Structural and Spectroscopic Characterization of an Einsteinium Complex

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Summary Paragraph

The transplutonium elements lie at the edge of the periodic table, where patterns and trends used to predict and control physics and chemistry for transition metals, main group elements, and lanthanides break down. Understanding properties of these heavier elements has traditionally been restricted by their scarcity and high radioactivity, and this is especially true for einsteinium (Es), the heaviest element on the periodic table that can currently be generated in sufficient quantities to allow for classical macroscopic studies.[1] Overcoming experimental hurdles due to radioactivity and scarcity to study Es is a long-standing challenge within actinide chemistry, and here we demonstrate that we were able to characterize a coordination complex of einsteinium (Es), using less than 200 ng of ^{254}Es ($t_{½}$ = 275.7 days), with an organic hydroxypyridinone-based chelating ligand. Structural studies resulted in the first measurement of the Es L_3 absorption edge energy and the first measurement of an Es bond distance. Photophysical measurements revealed antenna sensitization of Es^{III} luminescence and a hypsochromic shift upon metal complexation, which is unprecedented for earlier actinide elements, and indicative of an intermediate coupling scheme in which *j-j* coupling becomes prevalent over Russell-Saunders coupling. These results are presented within the larger context of previous actinide complexation studies[2] and highlight the need to continue thoroughly charting the unusual behavior of the 5*f*-elements, especially those that are scarce and short-lived.

Main Text

The high radioactivity, scarcity, and continuous decay of Es isotopes have precluded this element from receiving the same attention as its preceding neighbors within the actinide series, whose bonding, electronic structure, and chemical properties are assumed to be intermediate between those of the transition metals and the lanthanides.[1] This unusual chemical behavior is often attributed to the emergence of the 5*f*-orbital manifold, large spin-orbit coupling, and significant relativistic effects,[3] and all of these properties are known to increase across the actinide series.[4] Contemporary worldwide availability of Es is limited to small-scale quantities (ng to μg) of one of its two long-lived isotopes, ^{254}Es ($t_{½}$ = 275.7 days), which is ~300 times more radioactive than its longer-lived transplutonium neighbors ^{249}Bk and ^{249}Cf.[5] However, there are limited examples demonstrating how technical challenges associated with working with transplutonium elements can be overcome, even for elements that are difficult to handle like Es. Highlights from the few previous Es studies include establishing nuclear properties from Es isotopes,[6] purification of Es from neighboring actinides,[7-9] and initial reports documenting various Es ionization potentials and thermodynamic properties.[1,10] A few simple inorganic compounds - oxides and halides - of Es have also been previously prepared. These compounds have been characterized in terms of their unit cell parameters and some optical measurements have been reported.[1,11-14] Thermodynamic stability constants have also been measured for a limited series of common complexing agents (Cl^-, OH^-, SO_4^{2-}, SCN^-) and chelators (ethylene diamine tetraacetic acid and diethylene triamine pentaacetic acid), using radioactive tracer methodologies.[1,15-18] Beyond this, the chemistry of Es is completely unexplored and as a result there is insufficient experimental data available to validate theoretical predictions regarding structure and bonding. One reason it is difficult to make accurate predictions for Es is because of its unique location on the actinide series. For example, it is unclear which oxidation states will be stable in numerous chemical environments since Es is bracketed between larger minor actinides (Am, Cm, Bk, Cf) that favor the +3 oxidation state and smaller late actinides (Fm, Md, No, Lr), for which the +2 oxidation state becomes stable.[3] Predicting reactivity and electronic structure changes during a chemical process is often beyond reach for Es because – in comparison to other actinides – the Lewis acidity for Es is large, its ionic radius is small, and Es has a substantial number of unpaired 5f-electrons (Es^{III} is $5f^{10}$).[2]

Here, we report on how the challenges to working with small quantities of ^{254}Es (<200 ng) were overcome to characterize the first Es-coordination complex in both solution and as a solid, leading to a breakthrough in Es chemistry. In these studies, the octadentate hydroxypyridinone ligand 3,4,3-LI(1,2-HOPO) (Fig. 1), denoted HOPO hereafter, was chosen as the complexing agent for its well-established chelation properties with both transition metals and *f*-elements, and because of its propensity to act as a luminescence sensitization antenna. This latter characteristic allowed for the detection of the Es luminescence spectrum, even with less than 170 ng available for study. Moreover, these luminescence measurements strongly suggested that Es was in the +3 oxidation state when chelated by HOPO. These optical results complemented structural characterization of the corresponding complex using trace level X-ray absorption spectroscopy (XAS) measurements at the Stanford Synchrotron Radiation Lightsource (SSRL).

For XAS studies, ^{254}Es (17 μM, 40 μL) was complexed with HOPO at a 1:10 metal:ligand ratio in aqueous solution buffered at pH 7-8 to ensure full ligand deprotonation and formation of a single Es species, $[Es^{III}(HOPO)]^-$ (Fig. 1). The solution was then dropcast into a 3D-printed sample holder, the resulting solid residue triply-contained, and the sample cooled with liquid nitrogen (~77 K), prior to collecting the Es L_3-edge XAS spectrum in fluorescence mode. Balancing moderate brightness from SSRL with trace level detection capabilities provided by the 100-element Ge detector on beamline 11-2 enabled data collection over 84 hours at the Es L_3-edge, using only 175 ng of ^{254}Es. The X-ray absorption near edge structure (XANES) spectrum from $[Es^{III}(HOPO)]^-$ showed no systematic changes with time and no evidence of beam-induced damage was observed. In 1967, Bearden and Burr predicted the Es L_3-edge energy to be 20,410 eV, using Slater-Dirac energy level calculations;[19] herein we measured this absorption edge for the first time using $[Es^{III}(HOPO)]^-$ (Fig. 2). Energies for the main absorption peak maximum (white line) and the inflection point (E_0, which is directly correlated to the binding energy of the $2p_{3/2}$-core shell of the ionized electrons) were determined at 20,390.0(1) and 20,385.4(2) eV, respectively (calibrated to the K-edge of a Mo reference foil; 20,000.0 eV). Both values are broadly consistent with the calculations of Bearden and Burr.[19] Since this sample is the first Es sample ever measured, these XANES results cannot be used to determine valence, which is normally determined with XANES by comparing to known standards. However, since optical measurements (*vide infra*) confirm the Es in $[Es^{III}(HOPO)]^-$ is Es^{III}, this XANES measurement is foundational and now provides an Es^{III} reference point to evaluate Es oxidation states in other compounds within a variety of matrices. Additionally, the shape of the XANES spectrum is very similar to those from other measured $[An^{III}(HOPO)]^-$ complexes, further confirming the oxidation state assignment of Es in $[Es^{III}(HOPO)]^-$ (Extended Data Fig. 1).

The local structure around the metal cation within the $[Es^{III}(HOPO)]^-$ complex was characterized using Es L_3-edge extended X-ray absorption fine structure (EXAFS) (Fig. 2 and Extended Data Table 2), and the results were consistent with complexation of Es^{III} by HOPO. The spectrum showed two features in the Fourier transform (FT) of the data at ~1.8 Å and ~3.2

Å, and an appropriate model for these data was developed based on previously calculated [M^{III}(HOPO)]$^{-}$ complexes.[2] The model included eight oxygen atoms in the first shell and a combination of four C and four N atoms in the second shell. As the coordination environment around Es is assumed to be due to HOPO complexation, we expect four C and four N atoms at nearly the same bond length. Since the spatial resolution of these data is only 0.24 Å, these shells are fully constrained together, but C and N lineshapes are still used for completeness, even though lineshapes for these elements are nearly identical (see the methods section for more details). Given this model, the fit to the transformed data resulted in an average Es–O bond distance of 2.38(3) Å [Debye Waller factor σ^2= 0.009(2) Å^2] and an average Es-C/N distance of 3.40(3) Å [σ^2= 0.012(7) Å^2]. As there are inherent challenges to modeling EXAFS data with such a limited *k*-range, we validated the Es–O bond distance from our model against previously determined M–O bond lengths in [M^{III}(HOPO)]$^{-}$ (M = Am, Cm, Cf) complexes as a function of the maximum wave vector (k_{max}) from the FT of the EXAFS data (Fig. 2).[2] All three actinide complexes show changes in best-fit bond distance as a function of k_{max} before stabilizing at ~7 Å^{-1}, with the most extreme variations observed for Am and Cf. In those cases, the stable Am–O and Cf–O distances (k_{max} > 7 Å^{-1}) were only ~0.03 Å different from data sets with a k_{max} of 6.5 Å^{-1} (Extended Data Fig. 3). Based on these analyses, we estimate the uncertainty of the Es–O bond distances to be on the order of ~0.03 Å. While the short k_{max} of these data precluded further analysis of the σ^2 in the fit (see methods section, *vide infra*), we also note that the EXAFS measured Es–O bond distance is representative of all eight M–O$_{HOPO}$ distances, which can span a wide range (up to ~0.1 Å) for metals with ionic radii similar to Es (such as Eu^{III}).[21]

Interpreting the L$_3$-edge XAS data was guided by complementary solution-phase luminescence spectroscopy on the same [Es^{III}(HOPO)]$^{-}$ complex. Gutmacher *et al.* were first to optically investigate Es^{III} doped into GdI_3 crystals.[13] Subsequently, Nugent and colleagues demonstrated Es^{III} could be sensitized *via* the antenna effect in Es-doped $CsGd(hfac)_4$ crystals (where hfac=hexafluoroacetylacetonate),[14] which until now remained the sole example of einsteinium luminescence sensitization. Upon excitation of the [Es^{III}(HOPO)]$^-$ sample at 31,250 cm^{-1}, we observed a single, broad peak at 9,950 cm^{-1}. We assign this feature to a transition from a first excited ($J = 5$) electronic energy level to the ground state ($J = 8$) of Es^{III} (Fig. 3), attributed here to the $^5I_5 \rightarrow {}^5I_8$ transition. This optical response confirms complexation of Es in the +3 oxidation state by HOPO,[22] and while the broadness of the $^5I_5 \rightarrow {}^5I_8$ spectra peak is atypical for $f \rightarrow f$ transitions, it is consistent with the one other example of aqueous Es^{III} luminescence,[23] and could be a result of the wide slit widths (see the methods section for details) that were necessary to obtain the spectrum highlighted in Fig. 3. In contrast with observations from other +3 *f*-block cations, the spectral peak of [Es^{III}(HOPO)]$^-$ was not bathochromically shifted when compared to the Es-aquo ion, which has a luminescence maximum of 9,259.3 cm^{-1}.[23] Instead, HOPO complexation induced a blue shift (+690.7 cm^{-1}) that is consistent with, but almost an order of magnitude larger, than the 77.8 cm^{-1} blue shift reported for Es-doped $CsGd(hfac)_4$ (9,337.1 cm^{-1}).[14] While these examples of blue-shifted Es^{III} luminescence appear to contradict the nephelauxetic effect, the $^5I_5 \rightarrow {}^5I_8$ transition is known to be hypersensitive. Hence, changes in crystal field and spin-orbit coupling could result in hyperfine splitting of the first excited and ground states of Es^{III}, thereby changing the energy gap between these two levels and resulting in a hypsochromic shift.[24,25] Of note, such behavior radically departs from the red-shifted luminescence commonly reported upon binding lanthanides and earlier +3 actinides (Am, Cm), for which Russell-Saunders coupling is known to predominate. It is possible these shifts to higher wavenumbers observed upon Es complexation are due to an increase of effective nuclear charge, itself resulting from an intermediate coupling scheme in which *j-j* coupling becomes prevalent over Russell-Saunders coupling.[26] Such transition to a different spin-orbit coupling regime from the earlier $5f^6$ Am^{III} and $5f^7$ Cm^{III} (as well as $5f^7$ Bk^{IV}) ions to $5f^{10}$ Es^{III} would be remarkable, and analogous near-IR luminescence spectroscopy experiments with $5f^9$ Cf^{III}, as well as multiconfigurational CASSCF calculations, will be employed to explore this behavior in future studies.

In summary, the first Es coordination complex was synthesized and characterized using complimentary XAS and luminescence spectroscopies. XANES and EXAFS measurements on $[Es^{III}(HOPO)]^-$ provided the first experimental measurement of the Es L_3 absorption edge energy and the first measurement of an Es bond distance. Luminescence spectroscopy results revealed the second instance of Es sensitization, via the antenna effect, with hypsochromic luminescence shifts evidenced in both systems upon metal complexation, which is unprecedented for +3 actinide (and lanthanide) HOPO luminescence. Combined with the short Es–HOPO bond distances and XANES analyses, the distinctively sensitive Es^{III} luminescence underlines the potential uniqueness of Es in comparison to the rest of the actinides. Finally, as all data were collected with <200 ng of metal, these results highlight the significant potential to further advance coordination chemistry across both the actinide series and the periodic table, when samples are only available in limited quantities.

Data availability

All data is available in the main text or extended data. Additional details are available upon request to the authors for purposes of reproducing or extending the analysis presented here.

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Author Contributions

K.P.C., K.M.S., S.A.K., and R.J.A. conceived the study and designed the experiments. K.P.C., K.M.S, and S.A.K. prepared the XAS sample. S.A.K., Z.R.J., and J.N.W collected XAS data. K.F.S., L.M.M., and C.H.B analyzed XAS results. K.P.C. and K.M.S prepared the photoluminescence sample. L.A-S., K.P.C., and T.M.M. collected luminescence data and interpreted the results. All authors discussed the experimental results and contributed to the manuscript.

Competing Interests

The authors declare no competing interests.

Additional Information

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Figure 1 | The organic ligand 3,4,3-LI(1,2-HOPO) (denoted HOPO) was selected to form an Es^{III} coordination complex suitable for structural and spectroscopic studies. The octadentate chelator is composed of four 1-hydroxy-pyridin-2-one metal binding units attached to a spermine scaffold (blue) through amide linkages; eight oxygen metal-binding atoms (red) serve as the first coordination sphere around Es^{III} upon ligand deprotonation and metal complexation.

Figure 2 | Structural features of the Es^{III}(HOPO) coordination complex were probed using element-specific L_3-edge XAS at 77 K. (**a**) XANES spectrum, (**b**) EXAFS data and fit, and (**c**) Fourier transform (FT) of the *k*-space data and fit for solid residue of Es^{III}(HOPO). Data were transformed between 2.5-6.6 $Å^{-1}$ using a Gaussian window with a width of 0.3 $Å^{-1}$, and raw unfiltered data error bars are estimated by the standard deviation of the mean between individual traces. The full data range for the raw data is shown in Extended Data Fig. 2. (**d**) The Es–O bond distance was validated against bond lengths determined from previously characterized $[M^{III}(HOPO)]^-$ (M = Am, Cm, Cf) complexes, highlighting a substantially shorter M-O bond in the einsteinium complex;[2] ionic radii taken from Lundberg *et al.*[20] Reported errors utilize a profiling method from the fit together with an estimate of probable systematic error from the limited *k*-range.

Figure 3 | Einsteinium luminescence sensitization was achieved upon chelation by HOPO, confirming the +3 oxidation state for einsteinium and revealing an unusual hypsochromic shift in metal emission. (**a**) Normalized emission of $[Es^{III}(HOPO)]^-$ in 1 M TRIS, pH 7-8, at 298 K upon excitation at λ = 320 nm with a Y48 bandpass filter (λ = 480 ± 5 nm). (**b**) Energy level diagram for complexed HOPO and $Es^{III}_{(aq)}$.[22,27]

Methods

General Considerations

Caution! ^{254}Es (t$_{½}$ = 275.7 days, 70.9 TBq/g) and ^{249}Cf (t$_{½}$ = 351 years, 150 GBq/g) are highly radioactive and decay to α-, β-, and γ-emitting isotopes. These isotopes as well as their decay daughters present significant health risks, and were manipulated only in facilities specifically designed for the safe handling of long-lived radioactive materials. All measurements were taken either in controlled facilities and/or using multiple containment procedures.

Materials

The ligand HOPO was prepared and characterized as previously described,[28] and a ligand stock solution was prepared by direct dissolution of a weighted portion into dimethyl sulfoxide (DMSO). All other chemicals used in this study were obtained from commercial suppliers and were used as received.

Preparation of XAS sample

The X-ray absorption spectroscopy (XAS) sample of ^{254}Es/^{249}Cf was assembled from aliquots of the metal and ligand stock solutions with a final metal:ligand ratio of 1:10 and an ^{254}Es concentration of ca. 17 μM. The ^{254}Es stock (175 ng) was prepped via direct dissolution into 3 M HNO_3 (10 μL) and the final sample was prepared in the stock container. 25 μL of 1 M TRIS was added to buffer the solution and allow for HOPO binding. HOPO was subsequently added (1 μL, 20 mM) and then the sample was buffered to pH 7-8 with an additional 5 μL of 1 M TRIS, resulting in approximately 40 μL of sample. The ^{254}Es(HOPO) solution was dropcast into a 3D printed sample holder (Extended Data Fig. 7, below) in 3 μL increments, and then loaded into an indium-sealed, triply-contained aluminum holder with Kapton windows (developed in house) within one week of synchrotron measurement.

XAS data collection and data treatment

XAS data were collected at the Es L_{III}-edge on beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a Si(220) double-crystal monochromator, fully tuned with vertical and horizontal slit sizes of 0.8 and 5.5 mm. For these experiments, higher harmonics from the monochromatic light were removed using a 370 mm Rh coated harmonic rejection mirror. The Rh coating was 50 nm with 20 nm seed coating and the substrate was Zerodur. The harmonic rejection cut-off was set at 23500.0 eV by the mirror angle, thereby controlling which photons experience total external reflection. Samples were held in a LN_2-cooled cryostat at 77 K throughout analysis and all XAS measurements were collected in fluorescence mode using a 100 element Canberra Ge detector and corrected for dead time. The data were energy calibrated to the main edge from a spectrum of Mo foil, setting the first inflection point of the Mo K-edge to 20000.0 eV. The dataset consists of 120 scans and sets of ten scans were averaged into a new file, yielding twelve averaged scans. Due to high levels of noise, each averaged scan was background subtracted independently. Data reduction and analysis were conducted using the RSXAP software suite[29-31] in conjunction with backscattering lineshapes and phases calculated using FEFF9.6,[32] which included the EXCHANGE card to apply a +15 eV correction to the Fermi level of the standards. Data were transformed between 2.5 and 6.6 $Å^{-1}$ using a Gaussian window with a width of 0.3 $Å^{-1}$ and all fitting was conducted in *r*-space. Error analysis was performed using a profiling method and in all cases the total number of fitting parameters was less than two-thirds the total number of independent points.

Due to limited mass of ^{254}Es in the sample, an extended data acquisition time was required (~84 hours). Over this length of time, beam induced changes to the sample could occur, and thus extended checks on the integrity of the sample were conducted. Extended Data Fig. 4

shows the first eight single XANES spectra collected from the sample with no significant changes in edge position or XANES structure. Due to the large amount of data collected on ^{254}Es(HOPO), every ten samples were merged to give twelve averaged scans. Extended Data Fig. 5 shows these averaged scans from oldest (top) to newest (bottom) demonstrating no apparent changes to the XANES spectra over the length of the measurement. This conclusion was confirmed with measurements of E_0 (as defined by the first inflection point of the main edge), and the main peak density or 'white line', neither of which showed any change as a function of time throughout the experiment (Extended Data Table 1). Collectively the data shown in Extended Data Figs. 4 and 5 and tabulated in Extended Data Table 1 strongly support the stability of the $[^{254}\text{Es}^{\text{III}}(\text{HOPO})]^-$ complex throughout the XAS measurement.

The fit model used for these data is similar, but not identical, to that used by Kelley and colleagues.[2] Here, the *k*-range is more limited, and so scattering pairs beyond the Es-C/N shell are not included, nor is any water coordination considered. Backscattering lineshapes and phases were calculated with FEFF 9.6[33] using the calculated $[\text{Am}^{\text{III}}(\text{HOPO})]^-$ structure from Kelley *et al.*[2] Due to differences in fit range, and the more updated use of the EXCHANGE card mentioned above when calculating the line shapes, there could be some enhanced systematic differences in the An-O bond length results between this study and those reported previously, and there are likely even larger differences in the Debye-Waller factors.

Since fitting to EXAFS data over such a limited *k*-range is not usually reported, we conducted a brief study for the Extended Data focusing on the effect of the short *k*-range on $[\text{An}^{\text{III}}(\text{HOPO})]^-$ fits using the data from Kelley *et al.*[2] For a direct comparison, the older data is refit using the exact same model applied to the Es data, so some small differences in the fit results with the original report are expected. Here, we focus only on the An-O average bond length as a function of the maximum wave vector, $k_{\max}$, used in the fit, and the results are shown in Extended Data Fig. 3. Although the Cm-O distance remains fairly constant as a function of $k_{\max}$ even for $k_{\max}$ as low as 5 Å^{-1}, more significant differences exist at low $k_{\max}$ for Am-O and Cf-O pairs. Using this limited data set, the maximum deviation from 6.6 Å^{-1} (the value used in the Es data) to a higher $k_{\max}$ where the bond length has stabilized is about 0.03 Å.

In the course of this analysis (Extended Data Fig. 8, 9, and 10), it became clear that a glitch exists in the Cf data reported previously between about 5 and 5.5 Å^{-1}, and hence the data at those values of $k_{\max}$ is unreliable.[2] This glitch could have had an effect on the previously reported Cf-O bond length, and so we have estimated a larger error for that pair in Fig. 2d.

Luminescence Spectroscopy

The luminescence sample of ^{254}Es/^{249}Cf was assembled from reprocessing the XAS sample described above. After reprocessing, γ-spectroscopy was used to determine ^{254}Es/^{249}Cf activity, which can be used to calculate sample mass, and the γ-spectrum was collected on an Ortec IDM-200-V High Purity Germanium Detector (P-type single crystal, 88mm diameter x 30 mm length) and calibrated using ^{133}Ba and ^{60}Co point sources. Using XUNDL due to discrepancies in the ENSDF evaluated data file, the ^{254}Es 2.17% intensity line at 61.89 keV was used to determine the total activity and mass of the sample, which was found to be 38.24 ng of ^{254}Es.[34] Preparation of the luminescence sample followed a similar protocol to what was used for XAS preparation, with ^{254}Es dissolved in 3 M HNO_3 (15 μL) and then partially buffered with 1 M TRIS (25 μL). HOPO was subsequently added (1.5 μL, 20 mM) and then the sample was buffered to pH 7-8 with an additional 40 μL of 1 M TRIS, resulting in approximately 82 μL of sample and a final ^{254}Es concentration of 1.88 μM. Emission and excitation spectra were measured on a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer equipped with a xenon lamp and a NIR detector at the Molecular Foundry, using a 10 nm excitation slit and 10 nm emission slit for the excitation spectrum (Extended Data Fig. 6), and a 14 nm excitation slit and a 20 nm emission slit for the emission spectrum, which likely broadened the excitation and emission peaks. Additionally, a 0.75 s acquisition time and a Y48 (λ = 480 ± 5 nm) bandpass filter to remove the third harmonic peak were used to collect excitation and emission spectra, and the final spectra were an average of ten individual measurements.

Methods References

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Extended Data

Extended Data Figure 1 | Comparison of XANES data for [An^{III}(HOPO)]$^-$ complexes. Am^{III}, Cm^{III}, and Cf^{III} spectra were reported previously,[2] and are compared to Es^{III} data reported herein.

Extended Data Figure 2 | Raw EXAFS data for [Es^{III}(HOPO)]$^-$. Data is shown as in Fig. 2b, but extended beyond the transform range used in the fit. Data show the effect of a wide monochromator glitch near 7 Å^{-1} that limited the data range.

Extended Data Figure 3 | M-O bond distance vs. the maximum wave vector used for the Fourier transform, $k_{\max}$, for [M^{III}(HOPO)]$^-$ actinide complexes previously characterized via EXAFS spectroscopy.[2] Note the difference in the fit model from ref. 2 as discussed in the methods section (*vide supra*). The worsening of the fits below 6.5 Å^{-1} is at least partially related to the loss of fit degrees of freedom. For instance, the numbers of degrees of freedom decreases from 3.3 to 1.2 going from a $k_{\max}$ of 6.5 Å^{-1} to 5.5 Å^{-1}. Note that the data for Am^{III} and Cm^{III} are of higher quality due to there being more material available. Samples masses are 27.1 µg, 10.9 µg, and 3.3 µg for Am^{III}, Cm^{III}, and Cf^{III} data, respectively.

Extended Data Figure 4 | Comparison of the first eight Es L$_{III}$-edge XANES scans collected for [Es^{III}(HOPO)]$^-$ at 77 K. Samples go in order from oldest (top) to newest (bottom)). Each scan required about 40 minutes.

Extended Data Figure 5 | Comparison of the averaged (oldest (top) to newest (bottom)) Es L$_{III}$-edge XANES scans collected for [Es^{III}(HOPO)]$^-$ at 77 K. Each averaged scan is taken from ten individual scans, and represents nearly four hours of data acquisition time.

Extended Data Figure 6 | Normalized excitation spectrum of [Es^{III}(HOPO)]$^-$ in aqueous solution. Spectrum collected upon monitoring at Es^{III} emission maximum (1005 nm).

Extended Data Figure 7 | Schematic drawings of 3D printed sample holder used for XAS measurements.

Extended Data Figure 8 | Comparison of backscattering lineshapes and phases for calculated [An^{III}(HOPO)]$^-$ complexes. Backscattering lineshapes and phases were calculated using the FEFF code described in the methods section.[33] The lineshapes of the An-O pairs are shown for FEFF calculations using the same structure and only varying the An species to demonstrate the lack of change with species. Note that these amplitudes are not k^3-weighted, as in Fig. 2 and Extended Data Fig. 2, and so there is no decrease above 4 Å^{-1} in the lineshapes used for fitting, but rather a change in slope.

Extended Data Figure 9 | Comparison of calculated XANES spectra for [An^{III}(HOPO)]$^-$ complexes. Spectra were generated from FEFF 9.6 calculations using a self-consistent field cluster of 6 Å and a full-multiple scattering cluster of 4 Å. Calculations on actinides generally overestimate the amount of 5*f* charge transfer when included in the valence orbitals, and so these orbitals are treated as core orbitals here. Note that the core-hole lifetime broadening used by the code increase from 8.7 eV to 10.3 eV from Pu^{III} to Es^{III}, the effect of which is visible in the increased broadening of the spectra.

Extended Data Figure 10 | Comparison of local density of states for the d orbitals from the calculations in Extended Data Figure 9. The spectra are plotted relative to the vacuum energy. The Fermi energy in all these calculations is about -7.6 eV above which the states are unoccupied, and therefore accessible to XANES. The calculations clearly show the 6d splitting between -5 and 0 eV. Note that the splitting *decreases* by about 0.6 eV from Pu^{III} to Es^{III}, in contrast to the increase in core-hole lifetime broadening. These effects are, nevertheless, washed out in the final calculation in Extended Data Figure 9 by the much larger core-hole lifetime broadening.

Extended Data Table 1 | Summary of [Es^{III}(HOPO)]$^-$ XAS features. All energy values are calibrated against the first inflection point of the Mo K-edge set at 20000.0 eV. E_0 was defined as the peak in the first derivative of the Es L_3-edge data from the [Es^{III}(HOPO)]$^-$ sample.

Extended Data Table 2 | Summary of EXAFS fits for [Es^{III}(HOPO)]$^-$. * indicates fixed parameters. N represents coordination number assuming an amplitude reduction factor of 1.0, R denotes the interatomic distance, σ^2 represents the Debye-Waller factor, and ΔE_0 represents the energy shift from the calculated energy Fermi level which had a correction applied in the FEFF calculation (see methods text above). The data were transformed over a k-range of 2.50-6.60 Å^{-1} with a Gaussian window of 0.30 Å^{-1}. The data were fit over a R range of 1.2-3.6 Å giving a total number of independent points of 8.3. The fit uses 5 parameters and thus has 3.3 degrees of freedom. Reported errors utilize a profiling method from the fit together with an estimate of probable systematic error from the limited *k*-range (Extended Data Fig. 3).[31]