The decisive role of 5f-orbital covalence in the structure and stability of pentavalent transuranic oxo $[M_6O_8]$ clusters

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Abstract. Actinide metal oxo clusters are of vital importance in actinide chemistry, as well as in environmental and material sciences. They are ubiquitous in both aqueous and non-aqueous phases, and play key roles in nuclear materials (e.g. nuclear fuel) and nuclear waste management. Despite the importance, our structural understanding of the actinide metal oxo clusters, particularly the transuranic ones, is very limited, due to the experimental challenges such as the high radioactivity. Herein we report a systematic theoretical study on the structures and stabilities of seven actinide metal oxo-hydroxo clusters $[An(IV)_6O_4(OH)_4L_{12}]$ (An: Th to Cm; L: O_2CH^-) (**1-An**) along with their group-4 (Ti, Zr, Hf, Rf) and lanthanide (Ce) counterparts $[M(IV)_6O_4(OH)_4L_{12}]$ (**1-M**). The work shows the T_d -symmetric structures of all the **1-An/M**, and suggests the positions of the -OH functional groups, which are experimentally challenging to determine. Furthermore, by removing six electrons from **1-An**, we found that the oxidation could happen on the An(IV) metal ions producing $[An(V)_6O_4(OH)_4L_{12}]^{6+}$ (**2-An**; An: Pa, U, Np), or on the O^{2-} and OH^- ligands producing $[An(IV)_6(O^{\cdot-})_4(OH^{\cdot})_2(OH)_2L_{12}]^{6+}$ (**3-An**; An: Pu, Am, Cm). Based on the **2-An**, we constructed a series of tetravalent and pentavalent actinide metal oxo clusters $[An(IV)_6O_{14}]^{4-}$ (**4-An**) and $[An(V)_6O_{14}]^{2+}$ (**5-An**), which proves the feasibility of the highly important pentavalent actinyl clusters for the first time, demonstrates f-orbital's structurally directing role in the formation of linear $[O\equiv An(V)=O]^{1+}$ actinyl ions, and expands the concept of **actinyl-actinyl interaction** into pentavalent transuranic actinyl clusters.

1. Introduction. The chemistry of actinide oxo clusters has received increasing attention in the last decades,¹ not only because of their potential application in the nuclear-fuel cycle technologies, catalysis and the design of molecular magnets, but also thanks to the advances in quantum chemistry methods enabling to handle actinide systems with a high density of electronic states arising from degeneracy or near degeneracy of orbitals and treat relativistic effects at the same time.²⁻⁴ Actinide oxo/hydroxo clusters provide useful models for the nanosized species involved in spent nuclear fuel separation and the migration behaviour of actinide metals in the environment. The chemistry of these species is also important for understanding geochemical reactions and for the development of new nuclear waste remediation technologies. Notably, discrete clusters have been isolated from hydrolysis and condensation reactions of low valent actinides in the aqueous condition, in the presence of anionic ligands such as halides or carboxylic acids.⁵⁻⁸ However, the chemistry of actinide oxide clusters remains underdeveloped compared to the transition-metal counterparts, and our understanding of their underlying electronic configuration-cluster structure relationship is limited.

$[M_6O_4(OH)_4]^{n+}$ is a thermodynamically favourable cluster core structure. Such tetravalent transition-metal and lanthanide $[M(IV)_6O_4(OH)_4]^{12+}$ clusters are well-known and have been thoroughly investigated, both experimentally and theoretically, for decades.⁹⁻¹¹ The actinide counterparts, on the other hand, were unknown until 2010; since then, a few tetravalent actinide $[An(IV)_6O_4(OH)_4]^{12+}$ clusters have been synthesised where An is U, Th, Pu or Np.¹²⁻¹⁷ In spite of their synthesis, the structures of the $[An(IV)_6O_4(OH)_4]^{12+}$ clusters are far from being unambiguously characterised: it is experimentally challenging to distinguish between the two types of tetrahedron An-An-O(H)-An and An-An-O-An sites using the single-crystal X-ray diffraction (SCXRD) method, particularly when the O or OH centres are adjacent to the heavy actinide centres. To distinguish the O and OH sites, the SCXRD experimental method, or the single-crystal neutron diffraction (SCND) method, requires large and high-quality crystals, which is not feasible particularly for the highly radioactive trans-uranic elements. In this consideration, computational methods are essential to elucidate the structures of the actinide clusters, and in complement with the experimental methods. However, a comprehensive and comparative computational investigation of the $[An(IV)_6O_4(OH)_4]^{12+}$ clusters and their tetravalent

lanthanide/transition-metal counterparts are in absence.

Moreover, pentavalent actinide-oxo ions and clusters play crucial roles in actinide science and engineering. For instance, the uranyl reductive functionalisation and nuclear waste remediation both involve $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ species;¹⁸⁻¹⁹ $[\text{O}=\text{Np}(\text{V})=\text{O}]^{1+}$ is the most common form of neptunium in aqueous solutions. In the aqueous phases, the $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ is potentially formed via $[\text{O}=\text{An}(\text{V})-\text{OH}]^{2+}$ unit.²⁰ Thus, investigating the clusters of $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ and $[\text{O}=\text{An}(\text{V})-\text{OH}]^{2+}$ units are of necessary. However, there is no report of pentavalent $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4]^{6+}$ clusters, neither clusters featuring the $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ unit. A theoretical proof-of-principle investigation of the pentavalent $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ (**2-An** and **3-An**) clusters will be highly valuable by providing insight into the formation and functionalisation of the pentavalent actinyls.

Herein, we present a comprehensive theoretical investigation of the structures of the $[\text{M}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ clusters (**1-M**; M: group 4, Ce and Th to Cm) and their hypothetical 6-electron oxidation to pursue $[\text{M}(\text{V})_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$. Furthermore, based on the M(IV/V) oxo-hydroxo clusters, we construct a series of novel $[\text{M}(\text{IV/V})_6\text{O}_{14}]^{4-/2+}$ clusters, which act as a platform to develop a comprehension of f-orbital's structurally directing role in the pentavalent actinyl chemistry, as well as the **actinyl-actinyl interaction** in the pentavalent transuranic chemistry.

2. COMPUTATIONAL DETAILS

All DFT calculations were performed with the Amsterdam Density Functional program ADF 2016.101.²¹ The Perdew–Burke–Ernzerhof (PBE)²² exchange-correlation functional was used. Relativistic effects were accounted for by the SR and SOC Zero-Order Regular Approximations (ZORA).²³⁻²⁴ Slater-type basis sets of valence triple- ζ plus one polarization function (TZP) quality were used for all atoms in the free clusters and for the cores of the ligated clusters. In order to balance the time cost and the accuracy of the calculations for different metal atoms, the frozen core approximation was applied for all atoms with the following core/valence shells: C and O (1s/2sp), Ti, V and Cr (1s2p/3spd4sp), Zr, Nb and Mo (1s-3d/4spd5sp), Hf, Ta and W (1s-4f/5spd6sp), Rf and Sg (1s-5f/6spd7sp), Ce (1s-4d/4f5spd6sp), and An (1s-5d/5f6spd7sp). Geometry optimisations using analytical

gradients were performed with and without symmetry constraints for the free and ligated clusters. The optimised minimum-energy structures were verified by analytical vibrational frequency analysis. For the open An-5f shell cases, different spin states were investigated and the high spin state is the lowest in energy. Additionally, TDDFT calculations on the lowest energy state for each species have been performed to check the stability of the ground electronic state.²⁵ To investigate the solvent influence on the electronic and geometric structures of the clusters, the conductor-like screening model (COSMO)²⁶ was applied with the parameters for a pyridine (Py) solvent, because pyridine was the most common solvent used in the lab studies for comparison. The following atomic COSMO-default radii from the ADF code were used: Ti 199.2 pm, Zr 211.7 pm, Hf 210.8 pm, Ce 228.3 pm, Th 228.3 pm, O 151.7 pm, and H 135.0 pm. The chemical bonding was investigated in some detail by applying wave function analyses as suggested by the Weinhold²⁷⁻²⁸ and the Boldyrev groups.²⁹ Localised molecular orbitals (MOs) of direct chemical appeal were determined at first using the so-called “natural bond orbital” analysis of Weinhold et al. in the NBO 6.0 code; this yields the “natural atomic orbitals” as input for Boldyrev’s so-called “Adaptive Natural Density Partitioning” (AdNDP). The AdNDP analyses were performed using the Multiwfn code.³⁰ When the occupation number of localised pair MO lies below 2.00, the wave function would require respective delocalisation of the MO over additional atomic centers. To gain further insights into the chemical bonding pattern, we performed NBO analysis to generate the multi-centered localised orbitals using Gaussian09 codes.³¹ Energy decomposition analyses (EDA)³² were carried out using the combined Extended Transition State (ETS) with the Natural Orbitals for Chemical Valence (NOCV)³³⁻³⁴ theory to assess different orbital contributions to the total bonding energies. The population partitioning schemes of Mulliken³⁵ were used to determine the atomic charges of the atoms in these species. This procedure has shown reasonable results to support and explain experiments in the study of geometrical structure and electronic structure of actinide clusters.³⁶⁻³⁸

3. Results and discussion

3.1 Structures and stability of $[M(IV)_6O_4(OH)_4L_{12}]$ (1-M)

The $[M(IV)_6O_4(OH)_4]^{12+}$ clusters are known for group 4 metals, cerium and uranium.^{11, 39-40} Nonetheless, their structural characterisation, in particular, experimentally determining of the positions

of the OH sites, was impeded by the limit of single crystal X-ray diffraction. Thus, we calculated the relative energy values of the four kinds of isomers (Figure 1, A to D) for group 4 (Ti, Zr, Hf, Rf), lanthanide (Ce) and actinide (Th to Cm), to gain insight of their structures.

Figure 1. Four kinds of isomers for $[M(IV)_6O_4(OH)_4]^{12+}$ clusters. For clarity, the ligand (L) are not shown.

Table 1. Relative energies (kcal/mol) of the four isomers for closed-shell $[M(IV)_6O_4(OH)_4L_{12}]$ (M=Ti, Zr, Hf, Rf, Ce, An).

M	A	B	C	D
Ti	0.0	28.8	22.3	30.5
Zr	0.0	28.2	25.6	32.9
Hf	0.0	29.2	27.6	35.0
Rf	0.0	28.4	31.9	42.8
Ce	0.0	16.5	13.9	18.1
Th	0.0	20.6	18.2	24.0

Table 1 lists the relative energy values of the four isomers (A-D **Figure 1**) for the closed-shell systems, which all prefer the isomer A over other isomers by 13-30 kcal/mol. The data indicate that in the closed-shell $[M(IV)_6O_4(OH)_4L_{12}]$ clusters, the -OH groups are localised and stay as apart from each other as possible, to reduce the dipole-dipole repulsion. The result is in correspondence with the Th system calculated by Knope et al..^{15, 41}

In the subsequent work, we adopt the geometry of the isomer A as a computational model which has been experimentally assigned as the backbone structure of $[\text{U}_6\text{O}_4(\text{OH})_4]$ cluster⁴² and expand the scope of actinide metals from Th to Cm for further considering the effect of electronic structures and oxidation state of An on the skeleton structures of An_6 . The 12 calculated structures of $[\text{M}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ (**1-M**) are thermodynamically stable according to their formation energy, covering d-block early-transition metal (group-4), lanthanide and actinide, allow us to conduct a comprehensive and comparative study. The selected geometric parameters of **1-M**, in parallel with the available experimental data, are listed in Table 2.

Table 2. Electronic state, electronic configuration, bond length (Å) for $[\text{M}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ (**1-M**) at the SR-PBE level.

M	2S+1	Elec. Conf. of M	M...M	M–O _b	M–O _{OH}	M–O _L	
Ti	1	d ⁰	3.354	1.970	2.155	2.157	Calc.
Zr	1	d ⁰	3.847	2.256	2.458	2.458	Calc.
Hf	1	d ⁰	3.714	2.1737	2.374	2.357	Calc.
			3.549–3.554	2.203–2.211	2.146–2.194	2.222–2.269	Ref10
Rf	1	d ⁰	3.573	2.094	2.291	2.278	Calc.
Ce	1	d ⁰	3.582	2.101	2.297	2.270	Calc.
			3.7386(3)	2.186(2)	2.381(2)	2.240(2)	Ref11
Th	1	d ⁰	3.924	2.293	2.505	2.490	Calc.
			3.922	2.297(6)–2.318(5)	2.518(6)–2.525(6)	2.456(6)–2.546(6)	Ref8,15
			3.912	2.30(6)	2.49(8)	2.441(4)–2.667(4)	Ref36
Pa	7	f ¹	3.849	2.248	2.467	2.420	Calc.
U	13	f ²	3.825	2.234	2.445	2.428	Calc.
			3.82	2.233	2.442	2.448	Ref42,43
Np	19	f ³	3.806	2.227	2.426	2.423	Calc.
			3.81	2.23	2.43	2.43	Ref43
Pu	25	f ⁴	3.778	2.211	2.415	2.409	Calc.
			3.77	2.207	2.407	2.403	Ref44
Am	31	f ⁵	3.781	2.200	2.421	2.424	Calc.
Cm	37	f ⁶	3.840	2.229	2.467	2.424	Calc.

* M...M: intermetallic distance between the two neighbouring metal ions. M–O_b: metal-oxo bond. M–OH: metal-hydroxo bond. M–O_L: metal-formate bond.

The M...M distance is relatively long, exhibiting the “secondary periodicity” that is a generally increasing from 3.354 Å for Ti–Ti to 3.924 Å for Th–Th within the group 4 and exhibiting the actinides contraction that is decreasing trend from 3.849 Å for Pa–Pa to 3.778 Å for Pu–Pu within the actinide

series. The discrepancies between the calculated and experimental values can be explained by excluding consideration of the solvent effect, which shows a large effect on the ionic bonds, especially the metal-metal interactions in d-block complexes. All the M...M distances in the 12 calculated **1-M** are longer than the sum of their single-bond radius,⁴³ indicating that the intermetallic interaction must be weak if there is any. The M–O_L and M–OH bond lengths are close in the same cluster, ranging between 2.155 to 2.505 Å within group 4 elements and between 2.409 to 2.467 Å within actinides, slightly longer than the covalent single-bond range, with considering the covalent single-bond radius of O as 0.63 Å. Compared to the M–O_L/OH, the M–O_b bond lengths are much shorter, but still substantially longer than the fitted double bond length (Ti=O: 1.74, Zr=O: 1.84, Hf=O: 1.85, Rf=O: 1.97, Ce=O: 1.94, Th=O: 2.00, Pa=O: 1.95, U=O: 1.96, Np=O: 1.98, Pu=O: 1.96, Am=O: 1.95, Cm=O: 1.95 Å).⁴³

Pentavalent actinide oxo and hydroxo clusters play crucial roles in the nuclear industry and environmental science, but to the best of our knowledge, there is no experimental report on such An(V) oxo/hydroxo cluster to date. Based on the tetravalent actinide [An(IV)₆O₄(OH)₄L₁₂] (**1-An**) clusters, we conducted a hypothetical 6-electron oxidation, by removing six electrons from the **1-An**, and examining the thermodynamic feasibility of the resultant [An₆O₄(OH)₄L₁₂]⁶⁺ actually being [An(V)₆O₄(OH)₄L₁₂]⁶⁺ (**2-An**; An: Pa, U, Np), or on the O²⁻ and OH⁻ ligands producing [An(IV)₆(O⁻)₄(OH⁻)₂(OH)₂L₁₂]⁶⁺ (**3-An**; An: Pu, Am, Cm). The calculated geometric parameters and spin densities for the **2-An** and **3-An** clusters are listed in Table 3.

Table 3. Electronic state, electronic configuration, bond length (Å) for [An₆O₄(OH)₄L₁₂]⁶⁺ (**2-An**; An: Pa, U, Np; **3-An**; An: Pu, Am, Cm) at the SR-PBE level.

M	2S+1	Elec. Conf. of M	Bond length				Spin population			
			M–M	M–O _b	M–O _{OH}	M–O _L	M	O _b	O _{OH}	O _L
Pa	1	f ⁰	3.945	2.291	2.477	2.284	0.00	0.00	0.00	0.00
U	7	f ¹	3.889	2.219	2.462	2.280	1.22	-0.06	-0.02	-0.03
Np	13	f ²	3.897	2.266	2.451	2.272	2.38	-0.13	-0.05	-0.06
Pu	19	f ⁴	3.907	2.275	2.448	2.282	3.75	-0.27	-0.10	-0.12
Am	25	f ⁵	3.904	2.272	2.472	2.329	5.18	-0.39	-0.15	-0.19
Cm	31	f ⁶	3.885	2.268	2.498	2.422	6.45	-0.29	-0.11	-0.23

In the **2-An** and **3-An**, all clusters are potential to form open-shell structures, except for **2-Pa**. The spin population calculation suggests that depending on the electronic structure, the six $[\text{An}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ clusters can be divided into three groups. For **2-Pa**, the optimised structure features closed-shell $5f^0 6d^0$ Pa(V) centres and is best described as $[\text{Pa(V)}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$. For **2-U/Np**, the metal-based 1.22|e| and 2.38|e| spin populations fit with the U(V) and Np(V) oxidation states, respective. The U(V) is a 1-electron doublet centre and the Np(V) is a high-spin, 2-electron triplet centre. The oxo and hydroxo centres are largely closed-shell and with only negligible spin density. Thus, the **2-U/Np** can be formulated as $[\text{U(V)}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ and $[\text{Np(V)}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$, respectively.

On the other hand, for **3-Pu**, Am and Cm, the scenario changes substantially. In these cases, the actinide centres are best described as An(IV) with metal-based spin populations of 3.75|e| (Pu), 5.18|e| (Am) and 6.45|e| (Cm). Instead, there are significant increase of spin densities on the O_b , OH and O_L sites, indicating the ligand-based oxidation and formation of $\text{O}^{\cdot-}$, $\cdot\text{OH}$ and $\cdot\text{O}_2\text{CH}$ free radical species. Due to the fractional distribution of the spin population over the **3-Pu/Am/Cm**, it is not possible to formulate them as simple distributions. Instead, spin delocalization should be considered in the $[\text{An(IV)}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ (**3-An**, An: Pu, Am, Cm) clusters. The results show that Pa, U and Np can achieve the hypothesized pentavalent oxo-hydroxo clusters via oxidation. For the heavier transuranic elements (Pu, Am, Cm), the oxidation will take place on the O^{2-} , OH^- and $[\text{O}_2\text{CH}]^-$ ligands. Thus, the results provide a understanding for theoretically pursuing the An(V) oxo-hydroxo clusters under the framework of $[\text{AnO}_4(\text{OH})_4\text{L}_{12}]$.

While the spin density distributions change significantly from U to Cm, the M–M distances keep consistent and only vary in a range of circa 0.02 Å (Table 3). Taking into account of the differences in ionic radii, this result is surprising and unexpected. The formation of An–An bond is not impossible, though our attempts to obtain clear evidence were impeded by lack of suitable multireference methods for the high oxidation state U(V) and Np(V) systems, which are multi-configurational in nature. For the Pu, Am and Cm $[\text{AnO}_4(\text{OH})_4\text{L}_{12}]^{6+}$ clusters, the presence of $\text{O}^{\cdot-}$ spin centres complicated the calculation;

thus, unfortunately, we could not arrive a plausible conclusion concerning the intermetallic bonds.

Figure 2. Energy level diagram of SR-Kohn Sham molecular orbitals for $[M(IV)_6O_4(OH)_4(L)_{12}]$ (**1-M**).

To understand the factors underpin the different oxidation behaviours, we examined the HOMO–LUMO gaps for the parent $[M(IV)_6O_4(OH)_4L_{12}]$ (**1-M**). **Figure 2** shows the selected Kohn-Sham molecular orbitals in the HOMO–LUMO region involving the *nd*-, *5f*- orbitals of the metal fragments and the O 2p orbitals, represented as different energy bands. The MOs from the O 2p are fully occupied and basically remaining the same energies across the series from Ti to Cm, locates at the bottom in **Figure 2**. When traversing within the group 4 series from Ti to Th, the radial distribution functions of virtual *nd* orbitals extend and the orbital energetics increase, consequently, increasing the HOMO–LUMO gap from 2.398 eV in Ti to 6.537 eV in Th and thus largely increasing the stability of $[M(IV)_6O_4(OH)_4L_{12}]$ for heavy elements. As depicted in **Figure 2**, the Ce-4f and An-5f bands insert between O 2p and M *nd* energy levels with two features: (1) the Ce-4f orbitals is virtual yet being more inert than the An 5f orbitals and (2) the singly occupied An-5f AOs decrease substantially as the atomic number increases so they become nearly degenerate with the oxygen lone-pair orbitals.

This is a general feature of actinide chemistry, which has been observed in a number of actinide complexes with different ligands. Therefore, the HOMO–LUMO gap drops to 1.446 eV at $[Ce(IV)_6O_4(OH)_4L_{12}]$, whereas, the energy gap between singly occupied α spin molecular orbitals (SOMO) and LUMO in actinide complexes smoothly decline from 3.621 eV at An= Pa to 0.479 eV in

An = Am and then eventually to degenerate at An= Cm. Thus, for the heavy transuranic elements Pu, Am and Cm, the oxidation (removing electrons) is easier to take place from the occupied O-2p orbitals, instead of the An-5f based SOMOs.

3.2 Model complexes $[\text{An}(\text{V})_6\text{O}_{14}]^{2+}$ to understand the pentavalent actinyl(V) clusters.

Pentavalent actinyls $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ are essential species in actinide science and nuclear fuel/waste research.^{20, 44} The $[\text{O}=\text{U}(\text{V})=\text{O}]^{1+}$ exists in the chemical and biological uranyl remediation processes, and the $[\text{O}=\text{Np}(\text{V})=\text{O}]^{1+}$ is the most common form of Np in aqueous solutions. Thus, understanding the aggregation, structures and bonding characters of the $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4]$ cluster is of strategic requirement. However, research in this field significantly lags behind the corresponding transition-metal-oxo clusters, partially due to the experimental challenges relating to their radioactivity and their complexation in electronic structures and chemical bondings. Thus, the systematic theoretical study is valuable to provide fundamental understanding for $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4]$ clusters.

The pentavalent 2-An clusters, $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$, are potential precursors for the $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ clusters, by deprotonating the An(V)–OH functional groups. Based on the calculation in the previous section, the outer sphere L^- ligands coordinate to the An(V) via An(V)–O_L bonds, which have similar bond lengths to the An(V)–μO bonds. Thus, based on the $[\text{An}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ clusters 2-An or 3-An, by replacing the (OH)[−] and L[−] by one and 0.5 O^{2−}, respectively, we construct $[\text{An}(\text{V})_6\text{O}_{14}]^{2+}$ (An: Pa, U, Np, Pu, Am, Cm) clusters (5-An) and explore their thermodynamic feasibility and structures.

The 5-An are the first expedition into the $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ clusters. It turns out that the 5-An are feasible for all the six calculated actinide elements (Pa, U, Np, Pu, Am, Cm), but the structures divide into two groups. The Pa prefers cluster structure with bent $[\text{O}=\text{Pa}(\text{V})=\text{O}]^{1+}$ units, while the U, Np, Pu, Am and Cm prefer those of linear $[\text{O}=\text{An}(\text{V})=\text{O}]^{1+}$ units. The details are discussed herein.

First, we construct the tetravalent version $[\text{An}(\text{IV})_6\text{O}_{14}]^{4-}$ (4-An; An: Pa-Cm), based the $[\text{An}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ (1-An), and calculated their structures. All the six 4-An feature the same O_h symmetry with their tetravalent precursors 1-An (see SI for details), which justifies our choices of calculation methods.

We subsequently remove six electrons from the O_h -symmetry $[\text{An(IV)}_6\text{O}_{14}]^{4-}$ (**4-An**) to investigate that if the cluster symmetry will change upon the oxidation to $[\text{An(V)}_6\text{O}_{14}]^{2+}$ (**5-An**). The calculated charge and spin population are listed in Table 4. Different from the oxidation of the oxo-hydroxo clusters **1-M**, which took place on the ligands instead of metal and led to significant spin population on the O/OH ligands, here in the **5-An**, all the actinide metal ions can be described as An(V), despite slight diffusions of spin population to the oxo sites in **5-Pu** to **5-Cm**. Thus, the oxidation from **4-An** to **5-An** is majorly metal-based.

The most substantial impact on the cluster structures from the oxidation is the change of symmetry. Only **5-Pa** was optimized at the O_h -symmetry (Figure 3a). For the rest five clusters (**5-U** to **5-Cm**), the O_h -symmetry structure is only a saddle point with two sets of large imaginary vibrational frequencies for T_{1g} and T_{2u} . To verify whether the imaginary frequencies of the **5-An** (An: U, Np, Pu, Am, Cm) are due to numerical noises for low-frequency modes, we used very tight criteria for the self-consistent-field convergence and geometry optimizations and increased the integration accuracy from the default value of 6.0 to 8.0, and even further, to 10.0. It turns out that the imaginary frequencies remain unchanged for the 3-U to Cm clusters. Therefore, the **5-An** (An: U to Cm) indeed distort from the O_h symmetry to the *low* symmetry, as a result of the oxidation (**Figure 3b**).

Table 4. Mulliken net charge (q) and Populations (|e|) on atoms of $[\text{An(IV)}_6\text{O}_{14}]^{4-}$ and $[\text{An(V)}_6\text{O}_{14}]^{2+}$.

	[An(IV) ₆ O ₁₄] ⁴⁻ (4-An)			[An(V) ₆ O ₁₄] ²⁺ (5-An)			
Charge							
	M	O _t	O _b	M	O _t	O _b	O _{act}
Th	1.65	-0.90	-1.06	NA			
Pa	1.46	-0.84	-1.01	2.26	-0.56	-1.03	-0.56
U	1.53	-0.85	-1.01	2.19	-0.51	-1.03	-0.99
Np	1.49	-0.84	-0.99	2.08	-0.49	-0.98	-0.52
Pu	1.48	-0.84	-0.98	1.99	-0.48	-0.98	-0.60
Am	1.44	-0.83	-0.96	1.91	-0.47	-0.99	-0.69
Cm	1.50	-0.84	-0.99	5.82	-0.45	-1.01	-0.69
Spin Population							
Th	0.00	0.00	0.00	NA			
Pa	1.04	-0.02	-0.02				
U	2.16	-0.06	-0.07	1.08	-0.06	-0.05	-0.05
Np	3.27	-0.13	-0.11	2.25	-0.14	-0.08	-0.13
Pu	4.42	-0.19	-0.18	3.39	-0.21	-0.13	-0.19
Am	5.53	-0.23	-0.22	4.53	-0.29	-0.08	-0.21

Cm	6.44	-0.27	-0.13	5.41	-0.28	-0.01	-0.23
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a. $[\text{Pa(IV)}_6\text{O}_{14}]^{2+}$ (O_h -symmetry)

b. $[\text{An(V)}_6\text{O}_{14}]^{2+}$ (S_6 -symmetry)

Figure 3. Structures of $[\text{Pa(V)}_6\text{O}_{14}]^{2+}$ (**5-Pa**) (**a**) and $[\text{An(V)}_6\text{O}_{14}]^{2+}$ (**5-An**; An = U to Cm) (**b**). An in pink color and oxygen in red color.

Table 5. Calculated bond lengths (Å) and bond angles (°) for **5-An** $[\text{An(V)}_6\text{O}_{14}]^{2+}$ (An= Pa to Cm) at the SR-PBE level.

An	2S+1	Elec. Conf. of An	Symmetry	Bond Length				$\text{O}_t\text{--M--O}_{\text{act}}$
				M–M	M–O _t	M–O _b	M–O _{act}	
Pa	1	f ⁰	O_h	3.742	1.814	2.298	2.263	146.4
U	7	f ¹	S_6	3.635	1.798	2.353	2.076	163.8
Np	13	f ²	S_6	3.694	1.779	2.430	1.930	174.0
Pu	19	f ³	S_6	3.345	1.768	2.235	1.920	178.7
Am	25	f ⁴	S_6	4.078	1.782	2.419	1.916	175.5
Cm	31	f ⁵	S_6	3.510	1.801	2.415	1.988	172.8

The selected calculated bond lengths and angles in the **5-An** clusters are listed in Table 5. In both the O_h -symmetry **5-Pa** and the S_6 -symmetry **5-U** to **5-Cm**, there are three groups for the total 14 O^{2-} ligands. The 6 terminal O^{2-} ligands coordinate to the metal via terminal, abridging, short $\text{An}\equiv\text{O}_t$ (t: terminal) bonds (1.768 Å to 1.814 Å). The rest 8 $\mu^3\text{-O}^{2-}$ ligands can be further categorized into two groups. Six of which are a part of a $[\mu^3\text{-O}_{\text{act}}\text{=An(V)}\equiv\text{O}_t]^{1+}$ unit, which we denote as O_{act} (act: actinyl). The other two $\mu^3\text{-O}^{2-}$ ligands are not a part of any $[\mu^3\text{-O}_{\text{act}}\text{=An(V)}\equiv\text{O}_t]^{1+}$ unit, but act as purely bridging

ligand, which we denote as O_b (b: bridging).

From Table 4, it is evident that the changing from the O_h -symmetry of **5-Pa** to the *low*-symmetry of **5-U** to **5-Cm** is driven by: 1) elongating of the $An-O_b$ bonds (2.298 Å vs ca. 2.40 Å, except **5-Pu**); 2) shortening of the $An=O_{act}$ bond (2.263 Å vs ca. 2.0 Å); 3) the increasing of the $\angle O_{act}=An(V)\equiv O_t$ (146.4° vs ca. 170°). In comparison, the terminal $An(V)\equiv O_t$ bond lengths only change slightly, in spite of the difference of the ionic radii. In **5-Pa**, the $Pa(V)-O_b$ bond (2.298 Å) and the $Pa(V)-O_{act}$ bond (2.263 Å) are nearly equivalent, and are both in the region of $Pa-O$ single bond. In contrary, for the rest **5-An** clusters, the $An(V)-O_b$ (2.235 to 2.430 Å) are significantly longer than the $An(V)=O_{act}$ (1.916 to 2.076 Å). The former is best described as a dative bond $An(V)\leftarrow O_b$, while the latter is an $An(V)=O_{act}$ double bond. In summary, the elemental structural unit of the **5-An** clusters can be described in two categories:

1) type-A for **5-Pa**; 2) type-B for **5-U** to **5-Cm** (Figure 4).

Type-A
5-Pa
 $[Pa_6O_{14}]^{2+}$

Type-B
An:U,Np,Pu,Am,Cm
5-An
 $[An_6O_{14}]^{2+}$

Figure 4. Schemes for two categories of $[An(V)_6O_{14}]^{2+}$

Table 6. The selected natural localized molecular orbitals (NLMOs) between An atom and its coordinated oxygen atoms in $[\text{An}(\text{V})_6\text{O}_{14}]^{2+}$ complexes.

Species	$\text{An}=\text{O}_{\text{act}}$		$\text{An}\equiv\text{O}_{\text{t}}$	
Type	σ	π	σ	π
Pa	87.6% $\text{O}(\text{sp}^{2.00}) + 8.0\%$ $\text{Pa}(\text{s}^{0.36}\text{d}^{1.36}\text{f})$	83.1% $\text{O}(\text{p}) + 5.6\%$ $\text{Pa}(\text{d}^{0.68}\text{f})$	77.2% $\text{O}(\text{sp}^{6.68}) + 22.3\%$ $\text{Pa}(\text{d}^{0.42}\text{f})$	79.4% $\text{O}(\text{p}) + 20.4\%$ $\text{Pa}(\text{d}^{0.54}\text{f})$
				79.5% $\text{O}(\text{p}) + 20.2\%$ $\text{Pa}(\text{d}^{0.61}\text{f})$
U	82.8% $\text{O}(\text{sp}^{6.85}) + 13.1\%$ $\text{U}(\text{d}^{0.87}\text{f})$	84.3% $\text{O}(\text{p}) + 8.1\%$ $\text{U}(\text{d}^{0.69}\text{f})$	74.1% $\text{O}(\text{sp}^{5.73}) + 25.1\%$ $\text{U}(\text{d}^{0.24}\text{f})$	78.3% $\text{O}(\text{p}) + 21.3\%$ $\text{U}(\text{d}^{0.53}\text{f})$
		82.8% $\text{O}(\text{p}) + 7.8\%$ $\text{U}(\text{d}^{0.60}\text{f})$		78.4% $\text{O}(\text{p}) + 21.4\%$ $\text{U}(\text{d}^{0.52}\text{f})$
Np	83.7% $\text{O}(\text{sp}^{1.53}) + 14.8\%$ $\text{Np}(\text{d}^{0.34}\text{f})$	84.4% $\text{O}(\text{p}) + 11.3\%$ $\text{Np}(\text{d}^{0.65}\text{f})$	73.8% $\text{O}(\text{sp}^{4.57}) + 25.4\%$ $\text{Np}(\text{d}^{0.18}\text{f})$	80.6% $\text{O}(\text{p}) + 19.0\%$ $\text{Np}(\text{d}^{0.61}\text{f})$
		84.7% $\text{O}(\text{p}) + 8.9\%$ $\text{Np}(\text{d}^{0.58}\text{f})$		80.6% $\text{O}(\text{p}) + 19.2\%$ $\text{Np}(\text{d}^{0.62}\text{f})$
Pu	81.3% $\text{O}(\text{sp}^{1.69}) + 16.9\%$ $\text{Pu}(\text{d}^{0.26}\text{f})$	84.0% $\text{O}(\text{p}) + 10.6\%$ $\text{Pu}(\text{d}^{0.58}\text{f})$	70.1% $\text{O}(\text{sp}^{6.54}) + 28.9\%$ $\text{Pu}(\text{d}^{0.14}\text{f})$	79.7% $\text{O}(\text{p}) + 20.0\%$ $\text{Pu}(\text{d}^{0.49}\text{f})$
		84.4% $\text{O}(\text{p}) + 12.5\%$ $\text{Pu}(\text{d}^{0.54}\text{f})$		79.7% $\text{O}(\text{p}) + 20.1\%$ $\text{Pu}(\text{d}^{0.50}\text{f})$
Am	76.3% $\text{O}(\text{sp}^{7.51}) + 21.7\%$ $\text{Am}(\text{d}^{0.18}\text{f})$	83.8% $\text{O}(\text{p}) + 11.4\%$ $\text{Am}(\text{d}^{0.57}\text{f})$	74.4% $\text{O}(\text{sp}^{7.49}) + 24.1\%$ $\text{Am}(\text{d}^{0.18}\text{f})$	83.0% $\text{O}(\text{p}) + 13.7\%$ $\text{Am}(\text{d}^{0.52}\text{f})$
		84.6% $\text{O}(\text{p}) + 13.0\%$ $\text{Am}(\text{d}^{0.62}\text{f})$		83.8% $\text{O}(\text{p}) + 15.5\%$ $\text{Am}(\text{d}^{0.58}\text{f})$
Cm	77.3% $\text{O}(\text{p}) + 17.4\%$ $\text{Cm}(\text{d}^{0.24}\text{f})$	84.6% $\text{O}(\text{p}) + 13.4\%$ $\text{Cm}(\text{d}^{0.52}\text{f})$	74.4% $\text{O}(\text{sp}^{7.49}) + 24.1\%$ $\text{Cm}(\text{d}^{0.18}\text{f})$	82.7% $\text{O}(\text{p}) + 17.0\%$ $\text{Cm}(\text{d}^{0.54}\text{f})$
		84.0% $\text{O}(\text{p}) + 11.0\%$ $\text{Cm}(\text{d}^{0.59}\text{f})$		81.3% $\text{O}(\text{p}) + 17.5\%$ $\text{Cm}(\text{d}^{0.44}\text{f})$

The driving force of the structural changes is the electronic conformations of the An(V) ions and the resultant An(V)-O bonding scenarios. As the energetic levels of the 5f-orbitals of An(V) become closer to the O-2p orbitals traversing from Pa(V) to Cm(V), it is reasonable to expect more 5f-2p spatial overlapping covalence for the heavier actinide metals. We presume that the 5f-orbital participant drives the formation of the linear $[\text{O}_t\equiv\text{An}=\text{O}_{\text{act}}]^{1+}$ cations, denoted by the pentavalent actinyl(V) having linear structures, which is consistent with the proposal of 5f-orbital covalency plays an important role in structure-directing.⁴⁵ As a result, the change from the O_h -symmetry of **3**-Pa to the *low*-symmetry of **3**-U to **3**-Cm. The hypothesis was proven by molecular orbital composition analysis on the $[\text{O}_t\equiv\text{An}=\text{O}_{\text{act}}]^{1+}$ units (Table 5). In the $\text{O}_t\equiv\text{An}=\text{O}_{\text{act}}$ unit, the $\text{O}_t\equiv\text{An}$ linkage is largely consistent and barely changed. The $\text{An}=\text{O}_{\text{act}}$ linkage, on the other hand, is much more variable and underpin the $\text{O}_t\equiv\text{An}=\text{O}_{\text{act}}$ angle. In the $\text{An}=\text{O}_{\text{act}}$ linkage, the σ -component is much more pronounced and plays the structural directing role.⁴⁵ Our analysis indicates a linear correlation between the f-orbital contribution in the σ -component of the $\text{An}=\text{O}_{\text{act}}$ linkage and the $\text{O}_t\equiv\text{An}=\text{O}_{\text{act}}$ angle (Figure 5). The linear correlation unequivocally proves that the f-orbital covalence is the factor driving the formation of linear $\text{O}_t\equiv\text{An(V)}=\text{O}_{\text{act}}$ units, which subsequently promote the change of symmetry.

Figure 5. The correlation between the f-orbital contribution in the $\text{An}=\text{O}_{\text{act}}$ σ -component and the $\text{O}_t\equiv\text{An(V)}=\text{O}_{\text{act}}$ angle.

The results indicate that for the transuranic elements up to Cm, the 5f-orbital spatial overlapping covalence has a trans-directing structural influence, i.e. the inverse-trans-influence (ITI) operates in the U(V) to Cm(V) actinyl ions. This is further supported by the electron localization function (ELF) analysis of the type-A $[\text{O}_t\equiv\text{Pa}(\text{V})=\text{O}_{\text{act}}]^{1+}$ unit and the type-B $[\text{O}_t\equiv\text{Am}(\text{V})=\text{O}_{\text{act}}]^{1+}$ unit (Figure 6). There is significant electron-pair density between the An(V) and O (as displayed by the light-blue color) corresponding to 6d-orbital bonding for Pa and 5f-orbital bonding for Am, respectively.

Figure 6. ELFs for $[\text{Pa}(\text{V})_6\text{O}_{14}]^{2+}$ and $[\text{Am}(\text{V})_6\text{O}_{14}]^{2+}$ based on the PBE/TZ2P SR-ZORA level of theory optimisation. The surface defined by two actinyl units.

Another structural feature in the type-B $[\text{An}(\text{V})_6\text{O}_{14}]^{2+}$ clusters is the presence of **actinyl-actinyl interaction** between the linear $[\text{O}_t\equiv\text{An}(\text{V})=\text{O}_{\text{act}}]^{1+}$ cations (**Figure 4**). The **actinyl-actinyl interaction** is ubiquitous in the $[\text{O}=\text{U}(\text{VI})=\text{O}]^{2+}$ chemistry and has increasing description in $[\text{O}=\text{U}(\text{V})=\text{O}]^{1+}$.⁴⁶⁻⁴⁹ and $[\text{O}=\text{Np}(\text{V}/\text{VI})=\text{O}]^{n+}$ chemistry,⁵⁰ but is unknown for heavy transuranic elements beyond Np. For the first time, our calculations of **3-Pu**, **3-Am** and **3-Cm** clearly prove the presence of the **actinyl-actinyl interaction** in the Pu(V), Cm(V) and Cm(V) oxo clusters. In comparison, for the **3-Pa**, the Pa(V)–O_b bond (2.298 Å) and the Pa(V)–O_{act} bond (2.263 Å) are nearly equivalent, and are both in the region of Pa(V)–O single bond. Thus, the elemental structural unit of **3-Pa** is best described as Pa(V)≡O_t supported by multiple Pa(V)–O single bonds (Figure 4, type-A), instead of $[\text{O}=\text{Pa}(\text{V})\equiv\text{O}_t]$. Thus, there is no **actinyl-actinyl interaction** in the **3-Pa**.

Considering cleaved and created bonds, transition of type **A** to type **B** is comparable to isomerisation of hydroxide $[O=An(OH)_2]^+$ to hydrated actinyl, $(H_2O)(AnO_2^+)$, with hydrolytic energy gradually increasing from 0 kcal/mol for $An = Pa$ through 28 kcal/mol for $An = Pu$ and to 36 kcal/mol for $An = Am$. The results of hydrolytic conversion of two $An-OH$ to an $An=O_{yl}$ is analogous to transformation of **actinyl-actinyl interaction** structure type **A** to type **B**, indicating that $[PuO_2]^{1+}$ is predicted to be more favourable to being type **B** than that of $[PaO_2]^{1+}$, due to the well-known bonding transit in chemical bonding of actinyl(V). In most of the diamondshaped **actinyl-actinyl interaction** clusters, the uranyl units preserve a linear geometry. In addition, combination of two $[AnO_2]^{1+}$ yielding type **B** structure for the bare **actinyl-actinyl interaction** is the most favourable but still inherently unstable towards Coulomb dissociation, as quantified by the computed energy (kcal/mol), *i.e.* 35.6 at PBE, 46.4 at B3LYP and 40.3 kcal/mol at coupled cluster. Our results for the formation energy of $[An(V)_6O_{14}]^{2+}$ via the reaction of $2[An(V)_3O_7]^{1+} \rightarrow [An(V)_6O_{14}]^{2+}$ show that three AnO_2^+ linked by one O^{2-} anion within $[An(V)_6O_{14}]^{2+}$ framework the induce the **actinyl-actinyl interaction** structure type **B**, which is thermodynamically stable, with exoenergies of 17.3, 19.9, 18.9, 16.8, 12.2, 7.6 kcal/mol at PBE level for Pa, U, Np, Pu, Am and Cm, respectively.

3.3 $[Pa(V)_6O_{14}]^{2+}$ vs $[M(V)_6O_{14}]^{2+}$ (M: V, Nb, Ta)

To develop an understanding of the periodic trend of the $[M_6O_{14}]$ clusters, we calculated the structures of the group 5 metal oxo clusters at +4 and +5 oxidation states. The $[M(V)_6O_{14}]^{2+}$ (**3-M**) and $[M(IV)_6O_{14}]^{4-}$ (**4-M**) (M: V, Nb, Ta) are found to be all thermodynamic feasible. The $[M_6O_{14}]^{2+}$ ion has an O_h structure with a ground state of a M d^0 center double-bonded with an oxo ligand and ionically bonded with four close-shell peroxido(O_2^{2-}) unit, which renders +V oxidation state for transition-metals. To rationalise the different structural feature of the polyoxometalates of $[Pa(V)_6O_{14}]^{2+}$ vs $[M(V)_6O_{14}]^{2+}$, respectively, we the quantitative analysis of M–M bonds in **Figure 7**. We note that along the increment of atomic number, M–M bond length elongates largely and the BO_{G-J} increase slightly but remain very weak, reflecting the weaker d-d interactions of the *nd* metals V, Nb and Ta, respectively. In contrast, when the Pa–Pa bond is obviously stronger than the M–M bond, the BO_{G-J} of Pa–Pa bond is as large as 0.12, caused by the 5f-5f interactions within two actinides. And also, the extra 5f-2p interaction in

Pa–O_b of [Pa(V)₆O₁₄]²⁺ cluster leads to significantly stronger bonding comparing to the [M(V)₆O₁₄]²⁺ clusters, consistent with the following MO analyses.

Figure 7. The trend of M–M and M–O_b bond order verse their bond lengths for [M₆O₁₄]²⁺.

Concerning the electronic structure, the closed-shell [M₆O₁₄]²⁺, contains 14 oxide anions, each with 3 valence electron pairs, i.e., $14 \times 3 = 42$ pairs in total. Those oxygen 2p group orbitals yielding pairs of π_u and π_g bonding type are stabilised by the metal *nd* AOs, thus the low virtual valence shell of M(V)-*nd* AOs or Pa(V)-5f AOs possessing at least 2.100 eV above the filled oxygen ligand orbitals. **Fig. S1** displays the localised cluster MOs for the case of M = V and Pa under the *O_h* irreducible representation and **Figure 8** shows the MO diagram of the series of [M₆O₁₄]²⁺ clusters. In common, all HOMOs are mainly composed of antibonding ligand orbitals (4t_{1u} and 3t_{2g}) except for [Pa₆O₁₄]²⁺, where the HOMOs are composed by the orbitals for the Pa≡O_t triple bonds that for the V≡O_t triple bonds are so strong as to lie in relatively energetical lower region. Upon the *n* increasing across the group of [M₆O₁₄]²⁺, the nonbonding MO, 1a_{2u} becomes more stable than the M≡O_t bonding MOs accounting for enhanced bonding interactions between the M *nd_{xy}* orbital and the O_b 2p orbital, whereas the M–O_b distances in these species decrease slightly because of the increased orbital splitting of bonding and antibonding orbitals. However, this trend is broken-up at M = Pa where the antibonding MOs are in lower energy region due to the mainly ionic Pa–O_b bond comparing to the strong covalent V–O_b bond because the

increased of *nd* levels account for the poorer energy match between the interacting O 2p and metal *nd* orbitals. As a consequence, we find a much less contribution of the Pa 6d AOs to the 1t_{2g} and 1t_{1u} bonding MOs (17.99% and 8.63%) than of the V 3d AOs to those two MOs (33.72% and 31.5%), respectively. In addition, the LUMOs (3e_g for V and 3t_{2u} for Pa) are mainly metal-based orbitals where 3e_g is V 3d-based MO and 3t_{2u} is Pa 5f-based MO. Combined with increased HOMO–LUMO gaps traversing the column, therefore, the penta-valent [Pa₆O₁₄]²⁺ clusters indeed being structural stable which has unique bonding character orbital interactions in the group 5.

Table 7. the percentage contributions of the *nd*_{±1} and 2p_{±1} AOs to the 1t_{2g} and 1t_{1u} MOs in [M(V)₆O₁₄]²⁺ (TM: V, Nb, Ta and Pa).

[M(V) ₆ O ₁₄] ²⁺	1t _{2g}		1t _{1u}	
	O 2p	<i>nd</i>	O 2p	<i>nd</i>
V	64.12	33.72	64.13	31.5
Nb	67.48	30.51	63.27	28.68
Ta	69.90	26.34	72.98	15.31
Pa	76.14	17.99	79.40	8.63

Figure 8. Scalar relativistic MO energy levels of $[\text{Pa}(\text{V})_6\text{O}_{14}]^{2+}$ and $[\text{M}(\text{V})_6\text{O}_{14}]^{2+}$ (M: V, Nb, Ta).

4. Conclusions

In this work, employing comprehensive theoretical calculations, we resolved the problems of -OH location in the experimentally synthesised $[\text{M}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ clusters **1-M** (M: group-4, Ce, Th to Cm), and predicted the structures of the experimentally challenging tetravalent transuranic $[\text{An}(\text{IV})_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ clusters. By conducting 6-electron oxidation of the **1-An** *in silico*, we found that the oxidation could be metal-based or ligand-based, resulting in $[\text{An}(\text{V})_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$ (An: Pa, U, Np) or $[\text{An}(\text{IV})_6(\cdot\text{O})_4(\cdot\text{OH})_4\text{L}_{12}]^{6+}$ (An: Pu, Am, Cm), respectively. The factor underpins the divergent oxidation behaviours was identified as the relative valence-shell orbital energies of the metal-based f/d orbitals and the ligand-based 2p-orbitals.

Moreover, our calculations suggested that the pentavalent An(V)-oxo clusters $[\text{An}(\text{V})_6\text{O}_{14}]^{2+}$ (**5-An**) (An: Pa to Cm) are thermodynamically available. Their structures were found to be dependent on the f-orbital spatial overlapping covalence of the $\text{An}(\text{V})=\text{O}_{\text{act}}$ bonds. The An(V) except Pa(V) exhibit a

significant level of the f-orbital covalence in the $\text{An(V)=O}_{\text{act}}$ bonds, which favours linear $[\text{O}\equiv\text{An(V)=O}_{\text{act}}]^{1+}$ unit ensuing assemble via the a actinyl-actinyl interaction into the low-symmetric clusters.

This work will provide a guidance that the f-orbital covalence underpins the formation of linear pentavalent actinyls $[\text{O}=\text{An(V)=O}]^{1+}$, which aggregate into the $[\text{An(V)}_6\text{O}_{14}]^{2+}$ clusters via the actinyl-actinyl interaction, which could be some meaning for the experimental synthesis of the pentavalent transuranic oxo-hydroxo and oxo clusters.

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Supporting Information

Mulliken charge and spin density of $[\text{An}_6\text{O}_4(\text{OH})_4\text{L}_{12}]$ and $[\text{An}_6\text{O}_4(\text{OH})_4\text{L}_{12}]^{6+}$; Geometric parameters of $[\text{An(IV)}_6\text{O}_{14}]^{4-}$ (An=Th, Pa, U, Np, Pu, Am, Cm) clusters, $[\text{M(IV/V)}_6\text{O}_{14}]^{4-/2+}$ (M = V, Nb and Ta) and $[\text{Pa(V)}_6\text{O}_{14}]^{2+}$ at the SR-PBE level; Contour plots of frontier molecular orbitals of $[\text{Pa}_6\text{O}_{14}]^{2+}$ and $[\text{V}_6\text{O}_{14}]^{2+}$.

Conflict of Interest

There is no conflict of interest to report.

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A systematic theoretical study on the structures and stabilities of metal oxo-hydroxo clusters $[M(IV)_6O_4(OH)_4L_{12}]$ (M: Ti, Zr, Hf, Rf, Ce, Th to Cm; L: O_2CH^-) and $[An(V)_6O_4(OH)_4L_{12}]^{6+}$, metal oxo model clusters $[M(IV)_6O_{14}]^{4-}$ and $[M(V)_6O_{14}]^{2+}$ (M: V, Nb, Ta, Pa to Cm), predicting the feasibility of pentavalent actinyl clusters, demonstrating the structurally directing role of 5f-orbital in the formation of linear $[O\equiv An(V)=O]^{1+}$, and expanding the concept of actinyl-actinyl interaction into pentavalent transuranic actinyl clusters.