
Supplementary information

**Structural and spectroscopic
characterization of an einsteinium complex**

In the format provided by the
authors and unedited

Peer Review File

Manuscript Title: Structural and Spectroscopic Characterization of an Einsteinium Complex

Editorial Notes:

Redactions – Third Party Material

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

This is an extremely interesting manuscript describing the one of the first ever coordination complexes of Es(III), which is an extremely radioactive element and as such, there is immense difficulty in manipulating the sample, let alone to perform spectroscopic measurements. The first report of an Es(III) molecular complex and its emission spectrum in the solid state doped into the Gd(III) complex was in 1970 and the second in solution in 1983 by Beitz. The same paper by Beitz also documented an Es(III) complex in solution with HDEHP but the emission spectrum was not reported here (and only the emission lifetime was reported).

The authors have quite rightly used the coordination chemistry they have previously developed for lanthanide and actinide chemistry. The results presented are likely to open the door to trans-Cf chemistry and are instrumental to advancing this new and growing field.

However, although the use of XAS to characterise an Es complex is new and very challenging, it is not in itself a new concept in actinide chemistry, although ultra trace studies have been performed. This combined with the fact that the luminescence of Es(III) is not completely unprecedented, makes me wonder if this paper meets the requirements for publication in Nature, given there are 2 examples in the literature and one could argue that both techniques do not unambiguously assign the +III oxidation state. However, given its overall general importance and potential contribution to the field I do believe publication in a journal such as Nature can be justified, provided the authors can expand a little on my queries below (if not suitable for the main text, at least in the ESI).

Principally, this is because a blue shift (hypsochromic shift) in the Es(III) emission is a really important finding in light of other actinides which all (I believe) show a red shift (bathochromic shift) upon complexation with a ligand. This then says something about the nature of the excited state and indicates that emission spectroscopy is possibly an excellent way of characterising the physical properties of Es(III) coordination complexes.

However, the fact that the emission may be an admixture of f-f emission and some charge transfer (depending on the redox potentials of Es(III)/(II) cannot be completely discounted here. The redox potentials are not really known as far as I know) and/or the blue shift extra evidence for breakdown of

RS coupling-this can be explained in more detail (perhaps in the ESI) by adding in the approximate energy levels expected if j-j coupling dominated.

Perhaps a comparison of the excitation spectra from HOPO-An complexes compared to HOPO-Es can help? Are any other transitions observed in the excitation spectra (outside the spectral window shown in the ESI?)

I am not at all an expert in XAS, so I cannot really comment on this aspect, but all other aspects of the work appear to have been performed to a satisfactory level.

I have a few queries I would like the authors to expand upon.

1. Was a UV-vis-nIR spectrum of the sample obtained? (even if it just showed ligand absorption of the HOPO chromophore?) Can the authors comment on this at all?
2. Did the authors record the emission spectrum without the appropriate filter in effect to see the 3rd harmonic of the excitation wavelength to compare the spectra? This is important in discussing the line widths/fwhm, which are a very important aspect to comment on, especially in comparison with the previously reported beta-diketonate spectrum (which shows fine structure in the solid state) and the Beitz paper from 1983. What I suggest the authors do is repeat the luminescence experiment with just the ligand under the exact same conditions to look at the features of the 3rd harmonic and add this to the ESI with a comment.
3. Can the authors expand on the fact that j-j coupling seems to dominate over RS-coupling and its implications on the form of the emission spectrum? Are there any implications on the bonding and the hypsochromic shift that can be related to the XAS data at all? Are there any differences/comparisons that can be drawn from the absorption/excitation spectra? What is the shoulder in the excitation spectrum around 420 nm due to? (real feature or Raman band from water?)
4. Were the authors able to perform any lifetime measurements? In principle, this should be feasible with the set up and the lifetime should be microseconds.
5. In Figure 3, the wavelength of the filter should be included and in the caption 'free HOPO' changed to 'uncomplexed HOPO'.
6. The phrase in the introduction "Moreover, these luminescence measurements unambiguously established that Es was in the +3 oxidation state when chelated by HOPO" is a little strong in the absence of other data such as absorption spectroscopy, here since only 2 other examples with emission spectra are really reported in the literature. I suggest re-phrasing this sentence.

All references are appropriate and cite appropriate previous literature.

Referee #2 (Remarks to the Author):

Actinide elements are localized at the almost far end of the periodic table, they correspond to the filling of the 5f orbitals, just before what are called the "super heavy" elements (with 6d filling). Although the first half of the actinide series has been relatively well investigated, the second half has been much less studied. The element that is the subject of this article, Es, is very rarely reported and its chemistry is scarcely described.

A. Whether or not Es follows the trends of the second half of the actinide series (in terms of radius contraction and dominant stable oxidation state +III for instance) is a key question of fundamental chemistry at the bottom of the periodic table. The originality of this work is therefore to report on the first structural and electronic data of Es in a coordination complex with HOPO ligand.

The authors have performed two sets of spectroscopic measurements : XAS at the Es LIII edge

performed for the first time and luminescence spectroscopy. Both techniques enable to characterize the physical chemical state of the complex although the technical difficulties associated with Es itself limit interpretation of the data.

B. This work is therefore more of a technical challenge that makes a world premiere than a full scientific story. Nonetheless for its own technical achievement and new data set on a very rare element, I would recommend publication in Nature after considering the following remarks.

C-D, F

1) I-64 a solid state compound is mentioned. But there is no other mention in the text of a solid state compound. This should be clarified.

2) I-98 LIII edge is $2p_{3/2}$ core electron, j should be added at this level of details.

3) Fig2. I understand EXAFS noise must increase very quickly after $k = 6 \text{ \AA}^{-1}$. A noise estimate should be given. In order to judge of noise increase it would be of interest to see the EXAFS data up to a higher k value. In other words EXAFS data should be provided up to a k value larger than the FT window. Also on I-117 spatial resolution should be provided and discussed.

4) I-119. Given the spectral resolution it is difficult to believe that 3 Es shells are needed (and are significant) for the fit. From Table S2 it is not completely clear if Es-C and Es-N are the same contribution or if 2 contributions with only 1 set of parameters (but with the same distances ?) have been used. In any case, justification of the use of two additional shells must be provided (with significant improvement of Quality factor for instance). This also refers to the previous remark.

5) I-125. In this section, the error in M-O distance is estimated as a function of the EXAFS k range. Clearly, bond distances and uncertainties vary with k range (which is well known in EXAFS spectroscopy). The variation of this variation seems to increase from Am to Cf. This is particularly clear for Cf for which the error bar at $k = 6 \text{ \AA}^{-1}$ is about 0.1 \AA . This could be linked with the evolution of the shape of the amplitude function of M as Z increases. I suggest the authors discuss more carefully this part (that is essential because half of the paper is about the Es-O distance value). In particular the amplitude functions $f(k)$ for Am \rightarrow Es could be plotted as a function of k (using feff code for instance) and compared. Trend could even be extended after Es.

6) I-127 and Fig. 2. The trend in M-O distances from Am to Es is not really discussed. If purely electrostatic interaction would occur between M and HOPO, a decrease of distances following the actinidic contraction is expected. This is not the case in Figure 2. What is the conclusion ?

7) I-141 please use the entire state notation (I) and not just J.

G. To strengthen the discussion, comparison with M-O distances in hydrates and/or aquo species might be added (with related references). Crystallographic data of the M(III) hydrates up to Cf have been provided as well as EXAFS data in aqueous solution.

H. The nuclear characteristic of isotope ^{254}Es are briefly given in the summary but not in the introduction. It should be added as well in the introduction for general interest. More generally, introduction is too brief and should better highlight the originality of Es chemistry, what is expected from general trends along the actinide series and in particular within the second half of the series.

The manuscript reports the structural and spectroscopic characterization of an einsteinium coordination complex. Since the availability of einsteinium is limited to small quantities - It is undoubtedly important scientific achievement. However, from a practical point of view, this paper will be of interest to the narrow circle of scientists.

The manuscript is quite short and focused on data, obtained by two experimental methods: Luminescence measurements and X-ray absorption spectroscopy. The luminescence data is not quite unique – since it was previously reported on Es systems (authors cite nicely a previous works in that field). I am just impressed that Es(III)HOPO complex induced a blue shift.

One question, which authors address through the manuscript is the Es the oxidation state. I dont understand why authors focus on it since Es compounds can only be present in oxidation state III. The luminescence data itself perhaps can be used as confirmation of the oxidation state, but I believe the best is to compare luminescence data on Es(III) with Ho(III) and Ho(II) complexes. The number of the 4f and 5f electrons in Ho(III) ground state and Es(III) ground state is similar. Since Es(II) can not exist and no comparison can be made, the spectral profile of Ho can be discussed in details, since luminescence data is quite different between Ho(II) and Ho(III).

The XANES method was used by authors to proof the presence of the Es(III). XANES itself can not confirm the presence of the Es(III) oxidation state if only one spectrum is recorded. The general practice is to record data on reference systems and look at the energy shifts recorded in data of unknown compounds (as reported in Fig. below) – Pu(III) definitely has an oxidation state of (III), since it is shifted towards low incident energy for comparing to the Pu(IV). XAS data in the present manuscript is shown only on one system – I suggest that authors reformulate discussion and delete any statements that XANES proofs the existence of the Es(III). In fact, if nobody would say to me that this is the spectrum of Es, I would think that actinide compound is in the oxidation state (IV), since L3 spectral shape is very similar to the PuO₂ and UO₂.

[Figure redacted – third party material]

What is definitely new here is the experimentally recorded value of Es L3 edge energy. Moreover, the authors report the EXAFS results and structural characterization of Es complex. Even that data was recorded in short energy region (up to 6-7 Å⁻¹) and I have my doubts how correct the bond distances were estimated, still, its obviously new piece of data. What I am missing in the analysis of Es L3 XAS data is the electronic structure calculations and I am sure that a group of authors can easily perform it. Especially here, when the structure is determined by EXAFS. One can use several codes to obtain the shape of the Es L3 edge XANES and to compare it to the experimental results. I believe paper will be much stronger - I am curious to see the crystal field splitting of the Es 6d states near the Fermi level (and compare to other actinides in series of Am, Cm, Bk, Cf, Es etc).

Author Rebuttals to Initial Comments: (please note that the authors have quoted the reviewers in black and responded in red)

Referee 1 Comments:

This is an extremely interesting manuscript describing the one of the first ever coordination complexes of Es(III), which is an extremely radioactive element and as such, there is immense difficulty in manipulating the sample, let alone to perform spectroscopic measurements. The first report of an Es(III) molecular complex and its emission spectrum in the solid state doped into the Gd(III) complex was in 1970 and the second in solution in 1983 by Beitz. The same paper by Beitz also documented an Es(III) complex in solution with HDEHP but the emission spectrum was not reported here (and only the emission lifetime was reported).

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However, the fact that the emission may be an admixture of f-f emission and some charge transfer (depending on the redox potentials of Es(III)/(II) cannot be completely discounted here. The redox potentials are not really known as far as I know) and/or the blue shift extra evidence for breakdown of RS coupling-this can be explained in more detail (perhaps in the ESI) by adding in the approximate energy levels expected if j-j coupling dominated.

Our Response: Es has not been observed in the +2 oxidation state in solution; however, it is predicted to have an accessible redox couple between -1.2 and -1.5 V (per Hulet, *Radiochim. Acta*, 1983, 32, 7- 23). Thus we cannot rule out charge transfer contributions, but this was not something we could explore as part of this study due to the very limited quantity of Es we had to work with. In terms of the Es energy levels, those included in Figure 3B are taken from Carnall *et al.* (*J. Chem. Phys.* 1973, 59, 1785-1789). The calculations in this paper are for the $5f^{10}$ configuration and are free ion calculations only. As such, the matrices are calculated (and fit) for individual J levels and all the J levels are included in the calculations, thus there would be no difference in energy levels, except the labels used to describe them, if j-j or RS coupling dominated. However, Carnall *et al.* do note that eigenvectors for Es are so mixed in character that S and L are not meaningful quantum numbers, suggestive of a mixing of RS and j-j coupling in their analysis, which we have utilized here. To fully elucidate manifestations of j-

j or intermediate coupling systems for Es would require multiconfigurational CASSCF calculations similar

to those recently detailed by Celis-Barros *et al.* for Bk(IV) (Int. J. Quantum Chem., 2020,120, e26254), which are beyond the scope of this study and our current capabilities.

Action Taken: The last sentence of the luminescence section has been updated to incorporate what follow-up efforts will focus on with regards to luminescence spectroscopy and reads, “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.”

Perhaps a comparison of the excitation spectra from HOPO-An complexes compared to HOPO-Es can help? Are any other transitions observed in the excitation spectra (outside the spectral window shown in the ESI?)

Our Response: Based on the referee’s suggestion we revisited two of our recent studies where we looked at the luminescence spectroscopy of HOPO with Am(III) and Bk(IV) (Am(III)-Dalton Trans. 2016, 45, 9912-9919; Bk(IV)-Nat. Chem. 2017, 9, 843-849). Excitation spectra were collected in both studies and with Am(III) the spectra were collected to 520 nm (see Fig. 2 in the Dalton paper), which is beyond the spectral window of the excitation spectra for Es-HOPO (now Extended Data Fig. 6). The only additional feature seen in either the Am(III) or Bk(IV) spectra, was an Am(III) f-f transition at ca. 510 nm, and the shape and fwhm of the spectra in all three studies can be correlated to the slit width used to collect data on each complex. For the Es-HOPO excitation spectrum, 10 nm excitation and emission slits were used and this likely broadened the excitation peak. There is an additional query about the excitation spectra below, so additional discussion is included there, but in terms of providing insight about coupling schemes we do not feel there is any additional information we can extract from the excitation spectra included in the Extended Data. Further, given the limited quantity and concentration of material, the excitation spectra in the Extended Data represents the highest quality data that was obtainable for this measurement.

Action Taken: none

I am not at all an expert in XAS, so I cannot really comment on this aspect, but all other aspects of the work appear to have been performed to a satisfactory level.

I have a few queries I would like the authors to expand upon.

1. Was a UV-vis-nIR spectrum of the sample obtained? (even if it just showed ligand absorption of the HOPO chromophore?) Can the authors comment on this at all?

Our Response: A UV-vis-nIR spectrum was not obtained for the sample, which was one of the many challenges we encountered when working with Es. Highly radioactive samples limit the suite of available instruments for collecting data, and those UV-vis-nIR instruments that were available would not yield results, given the limited volume and concentration of our solution sample.

Action Taken: none

2. Did the authors record the emission spectrum without the appropriate filter in effect to see the 3rd harmonic of the excitation wavelength to compare the spectra? This is important in discussing the line widths/fwhm, which are a very important aspect to comment on, especially in comparison with the previously reported beta-diketonate spectrum (which shows fine structure in the solid state) and the Beitz paper from 1983. What I suggest the authors do is repeat the luminescence experiment with just the ligand under the exact same conditions to look at the features of the 3rd harmonic and add this to the ESI with a comment.

Our Response: This was not done as part of our original experiments, but we have now collected data by performing the experiment suggested by the referee. The results of the experiment are unremarkable and just show a narrow, sharp peak at the third harmonic, as one would expect for a spectrum without a bandpass filter. We do not feel a spectrum of an excitation wavelength harmonic is worthy of inclusion in the manuscript/ESI; however, in an effort to add clarity, in-line with the referee's comment, we have updated the luminescence section of the manuscript to comment on potential causes of the broadness in the observed Es transition. Finally, we must respectfully push back on the referee's characterization of fine structure in the Es spectra of the hfac complex (Nugent *et al.* Chem. Phys. Lett. 1970, 7, 179-182). Two small peaks are shown for Es in Fig. 2A of the Nugent paper, neither of which exhibit any luminescence fine structure. While fine structure may be something that can be observed with Es, it will likely take greater quantities of material, more concentrated solutions, stronger excitation sources, or a combination of all these characteristics to do so, which are beyond current capabilities.

Action Taken: The sentence in the luminescence paragraph relating to peak broadness was updated to read, "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."

3. Can the authors expand on the fact that j-j coupling seems to dominate over RS-coupling and its implications on the form of the emission spectrum? Are there any implications on the bonding and the hypsochromic shift that can be related to the XAS data at all? Are there any differences/comparisons that can be drawn from the absorption/excitation spectra? What is the shoulder in the excitation spectrum around 420 nm due to? (real feature or Raman band from water?)

Our Response: The fact that j-j or some form of intermediate coupling may predominate for Es does physically make sense, even though it is not a phenomenon that has been previously observed experimentally. Spin-orbit coupling is known to be proportional to effective Z^4 (per Edelstein *et al.* Coord. Chem. Rev. 250, 948-973), and RS-coupling is based upon the assumption that interactions between orbital angular momenta of individual electrons is stronger than the spin-orbit coupling between the spin and orbital angular momenta. While this (RS-coupling) assumption works well for rare earth cations, it is highly unlikely spin-orbit based splitting can be neglected for Es ($Z=99$), especially as a breakdown in the Russell-Saunders approach has already been observed for earlier actinides such as Pu (see Moore *et al.* Phys. Rev. Lett. 2003, 90, 196404). As the $J = 5$ to $J = 8$ transition of Es is known to be hypersensitive (see Barbanel Radiochim. Acta 1997, 78, 91-95), this may mean that the spectral band changes with coordination environment as is known for the 7F_2 transition of Eu(III), but this will require additional Es experiments to determine. L₃-edge XAS is not the right technique to ascertain any information about coupling regimes for actinides, instead spin-orbit splitting manifests as a doublet in the N_{4,5} edge white line (per Bagus *et al.* Chem Phys. Lett. 2008, 455, 331-334). Energy electron loss spectroscopy (EELS) is the means to observe N_{4,5} spectra and we are pursuing these measurements as a part of different study in our lab. Finally,

the feature at 420 nm in the excitation spectra may be an f-f transition of Es as it agrees reasonably well with the absorption spectra of Es shown in Fig. 1 of Carnall *et al.* J. Chem. Phys. 1973, 59, 1785-1789. However, since we were unable to obtain a complementary absorption spectrum for Es-HOPO we hesitate to make this assignment without further characterization.

Action Taken: None, but we thank the referee for this detailed and very thoughtful comment.

4. Were the authors able to perform any lifetime measurements? In principle, this should be feasible with the set up and the lifetime should be microseconds.

Our Response: We were also not able to collect lifetime data on the Es-HOPO sample with the instrumentation setup used for the data presented in the manuscript (the detector was just not sensitive enough). We even went as far as to purchase a near-IR detector for a new fluorescence instrument that would make this measurement possible, but installation of this piece of equipment has been put on hold (indefinitely) due to Covid-19 related travel restrictions.

Action Taken: none

5. In Figure 3, the wavelength of the filter should be included and in the caption ‘free HOPO’ changed to ‘uncomplexed HOPO’.

Our Response: These are valuable suggestions and we have made both updates suggested by the referee

Action Taken: Filter information has been added to Figure 3 caption and text has been changed to match referee’s suggestion.

6. The phrase in the introduction ‘Moreover, these luminescence measurements unambiguously established that Es was in the +3 oxidation state when chelated by HOPO’ is a little strong in the absence of other data such as absorption spectroscopy, here since only 2 other examples with emission spectra are really reported in the literature. I suggest re-phrasing this sentence.

Our Response: We appreciate the feedback and have updated the manuscript conclusions in-line with referee suggestions.

Action Taken: Introduction sentence has been changed to read, “Moreover, these luminescence measurements confirmed that Es was in the +3 oxidation state when chelated by HOPO.”

All references are appropriate and cite appropriate previous literature.

Referee 2 Comments:

Actinide elements are localized at the almost far end of the periodic table, they correspond to the filling of the 5f orbitals, just before what are called the "super heavy" elements (with 6d filling). Although the first half of the actinide series has been relatively well investigated, the second half has been much less studied. The element that is the subject of this article, Es, is very rarely reported and its chemistry is scarcely described.

Whether or not Es follows the trends of the second half of the actinide series (in terms of radius contraction and dominant stable oxidation state +III for instance) is a key question of fundamental chemistry at the bottom of the periodic table. The originality of this work is therefore to report on the first structural and electronic data of Es in a coordination complex with HOPO ligand. The authors have performed two sets of spectroscopic measurements: XAS at the Es L_{III} edge performed for the first time and luminescence spectroscopy. Both techniques

enable to characterize the physical chemical state of the complex although the technical difficulties associated with Es itself limit interpretation of the data.

This work is therefore more of a technical challenge that makes a world premiere than a full scientific story. Nonetheless for its own technical achievement and new data set on a very rare element, I would recommend publication in Nature after considering the following remarks.

- 1) 1-64 a solid state compound is mentioned. But there is no other mention in the text of a solid state compound. This should be clarified.

Our Response: We appreciate this opportunity to add clarity to the manuscript and the sentence in question has been updated per referee suggestions.

Action Taken: The first sentence of the second paragraph on pg. 3 has been updated to read, “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.”

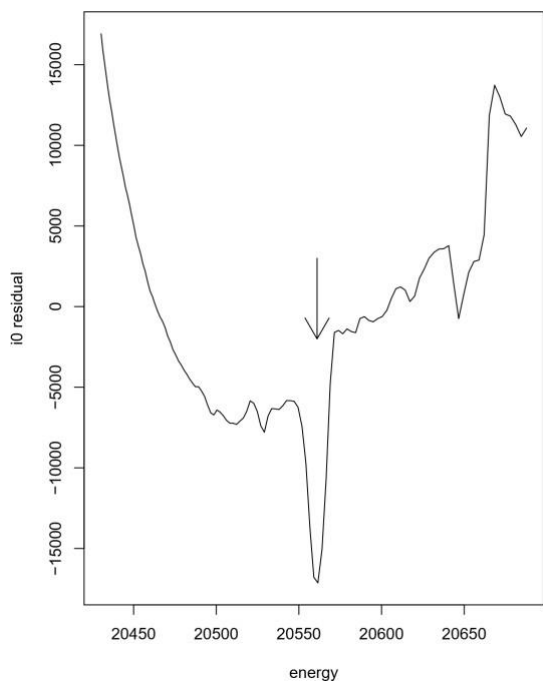
2) l-98 L_{III} edge is 2p_{3/2} core electron, j should be added at this level of details.

Our Response: We appreciate this opportunity to improve the precision of the text and have updated the manuscript in-line with referee suggestions.

Action Taken: Subscript has been added to the text to reflect j level of 2p electrons of L_{III} edge.

3) Fig 2. I understand EXAFS noise must increase very quickly after $k = 6 \text{ \AA}^{-1}$. A noise estimate should be given. In order to judge of noise increase it would be of interest to see the EXAFS data up to a higher k value. In other words EXAFS data should be provided up to a k value larger than the FT window. Also on l-117 spatial resolution should be provided and discussed.

Our Response: We agree and the noise level is, in fact, displayed in the figure in the paper, as noted in the caption, as the width of the band of the data lines, which is based on variations between many scans. This error bar (again, width on line) is easier to see for the raw data in grey, which is now included as Extended Data Fig. 2. The data are actually of excellent quality within the fit range. The limiting factor is not that the data noise becomes too large above 6.5 \AA^{-1} , but rather that there is a monochromator glitch near 7 \AA^{-1} that is too broad to remove reliably. Attempts to remove it and extend the fit to higher k produced very poor quality fits, thus we prefer to only show the data in the Extended Data for EXAFS experts to evaluate. Further we have also included below a plot of I0 with an arrow at the glitch energy (a linear background was removed to enhance the glitch in the plot). Finally, we have added the spatial resolution, which is about 0.24 \AA^{-1} ; however, we note that the referee’s request for this value is likely based on a misunderstanding regarding our fit methodology. We discuss that issue in the next point.



Action Taken: Full raw EXAFS data has been added as Extended Data Fig. 2, which is referenced in Fig. 2 caption. Details about spatial resolution have been added to EXAFS paragraph on pg. 7 of the manuscript.

- 4) I-119. Given the spectral resolution it is difficult to believe that 3 Es shells are needed (and are significant) for the fit. From Table S2 it is not completely clear if Es-C and Es-N are the same contribution or if 2 contributions with only 1 set of parameters (but with the same distances ?) have been used. In any case, justification of the use of two additional shells must be provided (with significant improvement of Quality factor for instance). This also refers to the previous remark.

Our Response: First, there has been a misunderstanding due to the terseness of the text in the manuscript, for which we apologize. We completely agree that if we were fitting two independent shells for the Es-C and Es-N that the resolution of the data would play a very important, and likely catastrophic role in the fit stability and reliability! However, we did not use the EXAFS data to justify using both C and N backscatters; rather, the HOPO coordination itself dictates their use. The methodology is fully explained in Kelley *et al.* (Inorg. Chem. 2018, 57, 5352-5363), as noted in the text, but we acknowledge we did not make this explicit here, and have updated the manuscript accordingly. We also want to highlight that we have made claims that EXAFS has somehow verified the species of this coordination, rather than the fit is consistent with HOPO coordination. Moreover, the C and N peaks are fit to a single bond length and a single Debye-Waller factor, so in fact, the number of free parameters is not affected. We only include both C and N neighbors to be correct regarding HOPO coordination. As the referee is likely aware, merely using a C or an N peak gives nearly identical results owing to the small difference in the scattering line shape of these species. This misunderstanding is serious, and we do not want any other readers to misconstrue the methodology. As we completely agree with the referee that the justification for the two peaks needs to be made clearer, we have made updates to the manuscript text and to the table of fit parameters in the Extended Data.

Action Taken: In the manuscript, we have updated text to read, “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.” In the extended data, Table 2 has been revised to explicitly show that this is, indeed, a two-shell, and not a three-shell, fit.

- 5) I-125. In this section, the error in M-O distance is estimated as a function of the EXAFS k range. Clearly, bond distances and uncertainties vary with k range (which is well known in EXAFS spectroscopy). The variation of this variation seems to increase from Am to Cf. This is particularly clear for Cf for which the error bar at $k = 6 \text{ \AA}^{-1}$ is about 0.1 Å. This could be linked with the evolution of the shape of the amplitude function of M as Z increases. I suggest the authors discuss more carefully this part (that is essential because half of the paper is about the Es-O distance value). In particular the amplitude functions $f(\pi)$ for Am - > Es could be plotted as a function of k (using feff code for instance) and compared. Trend could even be extended after Es.

Our Response: We have made the plot of EXAFS amplitude calculations using FEFF 9.6.4 for the An- O pair suggested by the referee and it is included in Supplementary Information (Supplementary Figure 1). As should be clear in the figure, there is no difference in the lineshape. Moreover, these data are not k -weighted. If they were, there would be no fall off above 4 \AA^{-1} , but rather a change in slope. Given these facts, but especially the similarity of these calculations, the amplitude lineshapes cannot be the reason for the increase in noise from Am to Cf. We also need to mention that FEFF has a Z limit of 99, which happens to be Es, so it is not (easily) possible to extend the Z range of these calculations. The reason for

the stabilization of the bond length may have more to do with the degrees of freedom of the fit. For instance, at a k_{max} of 5.5 \AA^{-1} , the degrees of freedom are only 1.2. Instead, the main difference in the experimental spectra with respect to the noise is simply the mass of material used to obtain the spectra, which were $27.1 \text{ }\mu\text{g}$ for $[\text{Am}^{\text{III}}(\text{HOPO})]^-$, $10.9 \text{ }\mu\text{g}$ for $[\text{Cm}^{\text{III}}(\text{HOPO})]^-$, and $3.3 \text{ }\mu\text{g}$ for $[\text{Cf}^{\text{III}}(\text{HOPO})]^-$.

Action Taken: Plot of FEFF amplitude for the An-O pair has been added to the supplementary information (Supplementary Figure 1) and additional details on change in fit quality have been added to caption of Extended Data Figure 3.

- 6) l-127 and Fig. 2. The trend in M-O distances from Am to Es is not really discussed. If purely electrostatic interaction would occur between M and HOPO, a decrease of distances following the actinidic contraction is expected. This is not the case in Figure 2. What is the conclusion ?

Our Response: The lack of discussion about the trend in M-O distances was an intentional choice. The referee is correct that purely electrostatic interactions should lead to a monotonic decrease in M-O distances that is a result of the actinide contraction. The lack of a distinct monotonic decrease in M-O distances can be caused by a number of factors, including some amount of covalency in the M-O bonds. As this is the first series where Es has been experimentally characterized, and limitations in the Cf data from Kelley *et al.* (Inorg. Chem. 2018, 57, 5352-5363) were discovered during the process of making Fig. 2D (see the methods section for details), we did not feel we had sufficient context to make larger claims about the trend in M-O distances. In future work, upon production of more Es at ORNL, this would absolutely be one of our aims, but here we felt it was not prudent to paint with a broad brush and make claims we could not fully experimentally elucidate.

Action Taken: none

- 7) l-141 please use the entire state notation (I) and not just J.

Our Response: The full state notation requested by the referee is used in the highlighted sentence; however, there was a second instance in the next sentence of using only J notation that has been updated.

Action Taken: The corresponding text in the luminescence section has been updated in-line with referee suggestions to read, “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 $^5\text{I}_5 \rightarrow ^5\text{I}_8$ transition. This optical response confirms complexation of Es in the +3 oxidation state by HOPO,²² and while the broadness of the $^5\text{I}_5 \rightarrow ^5\text{I}_8$ spectra peak is atypical for $f \rightarrow f$ transitions, it is consistent with the one other example of aqueous Es^{III} luminescence.”

- 8) To strengthen the discussion, comparison with M-O distances in hydrates and/or aquo species might be added (with related references). Crystallographic data of the M(III) hydrates up to Cf have been provided as well as EXAFS data in aqueous solution.

Our Response: The pioneering work on XRD and EXAFS of transplutonium aqua species by

Lindqvist- Reis *et al.* (Angew. Chem Int. Ed. 2007, 46, 919-922; Angew. Chem. Int. Ed. 2010, 49, 6343-6347), Soderholm *et al.* (Inorg. Chem. 2009, 46, 3485-3491), and Den Auwer *et al.* (Angew. Chem. Int. Ed. 2010, 49, 3811-3815) certainly laid the foundation for this manuscript. However, as the referee points out, these studies have only been extended to Cf(III). Comparing these results, which lack Es(III) data, to those included in the manuscript where we have a first data point for a Es(III)-O bond distance is not a comparison we feel adds value to the manuscript, and we must respectfully disagree with the referee that such additional text will strengthen the discussion. We thank the referee for this very thoughtful comment, which represents a logical next step for our Es(III) XAS work, and upon collecting this data in the future we will be sure to make the comparison suggested by the referee.

Action Taken: none

- 9) The nuclear characteristic of isotope ^{254}Es are briefly given in the summary but not in the introduction. It should be added as well in the introduction for general interest. More generally, introduction is too brief and should better highlight the originality of Es chemistry, what is expected from general trends along the actinide series and in particular within the second half of the series.

Our Response: We have moved the description of the nuclear characteristics of ^{254}Es to the introduction to update the manuscript in-line with the referee's suggestion along with shortening the summary paragraph, which was too long per Nature guidelines. As part of this revision, we have added the data on ^{254}Es at a spot in the first paragraph that puts Es work into greater context. Part of the challenge and the rationale for pursuing Es work is that actinide chemists do not know what to expect at Es. It is the current point where general trends experimentally break down for the actinide series in general, and the transplutonium elements in particular. This work should prove foundational for changing that going forward, and will lay the groundwork for future studies that elucidate details about trends in actinide structure and properties.

Action Taken: The summary paragraph was shortened, in-line with editorial guidelines. The first four sentences of the first paragraph of the main text have also been updated to read, "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 $5f$ -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 ($t_{1/2} = 275.7$ 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."

Referee 3 Comments:

The manuscript reports the structural and spectroscopic characterization of an einsteinium coordination complex. Since the availability of einsteinium is limited to small quantities - It is undoubtedly important scientific achievement. However, from a practical point of view, this paper will be of interest to the narrow circle of scientists.

The manuscript is quite short and focused on data, obtained by two experimental methods: Luminescence measurements and X-ray absorption spectroscopy. The luminescence data is not quite unique – since it was previously reported on Es systems (authors cite nicely a previous works in that field). I am just impressed that Es(III)HOPO complex induced a blue shift.

One question, which authors address through the manuscript is the Es the oxidation state. I don't understand why authors focus on it since Es compounds can only be present in oxidation state III. The luminescence data itself perhaps can be used as confirmation of the oxidation state, but I believe the best is to compare luminescence data on Es(III) with Ho(III) and Ho(II) complexes. The number of the 4f and 5f electrons in Ho(III) ground state and Es(III) ground state is similar. Since Es(II) can not exist and no comparison can be made, the spectral profile of Ho can be discussed in details, since luminescence data is quite different between Ho(II) and Ho(III).

Our Response: We must respectfully push back here as there are a couple facts stated by the referee that are incorrect. A few divalent Es compounds are known in the solid-state (see Inorg. Chem. 1981, 20, 3979-3983) and metallic Es is also known to be divalent (see Haire *The Chemistry of the Actinide and Transactinide Elements*, 2011, ch. 12, 1577-1620). While Es has not been observed in the +2 oxidation state thus far in solution, it is predicted to have an accessible redox couple of between -1.2 and -1.5 V (per Hulet, Radiochim. Acta, 1983, 32, 7-23). The combination of these factors led us to pursue confirmation of the Es oxidation state via luminescence spectroscopy, where Es(III) is known to exhibit near-IR luminescence upon sensitization (see J. Less-Common Metals, 1983, 93, 331-338). The referee's suggestion of comparing Es(III) to Ho(III) for the purposes of luminescence spectroscopy is also incorrect as it does not take into account changes in electrostatic interactions and spin-orbit coupling between the lanthanide and actinides. This is well-known for Gd(III) and Cm(III) (see Coord. Chem. Rev. 2006, 250, 948-973) and is known to extend to Es(III) as well, which electronically behaves like Yb(III). Yb also has an accessible divalent state and luminescence spectroscopy is a means for confirming oxidation states with this element, and given electronic similarities we did the same here for Es.

Action Taken: none

The XANES method was used by authors to proof the presence of the Es(III). XANES itself cannot confirm the presence of the Es(III) oxidation state if only one spectrum is recorded. The general practice is to record data on reference systems and look at the energy shifts recorded in data of unknown compounds (as reported in Fig. below) – Pu(III) definitely has an oxidation state of (III), since it is shifted towards low incident energy for comparing to the Pu(IV). XAS data in the present manuscript is shown only on one system – I suggest that authors reformulate discussion and delete any statements that XANES proofs the existence of the Es(III). In fact, if nobody would say to me that this is the spectrum of Es, I would think that actinide compound is in the oxidation state (IV), since L_3 spectral shape is very similar to the PuO_2 and UO_2 .

Our Response: We must respectfully push back as we do not assert anywhere in the manuscript that the XANES spectra were used to determine the Es oxidation state. As it seems that the referee misunderstood our assertions we have taken this opportunity to add clarity to the manuscript. Regarding the referee's observation about the similarity of the Es XANES and the Pu(IV) XANES, this is likely coincidental as the local structure around the central atom plays a large role in determining line shape, which is the primary reason for, say, the difference between the fluorite PuO_2 spectra and the plutonyl spectra. We have observed many instances of differing white line heights in An^{IV} spectra, even in eight-coordinate An-O systems, which are generally assigned to differences in the unoccupied 6d bandwidth due to differences in long-range order. A clear recent example is in UO_2 nanoparticles versus bulk material that we recently published (Chem. Sci. 2020, 11, 4648-4668). Interestingly, the reverse trend happens in ThO_2 nanoparticles versus bulk material in that same work. For $[\text{An}^{\text{III}}(\text{HOPO})]^-$ complexes, XANES spectra have very similar lineshapes owing to their similar coordination environments.

Action Taken: In the manuscript, we have updated the text to read, "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*) unambiguously confirm the Es in $[\text{Es}^{\text{III}}(\text{HOPO})]^-$ 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 $[\text{An}^{\text{III}}(\text{HOPO})]^-$ complexes, further confirming the oxidation state assignment of Es in $[\text{Es}^{\text{III}}(\text{HOPO})]^-$ (Extended Data Fig. 1).” In Extended Data Fig. 1, we have plotted XANES spectra for all measured $[\text{An}^{\text{III}}(\text{HOPO})]^-$ complexes, which demonstrates the significant similarities of all four species.

What is definitely new here is the experimentally recorded value of Es L₃ edge energy. Moreover, the authors report the EXAFS results and structural characterization of Es complex. Even that data was recorded in short energy region (up to 6-7 Å⁻¹) and I have my doubts how correct the bond distances were estimated, still, its obviously new piece of data.

Our Response: As discussed at length in the text, we have done everything we can to place an appropriate error estimate on the Es bond distances given the short *k*-range, and indeed the errors are quite large with +/- 0.03 Å (good data have errors in the first shell more on the order of 0.005 Å, see Li *et al.* Phys. Rev. B 1995, 52, 6332-6348). We are confident in the bond length of the first shell within this estimated error.

Action Taken: none

What I am missing in the analysis of Es L₃ XAS data is the electronic structure calculations and I am sure that a group of authors can easily perform it. Especially here, when the structure is determined by EXAFS. One can use several codes to obtain the shape of the Es L₃ edge XANES and to compare it to the experimental results. I believe paper will be much stronger - I am curious to see the crystal field splitting of the Es 6d states near the Fermi level (and compare to other actinides in series of Am, Cm, Bk, Cf, Es etc).

Our Response: First, we note that the DFT calculations on [Es^{III}(HOPO)]⁻ have been reported by Kelley *et al.* (Inorg. Chem. 2018, 57, 5352-5363), as referenced in the text. We are not entirely clear what the referee's experience is with actinide electronic structure calculations with regard to X-ray absorption spectra, but we must point out that codes such as FEFF have difficulties in the 5f series. The default for FEFF is to not allow charge transfer of the 5f electrons into valence orbitals. This is clearly wrong for the lighter actinides, but is now thought to be an issue potentially anywhere along the series. In fact, the calculations by Kelley *et al.* (ref. 3 in the manuscript) show potential covalency effects in the Bk/Cf/Es vicinity. It is possible to tell FEFF to unfreeze the 5f electrons; however, it grossly overestimates the amount of 5f covalence, which is a known problem in other methods like DFT when electron correlations are not explicitly taken into account. We performed the calculations suggested by referee with the 5f shell frozen so that the 6d splitting can be considered, and these plots can be found in the Extended Data and the Supplementary Information. In the case of the trivalent actinides (Am^{III}, Cm^{III}, Cf^{III}, and Es^{III}), which are highlighted in Extended Data Fig. 1, there is very little difference between the white line heights for the various [An^{III}(HOPO)]⁻ complexes. Subsequently, we used the [Am^{III}(HOPO)]⁻ complex from Kelley *et al.* and simply replaced the central atom. The calculations use a self-consistent field cluster radius of 6 Å and a full multiple-scattering radius of 4.0 Å, and are shown in Supplementary Information Fig. 2. FEFF calculations are relative to the vacuum energy, and these fits include calculations on Pu and Bk, for which there is no data currently available in the literature. One sees a similar systematic change in the white line height, but this is driven primarily by differences in the core-hole lifetime broadening (increases from 8.7 eV to 10.3 eV across the Pu-Es series). We also looked at the local density of states for the d-manifold and this is shown in Supplementary Information Fig. 3. The Fermi levels are near -7.6 eV relative to vacuum for all these calculations. The 6d splitting is clearly observed, and actually decreases with Z by about 0.6 eV from Pu to Es, counter to the lifetime broadening; however, this change in the d-splitting has a minimal

impact on the XANES due to the ~10 eV core-hole lifetime broadening. We included this information in the Supplementary Information, and not the manuscript since the 6d splitting has minimal potential impact on the Es L_{III}-edge lineshape. However, we agree that more advanced theories are known to be needed for the actinides, such as CASSCF methods that are only now being applied for XAS (including the necessary core hole) in the pioneering work of Jochen Autschbach at the State University of New York (Buffalo).

Action Taken: Plots comparing measured XANES spectra for [An^{III}(HOPO)]⁻ complexes as well as those calculated by FEFF have been added to the extended data and supplementary information,

respectively. Local density of states calculations for the d-manifold of trivalent An-HOPO species have been included in the Supplementary Information as well.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

Dear authors,

Thank you for taking the time to consider my comments on your manuscript. Overall, I am satisfied with your answers, which are comprehensive and I am happy to recommend your manuscript for publication with the minor amendments as detailed below:

Please include this information in the ESI: "10 nm excitation and emission slits were used and this likely broadened the excitation and emission) peaks"

Regarding the lack of UV-vis data, please also add this explanation to the ESI: "A UV-vis-nIR spectrum was not obtained for the sample, which was one of the many challenges we encountered when working with Es. Highly radioactive samples limit the suite of available instruments for collecting data, and those UV-vis-nIR instruments that were available would not yield results, given the limited volume and concentration of our solution sample."

Regarding lifetime measurements, also please state why these were unobtainable in the ESI: "We were also not able to collect lifetime data on the Es-HOPO sample with the instrumentation setup available to us; a more sensitive detector is needed for such measurements."

Point 6: I still think this sentence is a bit too strong in light of the data and evidence, so please tone down to: "Moreover, these luminescence measurements strongly suggested that Es was in the +3 oxidation state when chelated by HOPO." Here, it is important to be completely honest and does not affect the results of the paper or its potential impact in my view.

Referee #2 (Remarks to the Author):

*Please see attachment.

Referee #3 (Remarks to the Author):

The paper is now acceptable for publication. The authors have addressed almost all remarks I had and strengthen their conclusions.

Author Rebuttals to First Revision: (please note that the authors have quoted the reviewers in black and responded in red and blue)

Referee 1

Comments:

Dear authors,

Thank you for taking the time to consider my comments on your manuscript. Overall, I am satisfied with your answers, which are comprehensive and I am happy to recommend your manuscript for publication with the minor amendments as detailed below:

Please include this information in the ESI: "10 nm excitation and emission slits were used and this likely broadened the excitation and emission) peaks"

Our Response: The information requested by the referee has been added to the luminescence spectroscopy portion of the methods section.

Action Taken: Last two sentences of the luminescence spectroscopy portion of the methods section have been updated to read, "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, 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 yellow 48 ($\lambda = 480 \pm 5$ 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."

Regarding the lack of UV-vis data, please also add this explanation to the ESI: "A UV-vis-nIR spectrum was not obtained for the sample, which was one of the many challenges we encountered when working with Es. Highly radioactive samples limit the suite of available instruments for collecting data, and those UV-vis-n IR instruments that were available would not yield results, given the limited volume and concentration of our solution sample."

Our Response: We have added an explanation to luminescence spectroscopy portion of the methods section in-line with the suggestion provided by the referee.

Action Taken: Additional sentence has been added to the luminescence spectroscopy portion of the methods section that reads, "Finally, UV-vis-nIR spectra and luminescence lifetimes were not obtained for [Es^{III}(HOPO)] as highly radioactive samples limit the suite of available instruments for collecting data, and sufficiently sensitive instruments were not available for such measurements."

Regarding lifetime measurements, also please state why these were unobtainable in the ESI: "We were also not able to collect lifetime data on the Es-HOPO sample with the instrumentation setup available to us; a more sensitive detector is needed for such measurements."

Our Response: We have added an explanation to luminescence spectroscopy portion of the methods section in-line with the suggestion provided by the referee.

Action Taken: Additional sentence has been added to the luminescence spectroscopy portion of the methods section that reads, "Finally, UV-vis-nIR spectra and luminescence lifetimes

were not obtained for $[\text{Es}^{\text{III}}(\text{HOPO})]^-$ as highly radioactive samples limit the suite of available instruments for collecting data, and sufficiently sensitive instruments were not available for such measurements.”

Point 6: I still think this sentence is a bit too strong in light of the data and evidence, so please tone down to: “Moreover, these luminescence measurements strongly suggested that Es was in the +3 oxidation

state when chelated by HOPO.” Here, it is important to be completely honest and does not affect the results of the paper or its potential impact in my view.

Our Response: Sentence in question on pg. 4 of the manuscript has been updated to match referee’s suggestion.

Action Taken: Second to last sentence on pg. 4 has been updated to read, “Moreover, these luminescence measurements strongly suggested that Es was in the +3 oxidation state when chelated by HOPO.”

Referee 2

Comments:

Dear Editor,

Please find below in red my comments on the actions taken by the authors with regards to my review. In conclusion I agree that the present revised version is suitable for publication.

1) 1-64 a solid state compound is mentioned. But there is no other mention in the text of a solid state compound. This should be clarified.

Thank you for the action that clarifies the text. But I am sorry to say that this is still not totally clear for me what was measured in solution and what was solid. I think I understand XAS was performed on a dry sample but if this is really the case the state of the sample should be clearly mentioned in the legend of Figure 2.

Our Response: Figure 2 legend has been updated per the referee’s suggestion.

Action Taken: First sentence of figure 2 legend was updated to read, “(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).”

4) 1-119. Given the spectral resolution it is difficult to believe that 3 Es shells are needed (and are significant) for the fit. From Table S2 it is not completely clear if Es-C and Es-N are the same contribution or if 2 contributions with only 1 set of parameters (but with the same distances ?) have been used. In any case, justification of the use of two additional shells must be provided (with significant improvement of Quality factor for instance). This also refers to the previous remark.

I agree with author's modification, it is much clearer now. Could also the authors add somewhere (in the main text or in the extended data, Table 2 legend) the total number of free parameters ?

Our Response: We appreciate the opportunity to add clarity and have updated the manuscript per the referee’s suggestion.

Action Taken: The following sentences were added to the caption of Extended Data Table 2, “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.”

5) 1-125. In this section, the error in M-O distance is estimated as a function of the EXAFS k

range. Clearly, bond distances and uncertainties vary with k range (which is well known in EXAFS spectroscopy). The variation of this variation seems to increase from Am to Cf. This is particularly clear for Cf for which the error bar at $k = 6 \text{ \AA}^{-1}$ is about 0.1 \AA . This could be linked with the evolution of the shape of the amplitude function of M as Z increases. I suggest the authors discuss more carefully this part (that is essential because half of the paper is about the Es-O distance value). In particular the amplitude functions $f(\pi)$ for Am \rightarrow Es could be plotted as a function of k (using feff code for instance) and compared. Trend could even be extended after Es.

OK, this is convincing. Attention, typo in l 145.

Our Response: We thank the referee for their sharp eye and have corrected the typo in the caption of Extended Data Figure 8 (formally Supplementary Figure 1).

Action Taken: Extended Data Figure 8 caption has been updated to correct typo.

6) 1-127 and Fig. 2. The trend in M-O distances from Am to Es is not really discussed. If purely electrostatic interaction would occur between M and HOPO, a decrease of distances following the actinidic contraction is expected. This is not the case in Figure 2. What is the conclusion ?

I acknowledge the caution of the authors on this point. But being cautious is a quality and I still do think that this lack of explanation should be mentioned in the text. It would also have the advantage of introducing the continuation of work.

Our Response: We appreciate the feedback and direct the referee to the final paragraph of the main text where we have highlighted how this work will lead to future investigations. Specifically, in the last two sentences of the manuscript we have included the following text, “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.”

Action Taken: none

Referee 3

Comments:

The paper is now acceptable for publication. The authors have addressed almost all remarks I had and strengthen their conclusions.