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The formation and stability of $[EuP_5W_{30}O_{110}]^{12-}$ and $[AmP_5W_{30}O_{110}]^{12-}$

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Abstract

A comparison of the standard reduction potentials of Eu^{3+} and Am^{3+}, as well as their similar ionic radii, suggest that Am in the Preyssler anion, $[AmP_5W_{30}O_{110}]^{12-}$, may be reduced under an applied potential. However, cyclic voltammetric studies performed in a noncomplexing electrolyte, together with XANES and EXAFS data, consistently demonstrate that Am is trivalent when encrypted in $[AmP_5W_{30}O_{110}]^{12-}$. There is no evidence of Am^{3+} reduction, even at the lowest potentials probed. A comparison of bond distances of the trivalent Am analog, determined from EXAFS spectroscopy, with those of other tetravalent f ions shows a correlation with ionic radii that appears independent of the charge on the ion. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: $[EuP_5W_{30}O_{110}]^{12-}$; $[AmP_5W_{30}O_{110}]^{12-}$; Formation; Stability

1. Introduction

Heteropolyanions are well defined molecular clusters that typically vary in size from 50 to 200 atoms. Whereas a wide variety of these 'magic' clusters have been reported to date [1], there are only three anions, $[NaSb_9W_{21}O_{86}]^{18-}$ [2], $[NaAs_4W_{40}O_{140}]^{25-}$ [3] and $[NaP_5W_{30}O_{110}]^{14-}$ that have been reported to encapsulate rare-earth (R) ions. In the latter of these, $[NaP_5W_{30}O_{110}]^{14-}$, the so-called Preyssler anion, Na^+ is encrypted inside a central cavity formed by five PW_6O_{22} units arranged in a crown [4], as shown schematically in Fig. 1. It is not possible to synthesize a R analog of the Preyssler anion directly, however under suitable conditions the Na^+ can be exchanged for all of the rare earth ions [5], including La and Ce [6]. In addition to the R^{3+} exchange for Na^+, the actinide ions U^{4+} [5], Th^{4+}, Am^{3+} and Cm^{3+} [7] have also been successfully encrypted into the anion cavity. The encryption of actinide ions naturally raises the question of the Preyssler anions' suitability as an agent for separating, sequestering and/or storing radioactive waste. In order to assess this application, it is important to understand the speciation of the actinide ion in the P–W–O framework and its interactions with the framework.

All of the trivalent-R substituted Preyssler anionic clusters are electrochemically active and form heteropoly blues. Their CVs are qualitatively distinguishable from that of the parent cluster. Indeed, the charge on the substituted ion influences the CV, such that the electrochemical response from the heteropolyanion is characteristic of the formal charge on the ion in the central cavity. In this way, CV data can be used as a fingerprint of the charge on the encrypted ion. The cyclic voltammograms (CVs) of the R^{3+} -substituted $[RP_5W_{30}O_{110}]^{12-}$ are all similar to each other, with the exception of $[EuP_5W_{30}O_{110}]^{12-}$, in which Eu itself has been shown to be electroactive [8]. Eu is trivalent at rest potential but it is entirely reduced to Eu^{2+} under an applied potential of −0.55 V vs. Ag/AgCl [9]. This concomitant reduction of Eu and the framework results in a $[EuP_5W_{30}O_{110}]^{12-}$ CV that is unique. Although the exact formal potential at which trivalent Eu is reduced is difficult to access because of the concurrent electrochemical activity of the Preyssler–anion framework, X-ray absorption near-edge structure (XANES) data indicate a 50% reduction of the encrypted Eu at potentials more positive than −0.2 V in a non complexing electrolyte [10,11]. The standard potential for the Eu^{3+} reduction is −0.55 V [12]. Whereas Eu is trivalent at rest potential in $[EuP_5W_{30}O_{110}]^{12-}$, the observation that divalent Eu is stabilized over its trivalent counterpart by at least 0.35 V, relative to the standard reduction potential, when encrypted in an *anionic* cluster is quite remarkable.

The significant stabilization of reduced Eu in the Preyssler anion suggests the possibility of stabilizing Am^{2+} under similar conditions. Am^{3+} has a $5f^6$ configuration and as such it is the actinide analog of Eu^{3+}, which has the $4f^6$ configuration. The standard reduction potential of Am^{3+} has been estimated to be between −1.7 and −2.5

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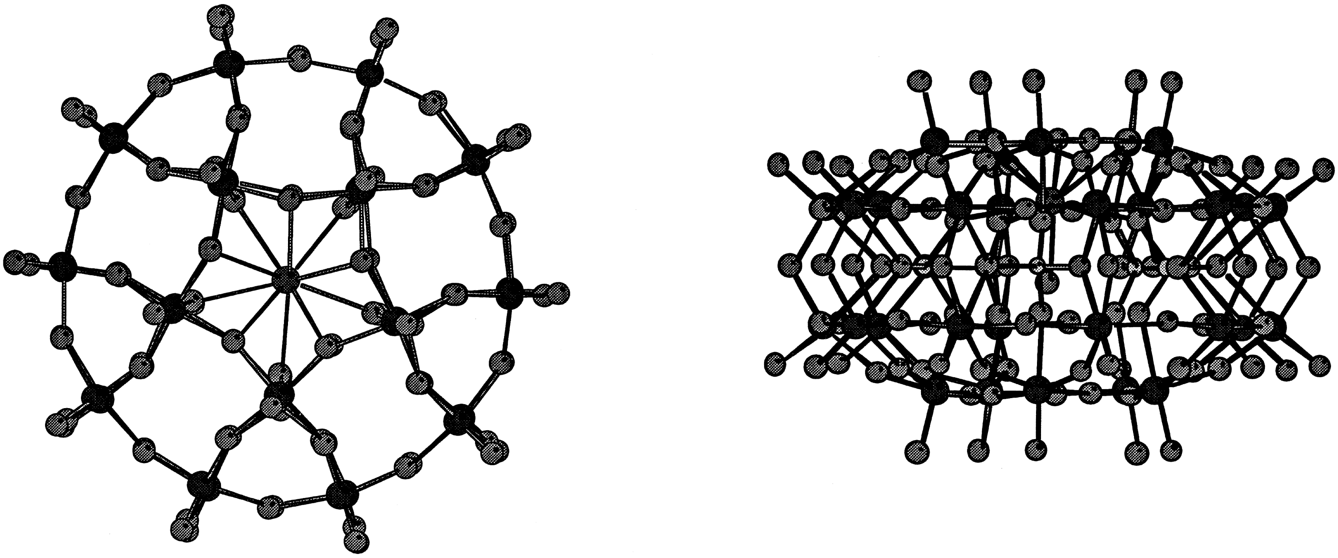

Fig. 1. The top (left) and side (right) view of the Preyssler anion $[RP_5W_{30}O_{110}]^{12-}$, which is shaped like a donut. The central ion seen in the top view, sits in the 'donut hole', and is exchangeable.

V vs. Ag/AgCl [13,14] and there is no direct evidence from CV data that Am^{3+} is reduced within the potential window afforded by the aqueous solvent [7]. Depending on the mechanism behind the stabilization of divalent Eu in an anionic cluster, this cluster may have an even more pronounced effect on a 5f ion. In other words, divalent Am may be even more stabilized than divalent Eu in the same environment. In order to understand better the influence of size and bonding on the unusual stabilization of lower valent hosts in the Preyssler anion, we report herein the speciation and coordination environment of Am in $[AmP_5W_{30}O_{110}]^{12-}$.

2. Experiments

The Eu- and Am-containing Preyssler anions were prepared according to literature methods as the K salts [7,8]. CV data were obtained in 1 M H_2SO_4 as described previously [7]. The low temperature Eu L_3 EXAFS (extended X-ray absorption fine structure) data for $[EuP_5W_{30}O_{110}]^{12-}$ were obtained at Wiggler station 4–3 at SSRL with a Si⟨220⟩ monochromator and ca. 0.8 mm vertical entrance slits. With ca. 80% detuning of the incident X-ray intensity, the Eu L_3-edge fluorescence data were collected using a 13-element detector (Canberra) without filters. The powdered sample was maintained at 17 K in a continuous-flow LHe cryostat (Oxford CF-1208). The room temperature XANES (X-ray absorption near edge structure) of an aqueous solution of $[EuP_5W_{30}O_{110}]^{12-}$ as well as the room temperature XANES and EXAFS of the solid $[AmP_5W_{30}O_{110}]^{12-}$ salt were obtained at the APS bending magnet station 12-BM-B, which is equipped with a Si⟨111⟩ monochromator. The X-ray energy for the Am experiments was calibrated by setting the maximum in the first derivative of a Nb foil spectrum to 18 986 eV. An Ar-filled ion chamber was used to detect the Eu Lα fluorescence. A multi-element detector was used to resolve the weak Am Lα signal from the strong W L fluorescence. The EXAFS were analyzed with the EXAFSPAK programs [15]. Single-scattering phase and amplitude functions were calculated with FEFF7.02 [16,17] and a scale factor fixed to 0.9.

3. Results

The CV data obtained from $[EuP_5W_{30}O_{110}]^{12-}$ and $[AmP_5W_{30}O_{110}]^{12-}$ are compared in Fig. 2. The CVs from these two samples are different. A comparison of the $[AmP_5W_{30}O_{110}]^{n-}$ CV data with data obtained in a similar fashion from clusters that encrypt a divalent ion, $[CaP_5W_{30}O_{110}]^{13-}$ [9] a trivalent ion, $[CeP_5W_{30}O_{110}]^{12-}$ [18] and a tetravalent ion, $[ThP_5W_{30}O_{110}]^{11-}$ [7] reveals that the Am data are effectively indistinguishable with those obtained from the Ce analog under similar conditions. Ce in $[CeP_5W_{30}O_{110}]^{12-}$ is trivalent and is not redox active over the potential range used for these experiments. Therefore, from the CV data we can conclude that Am is trivalent in the Preyssler anion. There is no evidence from the CV data that Am is electroactive in this anion, even under an applied potential of −0.6 V vs. Ag/AgCl.

The L_3-edge XANES data from a trivalent standard, AmF_3, are compared with those from a tetravalent standard, $Pb_2Sr_2AmCu_3O_8$ [19] in Fig. 3. The edge energies, determined from the maxima in their first derivatives, are 18 507 eV for the trivalent standard and 18 510 eV for the

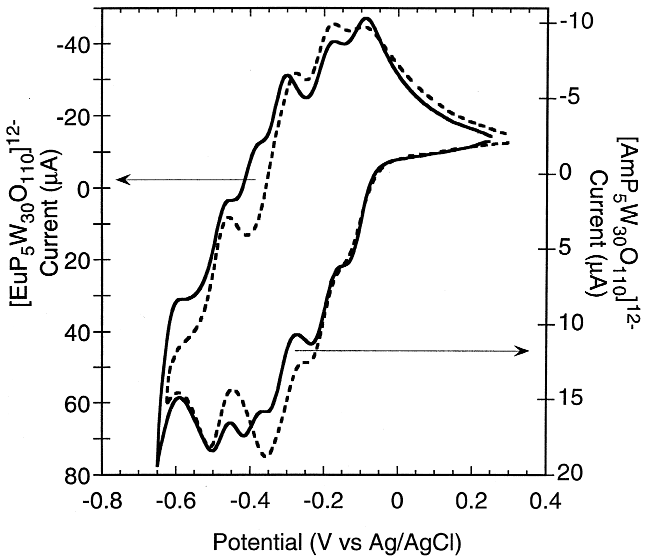

Fig. 2. The cyclic voltamograms of $[EuP_5W_{30}O_{110}]^{12-}$ and $[AmP_5W_{30}O_{110}]^{12-}$ are contrasted. Unlike the Eu analog [8], the Am analog has a cyclic voltamogram that is characteristic of an encrypted trivalent R that shows no redox activity. From these data it is assumed that Am is trivalent at all potentials probed in this experiment.

tetravalent standard, corresponding to a shift of 3 eV to higher energy for the tetravalent standard. If the absorption maxima instead of the derivative maxima are used to determine the edge positions, there is an edge shift from 18 513 eV for AmF_3 to 18 517.5 eV for $Pb_2Sr_2AmCu_3O_8$ for a shift of 4.5 eV. The difference in measured edge shifts using the two different methods is the result of the difference in white line shapes seen for the two edges. The shift of 3 eV to higher edge energy for the tetravalent compared with the trivalent standard may be slightly smaller than the 3.9 eV shift observed between data from Np^{3+} (NpI_3) and Np^{4+} (NpO_2) [20]. However, our result of 4.5 eV is very similar to the 4.8 eV shift between Np(III) and Np(IV) predicted from calculations on the metallic systems [21,22]. Finally, it should be noted that the L_3-edge from the tetravalent standard is much broader than that seen from the trivalent standard (this is the origin of the edge shift dependence on the method for determining the edge position). Whereas differences in edge shapes and intensities have been previously observed for a variety of lanthanide and actinide samples [11,20,23,24], there is currently no detailed understanding available of XANES spectra. However, it is clear that the edge positions and the gross spectral features are sufficient to determine the Am valence for the compound in question.

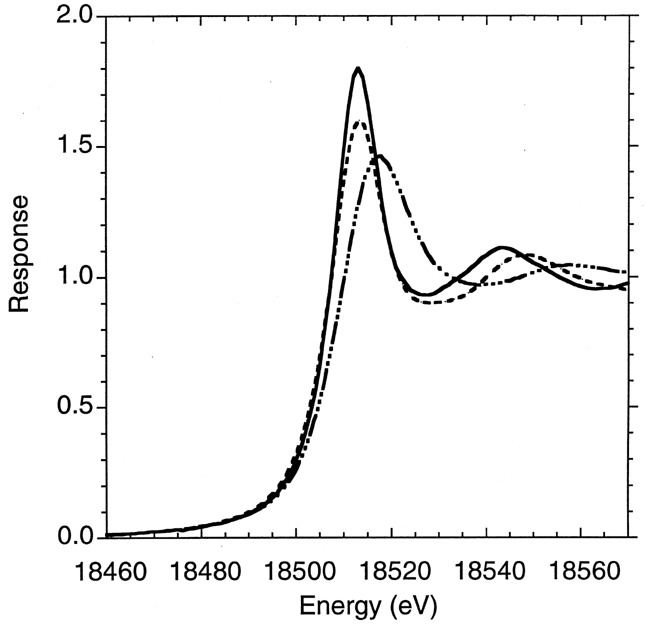

Fig. 3. The Am L_3-edge XANES spectrum of $[AmP_5W_{30}O_{110}]^{12-}$ (solid line) is compared to the trivalent standard AmF_3 (dotted line) and the tetravalent standard $Pb_2Sr_2AmCu_3O_8$ (dashed-dotted line). These data clearly demonstrate that Am is trivalent in $[AmP_5W_{30}O_{110}]^{12-}$.

Included in Fig. 3 are the XANES data obtained from $[AmP_5W_{30}O_{110}]^{n-}$. The edge energy and shape are very similar to those obtained from the trivalent standard. These data support the conclusions reached from the CV data that Am is trivalent in $[AmP_5W_{30}O_{110}]^{12-}$. The increased white-line intensity of the Am in the Preyssler anion over that observed for the fluoride sample may indicate very localized Am 6d and 5f-states in the cluster compound.

In addition to the information available about the valence of Am in $[AmP_5W_{30}O_{110}]^{12-}$ the extended X-ray absorption fine structure (EXAFS) also provides information about the Am coordinating environment. The Am L_3-edge EXAFS data obtained from $[AmP_5W_{30}O_{110}]^{12-}$ are shown in Fig. 4, together with their Fourier transform. In order to fit the data, advantage was taken of a partial crystal structure published for the Eu^{3+} analog [25], as well as previously published results from luminescence experiments that show Eu^{3+} is bound to 2 or 3 water molecules [8]. Similar results were also obtained thereafter by Lis et al. [26]. The Eu-framework P–W–O interactions are as follows: Eu–O_{10} at 2.61(1) Å; Eu . . . W_5 at 3.55(1) Å; Eu . . . P_5 at 3.82(3) Å; Eu . . . W_{10} at 6.07(1) Å and 1–2 water molecules with an Eu^{3+}–O bond length range of 2.39(4) Å. By analogy with the Eu analog, there may be water molecules within the tunnel in $[AmP_5W_{30}O_{110}]^{12-}$, one or more of which may be bound to Am. In order to address this issue of f-element hydration, we have included an R–O interaction in our modeling to account for R–water coordination. It is evident from the match between the experimental data and the best fit, also shown in Fig. 4, that the multi-shell modeling of the R ion environment is satisfactory. The results of the fit for the Am data are compared with EXAFS results obtained from several other encrypted f ions in Table 1 [27].

There is a paucity of experimentally determined Am–O distances that have been published with which the Am–O_{10} of 2.59 Å can be compared. Using the lattice constants for $AmScO_3$, and the oxygen parameters determined for

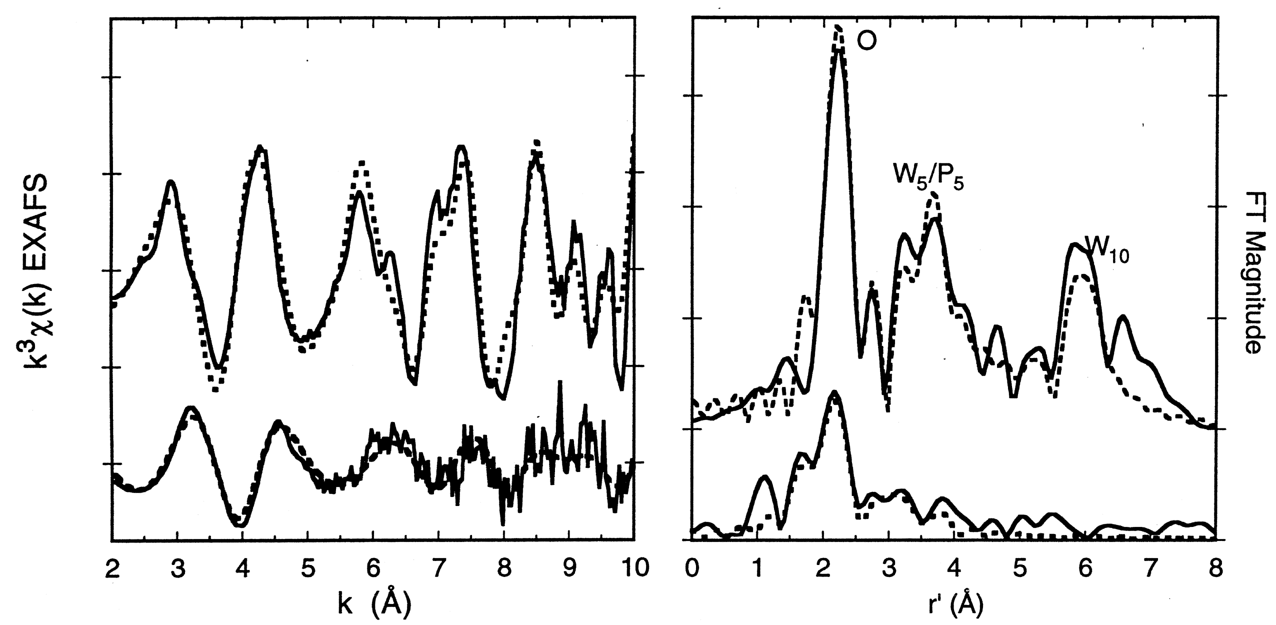

Fig. 4. Left panel. The Eu (top) L_3-edge EXAFS spectrum of $[EuP_5W_{30}O_{110}]^{12-}$ (solid line) is compared with the best fit (dotted line) and with the spectrum obtained from $[AmP_5W_{30}O_{110}]^{12-}$ (bottom, solid line) and its best fit (bottom, dotted line). The Fourier transforms of these data are shown in the right panel. The r' (distances) shown in the right panel are not corrected for phase shifts. The labels on the peaks correspond to the backscattering ion.

the isostructural $PrScO_3$, an $Am^{3+}–O_8$ distance of 2.53 Å is obtained [19]. This distance can be compared with tetravalent $Am–O_8$ distances of 2.327 Å estimated for AmO_2 and 2.22 Å for $Pb_2Sr_2AmCu_3O_8$. It is clear from these comparisons that EXAFS results are consistent with the CV and XANES data in revealing that the Am is trivalent in $[AmP_5W_{30}O_{110}]^{12-}$. The distance of 2.59 Å is within experimental error of the Am–O distance of 2.57 Å expected for the sum of their respective ionic radii.

4. Discussion and conclusions

The data discussed herein confirm that Am is trivalent in $[AmP_5W_{30}O_{110}]^{12-}$. The strong similarities between the CVs obtained from this anion and those obtained from other R^{3+}-encrypted Preyssler anions indicates that Am is not reduced under applied potentials low enough to reduce the solvent. This is in contrast to the behavior of Eu^{3+} in the same heteropolyanion, which has been shown to be completely reduced to Eu^{2+} at similar potentials [9]. Although the standard reduction potential of Eu^{3+} is less negative than the similar estimate for Am^{3+}, the unusual stabilization of a reduced ion by an anionic cluster suggested that the increased bonding interactions expected for the 5f ion over its 4f counterpart may have been sufficient to reduce at least a fraction of the Am. There is no indication of this partial reduction from the CV data.

Table 1
Encrypted R to water (R–O) distances for coordination number, n. Also included are R to cage-oxygen ($R–O_{10}$), cage tungsten ($R–W_5$) and cage-phosporus ($R–P_5$) interatomic distances in $[RP_5W_{30}O_{110}]^{n-}$. These data were obtained by fitting the $k^3\chi(k)$ L_3-EXAFS data following standard procedures as described elsewhere [28]. The number in parentheses represent the error (3σ)

	$R–(OH_2)_n$		$R–O_{10}$	$R–W_5$	$R–P_5$
	n	r (Å)	r (Å)	r (Å)	r (Å)
$[Eu^{3+}P_5W_{30}O_{110}]^{12-}$	1–2	2.39(4)	2.61(1)	3.55(1)	3.82(3)
$[Am^{3+}P_5W_{30}O_{110}]^{12-}$	1–2	2.32(2)	2.59(1)	3.59(2)	3.84(4)
$[Th^{4+}P_5W_{30}O_{110}]^{11-}$	2–3	2.34(3)	2.57(2)	3.56(1)	3.92(4)
$[U^{4+}P_5W_{30}O_{110}]^{11-}$	2–3	2.30(3)	2.54(2)	3.51(1)	4.01(5)

The distances found from EXAFS for the encrypted R ion to the framework oxygens compared in Table 1 are interesting. The $Am^{3+}–O_{10}$ should be very similar to that found for the trivalent Eu analog. Am^{3+} is the largest of the R ions in the Table. Th and U are smaller than Am and Eu because they are tetravalent. However, Eu has the longest Eu–O bond distance. In fact, a plot of the ionic radii of R^{n+} vs. $R–O_{10}$ distances reveals a direct correlation between the ionic radius and the experimentally determined bond distances for the actinide ions. This is a surprising result because the correlation appears independent of the charge on R. An Eu–O bond distance of about 2.57 Å would be required for Eu to follow the trends established by the actinide ions. This Eu–O bond distance is considerably smaller than the 2.61 Å determined from the EXAFS data. The much longer bond distance determined for the 4f ion over the distance expected from the trend established for the 5f ions may indicate that bonding interactions of the actinides with the heteropoly framework may be stronger than those of the lanthanide ions. This would be interesting because it would support our original hypothesis for these experiments in that the heteropolyanion framework may have a more pronounced effect on the relative stabilities of the 5f–redox couples than has been previously observed for Ce and Eu in these systems. Further work to elucidate these trends is currently underway.

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