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# Isolation and characterization of a new polyoxometalate ligand, $\text{H}_3\text{SbW}_{14}\text{O}_{50}^{10-}$ , and its interactions with f-elements†

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**We report the synthesis and characterization (Raman, FTIR, DLS, single crystal XRD) of  $\text{Cs}_{10}\text{H}_3\text{SbW}_{14}\text{O}_{50}\cdot 6\text{H}_2\text{O}$ , which contains a new polyoxometalate building block:  $\text{H}_3\text{SbW}_{14}\text{O}_{50}^{10-}$  ( $\text{SbW}_{14}$ ). Solution-state fluorescence, DLS, and UV-vis absorbance results with  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Am}^{3+}$ , and  $\text{Cm}^{3+}$  confirm that  $\text{SbW}_{14}$  acts as an efficient complexant and fluorescence sensitizer for f-elements.**

Polyoxometalates (POMs) represent a large family of molecules with numerous applications, and their range of compositions and structures covers most of the periodic table.<sup>1–3</sup> While the POM core structures are typically built upon d-block metals<sup>4</sup> (W, Mo, V, Cr, Nb, Ta), their compounds often incorporate other elements and complex metal ions, and are counter-balanced by cations. POM compounds that have been characterized thus far cover over 70 elements (from hydrogen to as heavy as curium<sup>5–8</sup>), representing one of the most diverse class of molecules.

POMs can be seen as the inorganic equivalents of organic chelators or as an ever-expanding family of molecules that uses d-block metal octahedra (e.g.,  $\text{WO}_6^{2-}$ ) as unitary blocks, instead of carbon–carbon bonds. POM core structures include the Lindqvist<sup>9</sup> (e.g.,  $\text{Mo}_6\text{O}_{19}^{2-}$ ,  $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$  and  $\text{H}_x\text{Ta}_6\text{O}_{19}^{x-8}$ ), Peacock–Weakley<sup>10</sup> (e.g.,  $\text{W}_5\text{O}_{18}^{6-}$ ), Keggin<sup>11</sup> (e.g.,  $\text{PMo}_{12}\text{O}_{40}^{3-}$ ,  $\text{SiW}_{11}\text{O}_{39}^{8-}$ ), Well–Dawson<sup>12</sup> (e.g.,  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ ), Anderson–Evans<sup>13,14</sup> (e.g.,  $\text{Mo}_7\text{O}_{24}^{6-}$ ), and Preyssler<sup>15</sup> (e.g.,  $\text{P}_5\text{W}_{30}\text{O}_{110}^{15-}$ ) ions. However, the Keggin, Wells–Dawson, and Lindqvist structures are the most widely studied.<sup>4,15–17</sup> For instance, in the Keggin structure ( $[\text{XW}_{12}\text{O}_{40}]^{7-}$ ), over 25 candidates are available to be incorporated as heteroelement (X). This leads to an overwhelming number of

Keggin derivatives,<sup>18</sup> all with potentially distinct physicochemical properties.

In this context, the subset of antimonopolytungstates (Sb-POTs), has been relatively overlooked, despite having truly unique properties. In previously reported examples of Sb-POTs, the stereoactive lone pair<sup>19</sup> of Sb(III) strongly influenced the structures, albeit still leading to Keggin derivatives.<sup>20</sup> In addition, the low charge density of  $\text{Sb}^{3+}$  shifts the POMs' stability window to slightly higher pHs, often leading to protonated Sb-POTs.<sup>21–23</sup> This often results in larger POMs, yet still all derived from the Keggin structure. Several Sb-POTs have been reported in the last few decades—all based on successive condensations of  $[\text{SbW}_9\text{O}_{33}]^{9-}$  ( $\text{SbW}_9$ ), which is a tri-lacunary Keggin ion.  $\text{SbW}_9$  is arguably the most used Sb-POT structure and has served as precursor for larger POMs ( $[\text{NaSb}_9\text{W}_{21}\text{O}_{86}]^{18-}$ ,  $[\text{Sb}_2\text{W}_{21}\text{O}_{69}]^{6-}$ ,  $[\text{H}_2\text{SbW}_{22}\text{O}_{76}]^{14-}$ ,  $[\text{Sb}_8\text{W}_{36}\text{O}_{132}]^{24-}$ ...<sup>20</sup>

In recent years, POMs have also received increasing attention for use as chelators for f-elements. In fact, POMs offer an interesting alternative relative to the more traditional organic chelators as they can act as oxygen-donor ligands but contain elements that are not easily incorporable in organic ligands. POMs can also stabilize usually unstable oxidation states of actinides, such as  $\text{Am}(\text{VI})$ .<sup>8</sup> The high-molecular weight of POMs also make them useful to perform microscale crystallization tests with radioisotopes.<sup>5</sup> In our quest to expand the chemistry of f-elements with POM ligands, we attempted to transpose our synthetic protocols recently used<sup>5,7,24</sup> for Keggin POMs with  $\text{B}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Ge}^{4+}$ , and  $\text{P}^{5+}$  to antimony ( $\text{Sb}^{3+}$  – Fig. 1). Unexpectedly, the substitution of the heteroelements mentioned above for  $\text{Sb}^{3+}$  did not yield the expected Keggin POM. Not only does the behavior of antimony depart from that of the other heteroelements, but it also yielded a novel POM structure. This therefore unlocked an opportunity to explore f-element chemistry with a new type of ligand.

Herein we report the single crystal XRD structure of the POM compound  $\text{Cs}_{10}\text{H}_3\text{SbW}_{14}\text{O}_{50}\cdot 6\text{H}_2\text{O}$ . This antimony(III) polytungstate is based on a new building block  $[\text{H}_3\text{SbW}_{14}\text{O}_{50}]^{10-}$  ( $\text{SbW}_{14}$ ). This POM was obtained by the typical synthetic route that has consistently led to Keggin-type structures with other

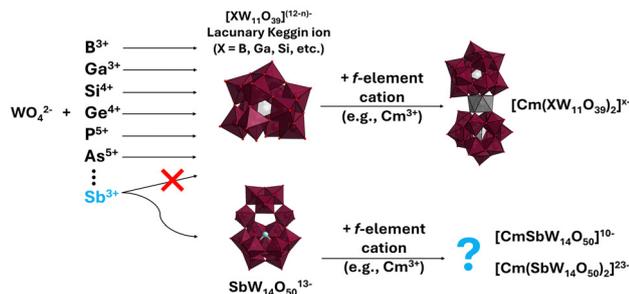
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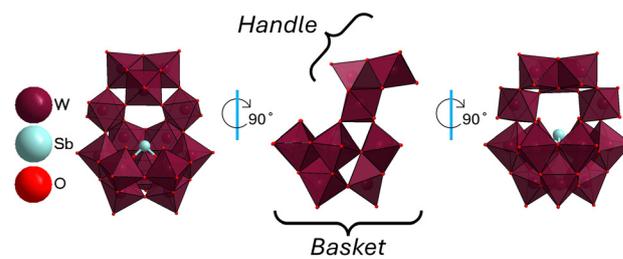


**Fig. 1** Comparative synthesis scheme for the Keggin ion POM ligands and the new antimony POM reported here (unprotonated formula:  $\text{SbW}_{14}\text{O}_{50}^{13-}$ ). While most p-block elements react with  $\text{WO}_4^{2-}$  (at pH 4–7) to form Keggin-type POMs, the same reaction with  $\text{Sb}^{3+}$  yield a different type of POM:  $\text{SbW}_{14}\text{O}_{50}^{13-}$ . This new POM can then be used to interact with lanthanide and actinides cations (e.g.,  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ).

p-block elements.<sup>15</sup> Additionally, we probed the potential binding of  $\text{SbW}_{14}$  to trivalent lanthanides ( $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$ ) and actinides ( $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ ) in solution.  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  were used for their fluorescence properties while  $\text{Nd}^{3+}$  and  $\text{Am}^{3+}$  were used for their absorbance properties. All four f-elements also have similar ionic radii, facilitating intercomparisons. The behavior of  $\text{SbW}_{14}$  was also contrasted with the previously known POM  $\text{SbW}_9$ . The results show that  $\text{SbW}_{14}$  can act as an effective aqueous ligand with f-elements. This represents the first study of interactions between antimony-containing ligands and heavy actinides.

$\text{SbW}_{14}$  was obtained by conversion of the precursor  $[\text{SbW}_9\text{O}_{33}]^{9-}$  ( $\text{SbW}_9$ ). This precursor was synthesized as reported by Bösing *et al.*<sup>20</sup> without modification. The  $\text{SbW}_9$  to  $\text{SbW}_{14}$  conversion reaction was found remarkably straightforward – happening at room temperature, ambient pressure, and in aqueous solution. From the synthesis by Bösing *et al.*, a 2 mM solution of  $\text{SbW}_9$  was prepared (30 mg in a 100 mM acetate buffer at pH 5.5). Then, an equal volume of 6 M CsCl was added (final concentration of 3 M). After 24–48 h crystals of  $\text{SbW}_{14}$  appeared. The pH was measured at various points during the crystallization period and was stable at 5.5. For a more detailed synthesis procedure see ESI.† Single crystals of  $\text{SbW}_{14}$  were collected for structure determination, plus Raman and FTIR analysis. Fig. S1 (ESI†) clearly shows distinct Raman and FTIR features between  $\text{SbW}_9$  and  $\text{SbW}_{14}$ .

Interestingly, the new Sb-POT could only be crystallized through the addition of caesium counterions, as opposed to pH variation. For POMs, the most conventional manner to control their speciation is by controlling the pH, to tune their hydrolysis and condensation reactions. We assume that  $\text{SbW}_{14}$  had thus far remained undiscovered because there is generally very little information in the literature about Sb-POTs with caesium counterions. This new crystal structure is unique in its synthesis, obtained through counterion-mediated reactions as opposed to pH-controlled reactions. The new structure, fully formulated as  $\text{Cs}_{10}\text{H}_3\text{SbW}_{14}\text{O}_{50}\cdot 6\text{H}_2\text{O}$ , crystallizes in the orthorhombic space group  $P2_12_12_1$  with a unit cell volume of 6609.5 (3) Å<sup>3</sup>; for more information see Table S1 (ESI†). One manner to describe the new Sb-POTs is as a combination of



**Fig. 2** Top. Structure overview of the isolated new polyoxometalate,  $\text{SbW}_{14}\text{O}_{50}^{13-}$ . Color code: W (maroon), O (red), Sb (cyan). Caesium and hydrogen atoms are omitted for clarity. Bottom. Raman spectra for  $\text{SbW}_9$  and  $\text{SbW}_{14}$ .

the  $[\text{SbW}_9\text{O}_{33}]^{9-}$  subunit, nicknamed the ‘basket’, with a  $[\text{W}_5(\text{OH})_3\text{O}_{14}]^-$  ‘handle’ subunit (Fig. 2). The structure itself has only one symmetry element; a mirror plane along its long axis. Thus, the structure falls under the point group  $C_s$ . The ‘basket’ subunit,  $\text{SbW}_9$ , is the original precursor and itself is often described as the tri-lacunary version of parent Keggin structure ( $[\text{XW}_{12}\text{O}_{40}]^{12-}$ ).<sup>25,26</sup> In other words, removal of three adjacent tungstates from a parent but hypothetical structure  $[\text{SbW}_{12}\text{O}_{40}]^{5-}$ , would result in the  $\text{SbW}_9$  subunit. We suspect that  $\text{SbW}_9$  does not convert to  $[\text{SbW}_{12}\text{O}_{40}]^{5-}$  due to the size of  $\text{Sb}^{3+}$  and steric hindrance created by its lone electron pair. In  $\text{SbW}_9$ , six tungstates surround the central  $[\text{SbO}_3]^{3-}$ , with the remaining three tungstates opposite to the lone pair on Sb.

Bond valence sum calculations in  $\text{SbW}_{14}$  confirms the oxidation state at +III for Sb (Table S2, ESI†). The six surrounding tungstates can be thought of as the ‘rim of the basket’ while the remaining three tungstates can be the ‘bottom’. The ‘handle’ itself,  $[\text{W}_5(\text{OH})_3\text{O}_{14}]^-$ , can further be subdivided and described as a  $[\text{W}_3(\text{OH})_3\text{O}_{10}]^{5-}$  with two edge-sharing *cis*-di-oxyl-tungstens,  $[\text{O}=\text{W}=\text{O}]^{2+}$ , binding to two of the three tungstates in the trimer. These two flanking tungstens then bind to the ‘basket’ completing their six-fold coordination. The ‘handle’ is attached to the basket *via* four out of the six tungstates surrounding Sb in the  $\text{SbW}_9$  subunit. As a result, all tungstates have a coordination number of six, as seen for most polyoxotungstates, with rare exceptions.<sup>27</sup> Bond valence sum calculation on the O and W positions additionally reveal the potential location of three protons on the POMs, leading to the formula  $[\text{H}_3\text{SbW}_{14}\text{O}_{50}]^{10-}$ , Table S3 (ESI†).

Due to its unique composition and structure, the complexation of  $\text{SbW}_{14}$  with f-elements became of particular interest. The solution behavior of this new POT was explored through fluorescent spectroscopy ( $\text{Eu}^{3+}$  vs.  $\text{Cm}^{3+}$ ) and UV-Visible spectrophotometry ( $\text{Nd}^{3+}$  vs.  $\text{Am}^{3+}$ ). This represents the first study on transplutonium elements with antimony-based ligands. To first probe the physicochemical properties and complexation behavior for  $\text{SbW}_{14}$ , excitation and emission spectra were taken with  $\text{Eu}^{3+}$  at a 1 : 2 ratio ( $\text{Eu}^{3+} : \text{SbW}_{14}$ ), as we expected a 1 : 1 or 1 : 2 complex based on potential binding sites of the  $\text{SbW}_{14}$  structure (Fig. 2). Excess POM to f-element was also used to ensure full complexation. Parallel experiments were done with  $\text{SbW}_9$ , for comparison purposes and to confirm that  $\text{SbW}_{14}$  does not convert back to its precursor upon binding to the



f-elements. Both  $\text{SbW}_9$  and  $\text{SbW}_{14}$  were found to spontaneously bind to the trivalent lanthanides and actinides.

Fig. 3a and b show the normalized excitation and emission spectra, respectively for  $\text{Eu}^{3+}$  with  $\text{SbW}_9$  and  $\text{SbW}_{14}$ . Both POMs bind to  $\text{Eu}^{3+}$  and sensitize its luminescence, but evidently *via* different pathways (Fig. 3a). The preferential excitation pathway for  $\text{Eu}^{3+}$  is *via* the POM band ( $\lambda_{\text{ex}} = 290\text{--}310$  nm) in the case of  $\text{SbW}_{14}$  but *via* direct excitation of  $\text{Eu}^{3+}$  ( $4f\text{--}4f$  sharp transitions at  $360\text{--}410$  nm, main peak  $\lambda_{\text{ex}} = 396$  nm) in the case of  $\text{SbW}_9$ . The excitation peak *via* the POM has a maximum at  $343$  nm for  $\text{SbW}_9$ , compared to  $303$  nm for  $\text{SbW}_{14}$ . When comparing the emission spectra,  $\text{SbW}_{14}$  results in more defined  $\text{Eu}^{3+}$  emission peaks, with intensities about 16-fold higher (Fig. S3, ESI†).

Lifetime dependent fluorescence further shows different complexation behaviors for  $\text{SbW}_9$  versus  $\text{SbW}_{14}$  (Table S4, ESI†). While both  $\text{SbW}_9$  and  $\text{SbW}_{14}$  yield mono-exponential decay curves with  $\text{Eu}^{3+}$  (suggesting only one type of complex(es) present), the lifetimes are significantly different, at  $336$   $\mu\text{s}$  and  $621$   $\mu\text{s}$ , respectively. Based on the Kimura equations,<sup>28</sup> which empirically correlate fluorescence lifetimes to hydration sphere, the number of coordinating water molecules decreases from three for  $\text{Eu}\text{--}\text{SbW}_9$ , to one for  $\text{Eu}\text{--}\text{SbW}_{14}$ . Although we were unable to crystallize a complex of  $\text{SbW}_{14}$  with an f-element, the solution-state fluorescence results suggest that  $\text{SbW}_{14}$  is more amenable to fulfil the f-element coordination sphere than  $\text{SbW}_9$ , leaving it less exposed to solvent molecules. Additional

fluorescence titration experiments (Fig. S6–S8, ESI†), revealed that the  $\text{Eu}\text{--}\text{SbW}_{14}$  likely undergoes a gradual complexation reaction when the ratio  $\text{SbW}_{14}:\text{Eu}$  is varied. By analogy to other POMs,<sup>4</sup> we tentatively ascribe the observed spectral changes to the sequential formation of 1:1 and 1:2 complexes, however the precise solution-state speciation of the f-element/ $\text{SbW}_{14}$  systems will require further investigations.

When studies were extended from 4f to 5f-elements ( $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ ) some deviations could be discerned in their binding behavior and physiochemical properties. Fluorescence results (Fig. 3c, d and Fig. S4, S5, ESI†) confirmed that  $\text{Cm}^{3+}$  also binds to both  $\text{SbW}_9$  and  $\text{SbW}_{14}$ . However, contrary to  $\text{Eu}^{3+}$ , the excitation spectra revealed that, for both  $\text{SbW}_9$  and  $\text{SbW}_{14}$ , sensitization of  $\text{Cm}^{3+}$  *via* the POM is more efficient than direct excitation. The POM excitation band is at  $276$  nm for  $\text{Cm}\text{--}\text{SbW}_9$  versus  $303$  nm for  $\text{Cm}\text{--}\text{SbW}_{14}$ . Sensitization of  $\text{Cm}^{3+}$  is also more efficient *via*  $\text{SbW}_{14}$  than  $\text{SbW}_9$ , by a factor of  $\sim 4$  (Fig. S4, ESI†). In other words,  $\text{SbW}_{14}$  leads to brighter complexes than  $\text{SbW}_9$  for both  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$ . The  $\text{Cm}^{3+}$  emission spectra are also distinct, with peak maximum at  $606.0$  nm for  $\text{SbW}_9$  and  $609.0$  nm for  $\text{SbW}_{14}$  and an increase in intensity of a factor of 1.5. Both  $\text{Cm}\text{--}\text{SbW}_9$  and  $\text{Cm}\text{--}\text{SbW}_{14}$  complexes exhibit a significant peak shift when compared to free  $\text{Cm}^{3+}$  under similar conditions ( $598.4$  nm).<sup>5</sup> While the Kimura equation has been shown to not be applicable for most reported curium POMs,<sup>5</sup> apart from the simplest polytungstate  $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$ ,<sup>6</sup> the time-dependent fluorescence herein is somewhat consistent with the  $\text{Eu}^{3+}$  analog (*i.e.*, lifetime longer for  $\text{Cm}\text{--}\text{SbW}_{14}$  vs.  $\text{Cm}\text{--}\text{SbW}_9$ ). The measured lifetimes for  $\text{Cm}^{3+}$  are  $133$   $\mu\text{s}$  for  $\text{SbW}_9$  to  $177$   $\mu\text{s}$  for  $\text{SbW}_{14}$  (Table S4, ESI†). This corresponds to four and three water molecules, respectively. The trend is consistent with the  $\text{Eu}^{3+}$  results and indicates a lower hydration number for the  $\text{Cm}\text{--}\text{SbW}_{14}$  complex, relative to  $\text{Cm}\text{--}\text{SbW}_9$ , but the absolute number of water molecules may not be accurate. The difference in hydration between  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  complexes could arise from different binding sites on  $\text{SbW}_{14}$ .

However, we posit that the Kimura equation fails to accurately describe the  $\text{Cm}^{3+}$  hydration for the Sb-POTs and starts to be less valid for  $\text{Eu}^{3+}$  as well, in this particular context. We attribute this to the alkali counterions, which are typically considered inert but have been shown to form strong ion pairs with certain POM complexes. Herein,  $\text{SbW}_9$  uses  $\text{Na}^+$  whereas  $\text{SbW}_{14}$  uses  $\text{Cs}^+$ , which could impact fluorescence properties. Based on the emission spectra for  $\text{SbW}_9$ , the observed species are 1:1 complexes,  $[\text{Eu}(\text{SbW}_9\text{O}_{33})(\text{H}_2\text{O})_3]^{6-}$  and  $[\text{Cm}(\text{SbW}_9\text{O}_{33})(\text{H}_2\text{O})_4]^{6-}$ , but the speciation for  $\text{Cm}/\text{Eu}\text{--}\text{SbW}_{14}$  remains ambiguous as we do not know its coordination mode. We also performed dynamic light scattering (DLS) experiments on  $\text{SbW}_{14}$  and  $\text{SbW}_9$ , with and without  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  (Fig. S9 and Table S5, ESI†). The measured hydrodynamic diameters could support the formation of 1:1 complexes for both POMs under the tested conditions, although the size difference between 1:1 and 1:2 complexes may not be enough to discriminate with this technique. The role of counterions on the apparent hydrodynamic size measured by DLS also adds some uncertainty to the applicability of DLS to POM complexes.

To gain more insight into the speciation, UV-Vis absorbance experiments with  $\text{Nd}^{3+}$  and  $\text{Am}^{3+}$  were performed (Fig. 4). Both

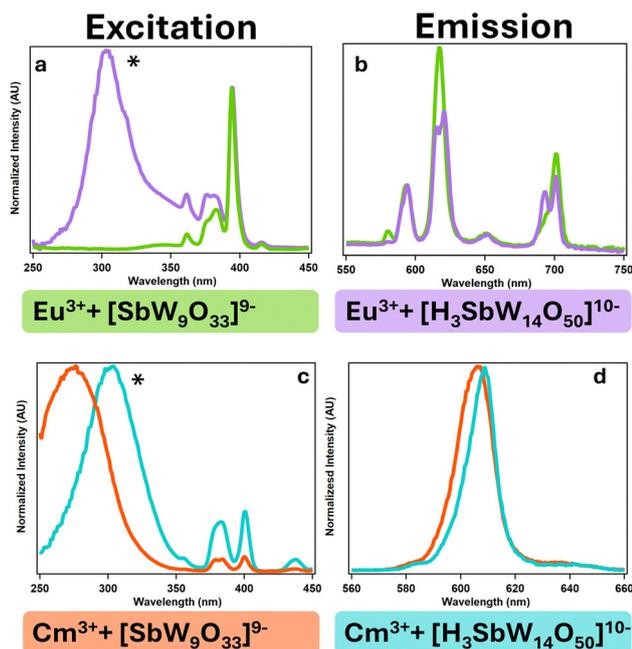


Fig. 3 Fluorescence studies on  $\text{Eu}\text{--}\text{SbW}_{14}$  (purple curves) and  $\text{Cm}\text{--}\text{SbW}_{14}$  (blue curves) compared to  $\text{Eu}\text{--}\text{SbW}_9$  (green curves) and  $\text{Cm}\text{--}\text{SbW}_9$  (orange curves).  $\text{Eu}^{3+}$  fluorescence: (a) excitation and (b) emission.  $\text{Cm}^{3+}$  fluorescence: (c) excitation and (d) emission. Fig. 3a is normalized to the excitation peak at  $396$  nm as  $\text{Eu}^{3+}$  sensitization *via* the POM band of  $\text{SbW}_9$  is inefficient. See Fig. S1–S5 (ESI†) for raw intensity spectra. Solution conditions were as follows:  $[\text{Eu}^{3+}] = 1$  mM, and  $[\text{Cm}^{3+}] = 100$   $\mu\text{M}$ ,  $[\text{SbW}_9]$  and  $[\text{SbW}_{14}]$  at  $2$  mM and  $200$   $\mu\text{M}$ , respectively. Sb-POTs were dissolved in  $0.1$  M acetate at pH of  $5.5$ . \*Indicates the POM excitation band.



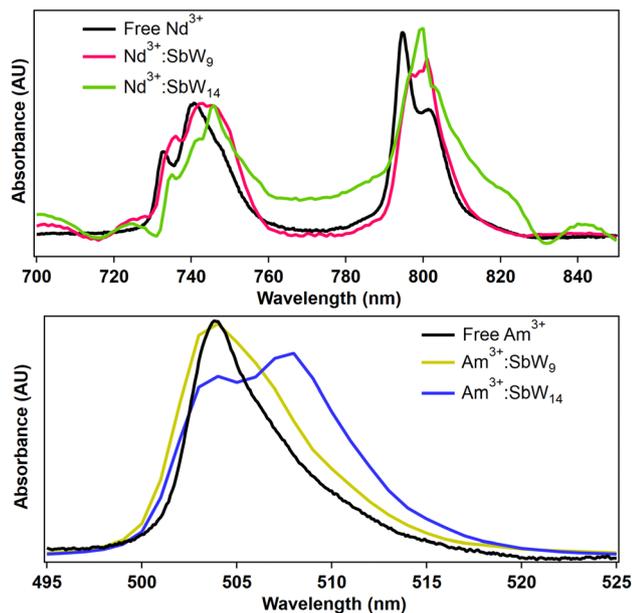


Fig. 4 UV-Vis spectra for  $\text{Nd}^{3+}$  (top) and  $\text{Am}^{3+}$  (bottom) with  $\text{SbW}_9$  and  $\text{SbW}_{14}$ . Solution conditions:  $[\text{Nd}^{3+}] = 1 \text{ mM}$ ,  $[\text{Am}^{3+}] = 20 \text{ }\mu\text{M}$ ,  $[\text{SbW}_9]$  and  $[\text{SbW}_{14}] = 2 \text{ mM}$  and  $40 \text{ }\mu\text{M}$ , respectively. Sb-POTs dissolved in 0.1 M acetate buffer (pH 5.5).

metals previously demonstrated sensitive absorbance peak shifting for different  $\text{Nd}^{3+}/\text{Am}^{3+}$ -POT species.<sup>5,8</sup>  $\text{Am}^{3+}$  typically exhibit significant peak shifting with the free ion absorbance at 504 nm, 1:1  $\text{Am}^{3+}$ :POT complexes at 506–512 nm, and 1:2 complexes at 514–520 nm.<sup>5</sup> For both  $\text{Nd}^{3+}$  and  $\text{Am}^{3+}$ , there is evidence of complexation with both  $\text{SbW}_9$  and  $\text{SbW}_{14}$  (Fig. 4). The absorbance bands of  $\text{Nd}^{3+}$  and  $\text{Am}^{3+}$  are both affected in the presence of  $\text{SbW}_9$  and  $\text{SbW}_{14}$ , relative to their free ion state. In the case of  $\text{Am}^{3+}$ ,  $\text{SbW}_9$  leads to asymmetric broadening of the peak, likely indicative of a lower symmetry relative to the aqua ion. For  $\text{Am}^{3+}$  with  $\text{SbW}_{14}$ , the peak exhibits a more obvious change with a dominant peak appearing at 508.0 nm. Note that the  $\text{Am}^{3+}$ -Sb-POT experiments were limited to 20  $\mu\text{M}$  concentrations, as opposed to 1 mM for  $\text{Nd}^{3+}$  or 100  $\mu\text{M}$  for  $\text{Cm}^{3+}$ , which may have limited the complexation efficacy of the POMs. The results nonetheless confirm that both  $\text{SbW}_9$  and  $\text{SbW}_{14}$  bind to trivalent lanthanides and actinides in solution. The similar extinction coefficient also supports the formation of 1:1 complexes under these conditions.

In conclusion, this study reports a new antimonopolytungstate structure,  $\text{SbW}_{14}$ , and its solution behavior with lanthanide and actinide elements. The  $\text{Cs}_{10}\text{H}_3\text{SbW}_{14}\text{O}_{50}\cdot 6\text{H}_2\text{O}$  structure was synthesized by an unconventional route of counterion-mediated conversion (*versus* traditional hydrolysis and condensation reactions). This compound was characterized *via* single crystal XRD, FTIR, Raman microscopy and compared to its precursor,  $\text{SbW}_9$ . Solution-state fluorescence, UV-Vis spectroscopy, and DLS experiments with  $\text{Eu}^{3+}$  vs.  $\text{Cm}^{3+}$ , and  $\text{Nd}^{3+}$  vs.  $\text{Am}^{3+}$ , revealed consistent complexation of  $\text{SbW}_9$  and  $\text{SbW}_{14}$  to the lanthanides or actinides. Furthermore, we demonstrate that the new structure functions as a more efficient sensitizer and for both  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$ , relative to

$\text{SbW}_9$ . Future work will focus on elucidating the solution-state speciation and expand the counterion conversion of other Sb-POTs and interactions with other f-elements.

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## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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