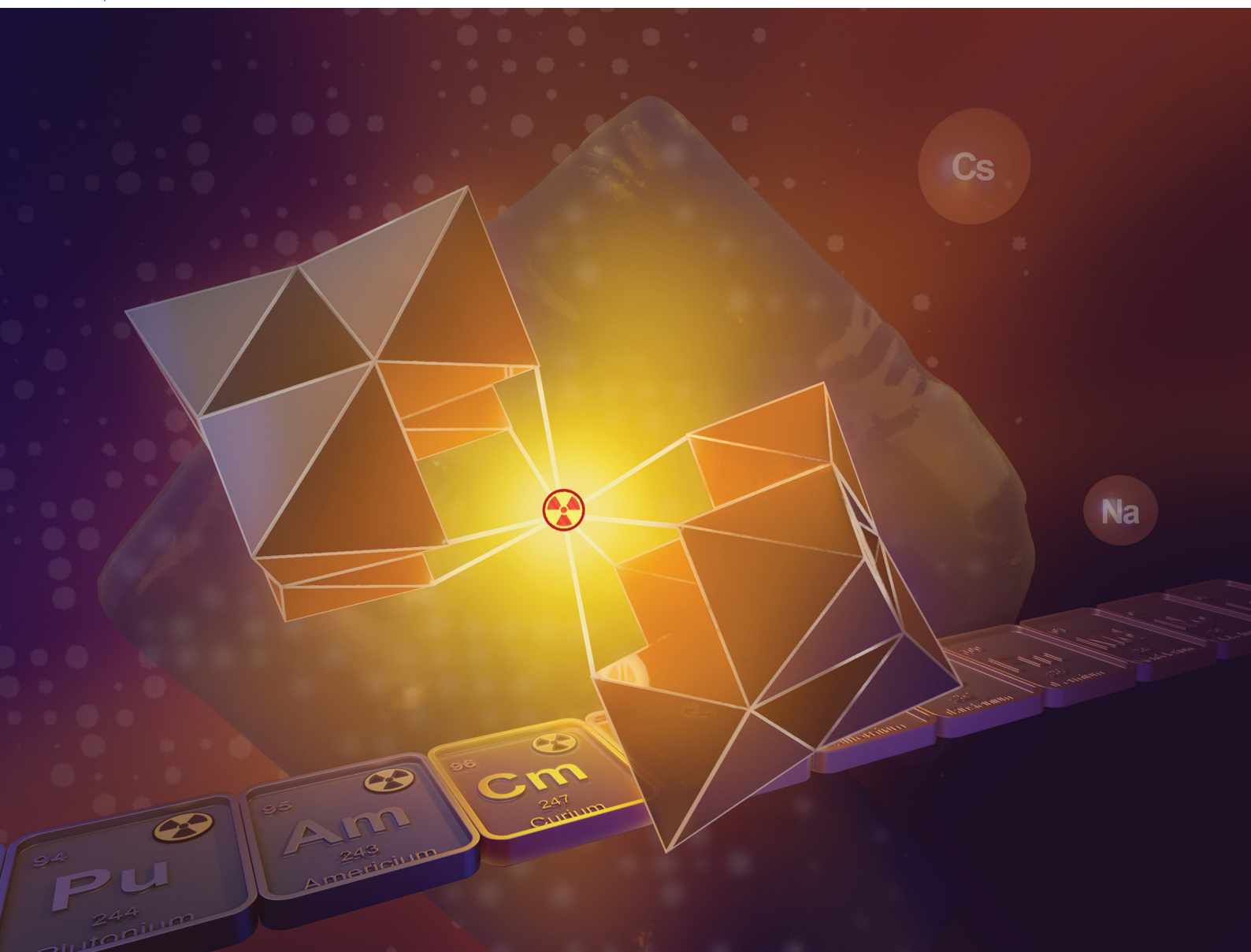


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# Characterization of the first Peacock–Weakley polyoxometalate containing a transplutonium element: curium bis-pentatungstate $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$ †

 Ian Colliard\*<sup>ab</sup> and Gauthier J.-P. Deblonde  <sup>ac</sup>

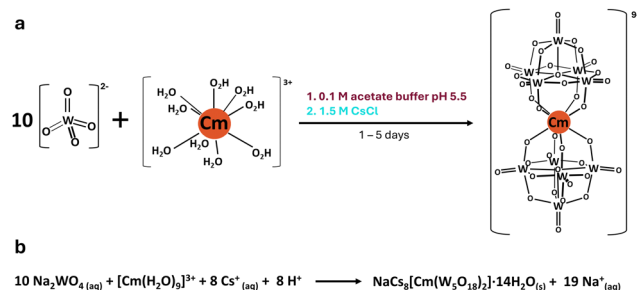
**Leveraging microgram-level techniques, we here present the first transplutonium bis-pentatungstate complex:  $\text{NaCs}_8\text{Cm}(\text{W}_5\text{O}_{18})_2 \cdot 14\text{H}_2\text{O}$  ( $\text{CmW}_5$ ). Single crystal XRD, Raman, and fluorescence characterization show significant differences relative to analogous lanthanide compounds. The study reveals the unsuspected impact of counterions on fluorescence and vibrational modes of the curium complex and its lanthanide counterparts.**

Interests in polyoxometalates can be traced as far back as the 19th century, with the synthesis of ammonium phosphomolybdate  $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$  first reported in 1826.<sup>1</sup> Since then, polyoxometalates, POMs, have permeated into various other fields, ranging from drug delivery to microelectronics, catalysts, energy storage, and more.<sup>2–6</sup> POMs can also act as metal chelators and, while their chemistry is incredibly diverse, POMs are typically derived from a handful of major structures, with notably, the Peacock–Weakley<sup>7</sup> *e.g.*,  $[\text{M}^{n+}(\text{W}_5\text{O}_{18})_2]^{15-n}$ , the Lindqvist<sup>8</sup> (*e.g.*,  $\text{Nb}_6\text{O}_{19}^{8-}$ ), the Keggin<sup>9</sup> (*e.g.*,  $\text{PMo}_{12}\text{O}_{40}^{n-}$ ), the Well–Dawson<sup>10</sup> (*e.g.*,  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ ), the Preyssler<sup>11</sup> (*e.g.*,  $[\text{M}^{n+}\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-n}$ ) ions, *etc.*

Perhaps not surprisingly, compared to other fields, POM chemistry has had little overlap with actinide chemistry thus far, and particularly for heavy actinides (Am, Cm, Bk, Cf...). The first instance of a polyoxometalate compound containing an actinide was reported in 1914, with the synthesis of a thorium(IV) polymolybdate  $(\text{NH}_4)_8(\text{ThMo}_{12}\text{O}_{42})$ .<sup>12</sup> However, it is not until after the 1970's that a renewed interest in incorporating actinide elements into polyoxometalate chemistry yielded additional structures. Moreover, while the

actinide group consists of fifteen members, most of the data published on actinide POMs is about thorium and uranium. The high specific activity and isotope scarcity are only some of the constraints that have limited studies with transuranic elements. Recently, certain POMs have been leveraged to crystallize their complexes in microgram quantities,<sup>13,14</sup> opening the avenue to studying their interactions with elements beyond plutonium (Fig. 1a). However, the number of known actinide POMs with transplutonium elements is still very limited: only one with Am(IV),<sup>15</sup> one with americium(VI),<sup>16</sup> and three with Cm(III).<sup>13</sup>

One class of POMs that has historically received strong interest is the bis-pentatungstate–metal complex  $[\text{M}^x(\text{W}_5\text{O}_{18})_2]^{(12+x)-}$ . Intense luminescent and optical properties when complexing lanthanide (Ln) ions, in solution and solid-state,<sup>17–20</sup> provide strong motivation to pursue analogous compounds with transplutonium ions, notably  $\text{Cm}^{3+}$ , as it can undergo fluorescence with a wide variety of ligands.<sup>21–23</sup> Unlike the other POM structures that can complex metal ions, such as the Keggin or the Well–Dawson anions, the pentatungstate anion  $[\text{W}_5\text{O}_{18}]^{6-}$  ( $\text{W}_5$ ), is often considered as the smallest and simplest POM ligand, both in terms of structure and synthesis. Fluorescence studies on aqueous solutions of  $\text{W}_5$  and  $\text{Cm}^{3+}$  previously showed<sup>13</sup> a ~500 times increase in the luminescence of  $\text{Cm}^{3+}$  upon complexation to  $\text{W}_5$ ,



**Fig. 1** Reaction scheme (a) and equation (b) for forming the curium bis-pentatungstate complex  $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$ . The starting curium(III) aqua ion is considered to have 9 water molecules, as previously reported by Skanthakumar *et al.*<sup>24</sup>

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with a shift and splitting of the emission peaks (598.4 to 604.6 nm with multiple Stark levels). By analogy to the lanthanides, the expected complex formed in solution was  $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$  ( $\text{CmW}_5$ ).  $\text{CmW}_5$  solutions exhibit the longest fluorescence lifetime for a  $\text{Cm}^{3+}$  complex reported so far (780  $\mu\text{s}$ ), and we hypothesized<sup>13</sup> it was due to the complete removal of water molecules from the starting  $[\text{Cm}(\text{H}_2\text{O})_9]^{3+}$  aqua ion (Fig. 1b).<sup>24</sup> However, the crystal structure of this kind of heavy actinide complex has remained elusive.

Herein we report the single crystal XRD structure of  $\text{CmW}_5$ , which represents the first heavy actinide compound of the Peacock–Weakley POM class. The cesium salt of  $\text{CmW}_5$ , fully formulated as  $\text{NaCs}_8[\text{Cm}(\text{W}_5\text{O}_{18})_2]\cdot 14\text{H}_2\text{O}$ , crystallizes in the anorthic space group  $P\bar{1}$  ( $V = 2711.36(6) \text{ \AA}^3$ ). We further report the first  $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$  compound with cesium counterions,  $\text{Na}_3\text{Cs}_6[\text{Nd}(\text{W}_5\text{O}_{18})_2]\cdot 18\text{H}_2\text{O}$ , which crystallizes in the anorthic space group  $P\bar{1}$  ( $V = 2811.36(6) \text{ \AA}^3$ ). While the only distinguishable feature between the heavy actinide and the lanthanide is a difference in the number of  $\text{Na}^+$  and  $\text{Cs}^+$  counterions, the apparent crystallographic divergence precludes the spectroscopic differences observed for these compounds both in solution and solid-state, as discussed below.

A prior attempt to isolate this compound as a rubidium or cesium salt failed,<sup>13</sup> but a cesium salt of  $\text{CmW}_5$  was here successfully isolated as single crystals (Fig. 3) by modifying our recently developed microgram-level POM–metal complex synthesis.<sup>13</sup> In this optimized synthesis, we only used 1.2  $\mu\text{g}$  of  $^{247/246/248}\text{Cm}^{3+}$ , starting from a HCl solution (see Experimental section in the ESI†). Note that XRD-quality single crystals of  $\text{CmW}_5$  could only be grown with  $\text{Cs}^+$  counterions (Fig. 3c and d). Yet, the structure is isomorphic with previously reported sodium and potassium salts of  $[\text{Ln}^{\text{III}}(\text{W}_5\text{O}_{18})_2]^{9-}$  (Table S1, ESI†) and  $[\text{An}^{\text{IV}}(\text{W}_5\text{O}_{18})_2]^{8-}$  ( $\text{An} = \text{Th}, \text{U}, \text{and Np}$ ).<sup>17,25</sup> Briefly, the structure is comprised of two  $[\text{W}_5\text{O}_{18}]^{6-}$  ligands coordinating a central  $\text{Cm}^{3+}$ . The  $\text{W}_5$  ligand is built upon five edge-sharing octahedral tungstates, four of which corner-share to the central  $\text{Cm}^{3+}$  ion, forming an eight-coordinate square antiprismatic coordination environment for curium, with a nearly ideal  $D_{4d}$  symmetry. Bond lengths range 2.459(9)–2.508(9)  $\text{ \AA}$  for  $\text{Cm}-\text{O}$ , 1.715(6)–1.740(10)  $\text{ \AA}$  for  $\text{W}-\text{O}^{\text{terminal}}$ , 2.348–1.776  $\text{ \AA}$  for  $\text{W}-\text{O}^{\text{bridging}}$ , and 2.967(10)–3.762(10)  $\text{ \AA}$  for  $\text{Cs}-\text{O}^{\text{Cm}^{\text{s}}}$ . See ESI† for additional information on the synthesis and structure of  $\text{CmW}_5$ .

Interestingly, no water molecule is present in the first coordination sphere of the  $\text{Cm}^{3+}$  ion, which contrasts with previously studied heavy actinide complexes with organic ligands which are typically 9-coordinated and often have actinide-bound water molecules.<sup>24,26,27</sup> Moreover, in all the other  $\text{W}_5$  reported structures with trivalent lanthanides (Table S1, ESI†), the  $\text{Na}^+$  counterions bind to several water molecules instead of direct ion-pairing with the POM observed for the  $\text{Cs}-\text{CmW}_5$  structure. The lanthanide structures mainly featured hydrogen bonding interactions between the  $[\text{Ln}^{\text{III}}(\text{W}_5\text{O}_{18})_2]^{9-}$  and the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  counterions. On the other hand, the  $\text{CmW}_5$  salt reported herein is the only instance thus far of the  $\text{W}_5$  complex crystallizing with  $\text{Cs}$  counterions.

The most noticeable effect of the  $\text{Cs}$  counterions is the complete removal of the 9 water molecules from the  $\text{Cm}^{3+}$  aqua ion,<sup>24</sup> and it manifests as increased bonding interactions

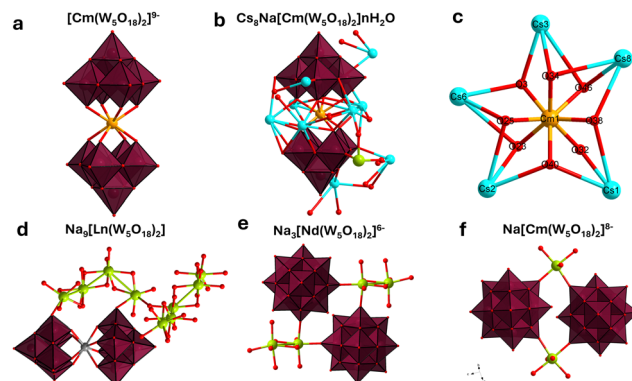
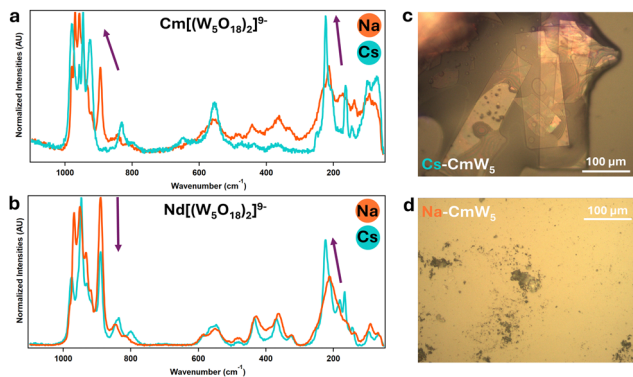


Fig. 2 Polyhedral representations of the  $\text{CmW}_5$  and  $\text{NdW}_5$  compounds. (a) The  $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$  complex, with counterions and solvated water molecules for clarity. (b) Asymmetric unit of the  $\text{Cs}-\text{CmW}_5$  crystal, fully formulated as  $\text{NaCs}_8[\text{Cm}(\text{W}_5\text{O}_{18})_2]\cdot 14\text{H}_2\text{O}$ . (c) Closeup view of the  $[\text{CmO}_8]$  square antiprismatic coordination, with five  $\text{Cs}$  counterions binding to all eight oxygens. (d) Asymmetric unit of the  $\text{Na}_9\text{NdW}_5$  structure,<sup>13</sup> showing no connectivity between complexes. (e) Connectivity between complexes for  $\text{Na}_3\text{Cs}_6[\text{Ln}(\text{W}_5\text{O}_{18})_2]$ . (f) Connectivity between complexes for  $\text{NaCs}_8[\text{Cm}(\text{W}_5\text{O}_{18})_2]\cdot n\text{H}_2\text{O}$ . Color code:  $\text{Cm}$  (orange),  $\text{Cs}$  (light blue),  $\text{Na}$  (green),  $\text{W}$  (maroon octahedra),  $\text{O}$  (red).

among  $\text{Cs}^+$  ions, the POM, and the central actinide ion. Of the eight  $\text{Cs}$  counterions in the  $\text{CmW}_5$  structure, five are close to curium ( $\text{Cs}-\text{Cm}$  distance of 4.48–4.54  $\text{ \AA}$ ) and bind directly to the bridging  $\text{O}$  in  $\text{Cm}-\text{O}-\text{W}$  ( $\text{Cs}-\text{O}^{\text{Cm}}$  distance of 2.967(10)–3.762(10)  $\text{ \AA}$ ). The lone  $\text{Na}^+$  counterion found in the structure at  $\sim 7 \text{ \AA}$  from  $\text{Cm}^{3+}$  favors binding with solvated water molecules, similar to what is observed in the lanthanide structures, and it only binds with the tungstate POMs *via* one yl oxygen between two complexes (Fig. 2). The interplay among  $\text{Cm}^{3+}$ ,  $\text{W}_5$ , and  $\text{Cs}^+$  ion leads to a unique geometry where  $\text{Cm}^{3+}$  is completely shielded from solvent molecules and surrounded by eight oxygens at  $\sim 2.48 \text{ \AA}$ , and five  $\text{Cs}^+$  at  $\sim 4.51 \text{ \AA}$  (Fig. 2).

Control experiments were performed with  $\text{Nd}^{3+}$  (Fig. 2 and 3), as its size<sup>28</sup> is similar to  $\text{Cm}^{3+}$ , by synthesizing both a cesium salt ( $\text{Cs}-\text{NdW}_5$ ) and a sodium salt ( $\text{Na}-\text{NdW}_5$ ). For  $\text{Cm}$ , a solid sample was also prepared with  $\text{Na}^+$  counterions ( $\text{Na}-\text{CmW}_5$ ) but only micro to sub-microcrystals could be obtained (Fig. 3d) so that no single crystal XRD characterization could be performed. Raman microscopy experiments on  $\text{Na}_9[\text{Ln}^{\text{III}}(\text{W}_5\text{O}_{18})_2]$  previously assigned the characteristic bands<sup>13,17</sup>: 980–920  $\text{ cm}^{-1}$  for the terminal yl'O stretching ( $\text{W}=\text{O}$ ), 850–500  $\text{ cm}^{-1}$  for the bridging  $\text{O}$  stretching in  $\text{W}-\text{O}-\text{W}$ ,  $< 350 \text{ cm}^{-1}$  for various vibrational modes for the entire complex, and lastly peaks at 890 and 200  $\text{ cm}^{-1}$  correspond to the bridging  $\text{O}$  stretching in  $\text{Ln}-\text{O}-\text{W}$ . The Raman spectrum of  $\text{Na}-\text{NdW}_5$  is consistent with previously reported spectra.<sup>13,17</sup> Interestingly, we observed a clear effect of the  $\text{Cs}^+$  counterions (Fig. 3b) with combined changes in Raman peak intensities and peak shifting. Although Raman intensities can typically vary slightly from crystal to crystal, significant differences were observed between  $\text{CmW}_5$  and  $\text{NdW}_5$ . For  $\text{CmW}_5$ , the intensities of the terminal yl oxygens ( $\text{W}=\text{O}$ ) increase, which could be due to increased  $\text{Cs}$ -complex interactions. For  $\text{Nd}-\text{O}-\text{W}$ , there is a decrease in intensity for the 890  $\text{ cm}^{-1}$  peak and an increase for the 211  $\text{ cm}^{-1}$  peak, which

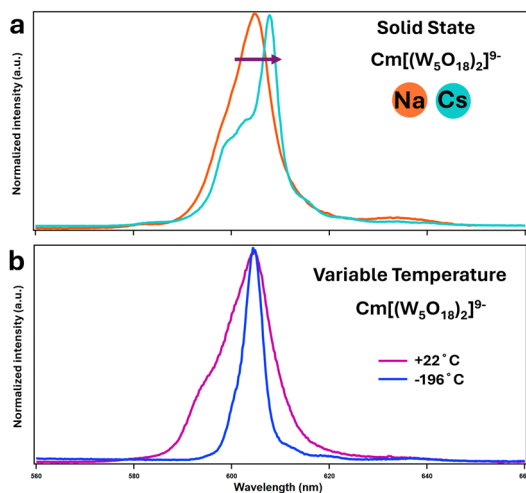




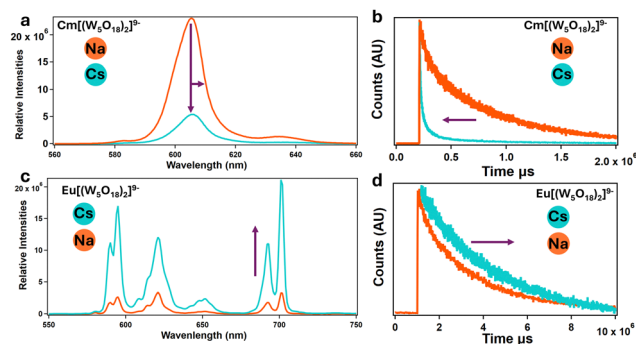
**Fig. 3** Solid-state Raman microscopy of CmW<sub>5</sub> and Nd–W<sub>5</sub> (a) [Cm(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9–</sup> with sodium (in orange) and cesium (in blue) counterions. (b) Similar experiments with [Nd(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9–</sup>. (c) CCD image capture of Cs–CmW<sub>5</sub> single crystals. This picture was taken under UV-light – the pink-orange fluorescence highlights the presence of Cm<sup>3+</sup>. (d) Na–CmW<sub>5</sub> solution evaporated onto a microscopy slide. The material was crystalline, but the crystals were too small for XRD analysis. See Fig. S1 (ESI<sup>†</sup>) for additional crystal pictures.

also shifts to 223 cm<sup>–1</sup>. For CmW<sub>5</sub>, an increase in Raman intensity for the terminal O and bridging O and peak shifting from 211 to 223 cm<sup>–1</sup> is also observed (Fig. 3a). However, the 890 cm<sup>–1</sup> peak corresponding to Cm–O–W is shifted to higher energy by 35 cm<sup>–1</sup> to 925 cm<sup>–1</sup>, *i.e.*, the opposite of what is observed for the Na/Cs–NdW<sub>5</sub> compounds. The blue shifting caused by the Cs on the bridging O in Cm–O–W is a clear indicator of the outsized role Cs<sup>+</sup> ions on the [Cm(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9–</sup> complex as opposed to its lanthanide analogs. To the best of our knowledge, this represents the first observation of cesium-actinide interactions within a molecular complex.

The impact of Cs counter ions on CmW<sub>5</sub> was further investigated *via* fluorescence spectroscopy (Fig. 4 and 5). We recently



**Fig. 4** (a) Solid-state emission spectra of [Cm(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9–</sup> with Na and Cs counterions (b) fluorescence emission of aqueous solutions of Na–CmW<sub>5</sub> at room temperature (22 °C – pink curve) and after flash-freezing in liquid nitrogen (–196 °C – blue curve). Solvent: 1:4 vol/vol glycerol:H<sub>2</sub>O. Excitation wavelength: 271.0 nm. See Fig. S2 and S3 (ESI<sup>†</sup>) for corresponding excitation spectra.



**Fig. 5** Solution and time-resolved fluorescence. (a) and (b) Emission spectra of solutions of CmW<sub>5</sub> with sodium and cesium counterions, showing fluorescence quenching and lifetime shortening. (c) and (d) Similar experiments with NdW<sub>5</sub>, showing opposite behavior. Both CmW<sub>5</sub> and EuW<sub>5</sub> complexes are under 100 mM acetate buffer at a pH of 5.5. [EuW<sub>5</sub>] = 1 mM. [CmW<sub>5</sub>] = 100 μM (Cs–CmW<sub>5</sub> spectra was adjusted to compensate for the dilution for the addition of 3 M CsCl, final concentration of Cs–CmW<sub>5</sub> was 50 μM). See Fig. S4 and S5 (ESI<sup>†</sup>) for corresponding excitation spectra.

reported<sup>13</sup> solution-state fluorescence experiments on Na–CmW<sub>5</sub>. The Cm<sup>3+</sup> emission peak is centered at 604.6 nm and the fluorescence lifetime decay of 780 μs is the longest observed for a Cm<sup>3+</sup> complex in solution. We performed similar Cm<sup>3+</sup> fluorescence experiments with and without cesium counterions, and both in the solid-state (Fig. 4) and solution-state (Fig. 5). Consistent with the Raman spectroscopy results, the fluorescence properties of CmW<sub>5</sub> were also found to be impacted by the nature of the counterions. Fig. 4a shows the emission spectrum of single crystals of Cs–CmW<sub>5</sub> and a crystalline precipitate of Na–CmW<sub>5</sub>. Switching the counterions from Na to Cs, the Cm<sup>3+</sup> emission peak shifts from 604.6 to 608.0 nm. The structure of the emission peak of Cs–CmW<sub>5</sub> is also more pronounced, likely indicative of less disorder in the structure. We also measured the emission spectrum of Na–CmW<sub>5</sub> in solution at room temperature and as a flash-frozen solution at liquid-nitrogen temperature (–196 °C). The spectrum of the Na–CmW<sub>5</sub> solution (Fig. 4b) at room temperature is consistent with that of the solid (Fig. 4a). Upon cooling, the Na–CmW<sub>5</sub> emission peak becomes more structured, and we could confirm the main emission band is at 604.6 nm, consistent with the solid-state data. The results clearly indicate that the nature of the counterion impacts the energy levels of CmW<sub>5</sub>.

To further confirm the results, Fig. 4a shows the emission spectra of a Na–CmW<sub>5</sub> solution (consistent with previously reported data<sup>13</sup>) and the same sample after addition of Cs<sup>+</sup> counterions. A significant quenching of the luminescence is observed, with the emission intensity decreasing by an order of magnitude. A shortening of the lifetime to about 515 μs and a peak shifting from 604.6 to 606.0 nm were also observed (Fig. 5a and b). This strongly indicates that Cs<sup>+</sup> counterions, typically considered spectator ions, actually influence bonding and energy levels within the CmW<sub>5</sub> complex.

The relatively close proximity between Cm<sup>3+</sup> and Cs<sup>+</sup> ions in the crystal structure (Fig. 2) suggests that Cs<sup>+</sup> may provide a relaxation pathway for Cm<sup>3+</sup> upon excitation, akin to water



molecules, hence leading to shortening of the luminescence lifetime. Another hypothesis is that ion-pairing formation between Cs and  $W_5$  is strong enough to change the excited state energy levels of the POM, leading to less efficient fluorescence sensitization of  $Cm^{3+}$  luminescence.

Similar solution-state experiments were performed with  $Eu^{3+}$ , due to its relatively similar size to  $Cm^{3+}$  and fluorescence properties (Fig. 5c and d). Solutions of Na- $EuW_5$  exhibit the typical multi-peak emission band of a  $Eu^{3+}$  complex, with main peaks at  $\sim 680$ ,  $\sim 620$ ,  $\sim 650$ , and  $\sim 700$  nm (Fig. 5c). The measured fluorescence lifetime of 2385  $\mu s$  indicates that no water molecule is present.<sup>29</sup> However, contrary to curium, when an excess of  $Cs^+$  ions is added, the emission intensity of  $EuW_5$  increases significantly, by a factor of  $\sim 10$ , and the lifetime increases from 2385 to 3431  $\mu s$ . This, combined with the Cm results indicate the Cs ions impact the energy levels of the POM.

In conclusion, this study reports the first example of a Weakley–Peacock-type polyoxometalate complex with a transplutonium element, namely the curium bis-pentatungstate  $NaCs_8Cm(W_5O_{18})_2 \cdot 14H_2O$ . This compound was synthesized at the microscale and characterized *via* single crystal XRD, Raman microscopy, as well as solid-state and solution-state fluorescence. Comparative experiments with  $Nd^{3+}$  and  $Eu^{3+}$  analogous compounds revealed a divergence between lanthanide and actinide coordination chemistries. This study further highlights the unsuspected but critical impact that counterions, particularly cesium, have on the fluorescence and vibrational modes of  $[Cm(W_5O_{18})_2]^{9-}$ . These results show that, even within the same coordination chemistry framework (*i.e.*, 8-coordinated complexes with square antiprismatic geometry), 4f and 5f cations exhibit fundamental chemical differences that can be manifested at long-range and even *via* interactions with other cations present in the structure. Given the high number of heavy tungsten atoms in the POM compounds, in addition to many oxygens and presence of the heavy actinide, computational work (*e.g.*, density functional theory) to explain the fundamental origin of these experimental observations are currently too expensive. Further compounding this, the results presented herein indicate that computational treatment of f-element POM complexes will require considering the full lattice (not just  $[Cm(W_5O_{18})_2]^{9-}$ , for example), including all cesium or sodium counterions and water molecules. Future work will focus on expanding the experimental space for actinide–POM compounds in order to provide a consistent framework for future theoretical work on this, so far, overlooked class of actinide compounds.

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## Conflicts of interest

There are no conflicts to declare.

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