20, 46, and 56; ΔH_{OK} AnO₂²⁺ relative energies graphs at different levels of theory; figures showing additional trends in optimized geometries, energies, spins, and electronic occupancies for different oxidation states in actinides; reaction energies for reaction 2 M²⁺O₂ → M²⁺ + O₂; optimized geometry parameters; summary of all the different OS structures; the total electronic energies in au; T1 values; NPA and QTAIM charges; NBOs and spins (natural spin densities) for the oxygen atoms; calculated QTAIM bond critical points; NIST ionization potentials; and coulombic energies estimates (PDF)

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Notes

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