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Article

The Curium Aqua Ion

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The coordination environment of the hydrated Cm^{3+} ion is probed both in the solid state and in solution. The analysis of single-crystal X-ray diffraction data from $[Cm(H_2O)_9](CF_3SO_3)_3$ determines that the Cm species is surrounded by nine coordinating waters with a tricapped-trigonal-prismatic geometry involving six short Cm–O distances at 2.453(1) Å and three longer Cm–O distances at 2.545(1) Å. The Cm nona-aqua triflate is isostructural with the series of lanthanide and actinide $[R(H_2O)_9](CF_3SO_3)_3$ ($R = $ La–Lu, Pu) compounds. A similar nona-aqua geometry is seen for the coordination environment of Cm in aqueous solution, as probed by high-energy X-ray scattering and extended X-ray absorption fine structure spectroscopy, although the splitting in the first coordination shell is increased from 0.092(2) in the solid to 0.16(2) Å in solution. This increase in splitting of the Cm–water distances in the first coordination sphere is discussed in terms of its potential relevance to the previously observed decrease in coordinating waters with decreasing ionic radius about the f-ion in solution.

Introduction

In its most stable trivalent oxidation state, curium ($Z = 96$) has a spherically symmetric, half-filled $5f^7$ shell and a $^8S_{7/2}$ electronic ground state, assuming Russell−Saunders coupling. As a result, Cm^{3+} is often used as a probe of heavier actinide speciation.[1] For example, Cm^{3+} was recently used to assess the impact of including a second coordination sphere on the calculated aqua-coordination complex.[2] With the use of density functional theory (DFT), it was determined that Cm^{3+} is surrounded by nine water molecules, in a trigonal prismatic arrangement of six prismatic waters with a Cm−O distance of 2.47 Å and three equatorial waters with a Cm−O distance of 2.48 Å. Studies of this type are significantly simplified by a spherically symmetric valence shell, which eliminates the need to assign unpaired valence electrons to specific orbitals. Another important feature of a half-filled shell is the resultant large energy gap to the first excited $J = {}^7/_2$ state, which results in a long luminescence lifetime that is sensitive to coordinating ligands through hybridization effects.

The Cm luminescent lifetime has been shown to correlate with water coordination[3] and is considered a sensitive probe of complexation in solution.[4,5] The absolute number of coordinating waters is predicted assuming that in an aqueous solution of noncoordinating ligands there are nine waters in the first coordination shell, an assumption based largely on lanthanide work.[6−8] Although luminescence measurements are now considered a useful tool to probe Cm^{3+} speciation, a detailed structural study of the coordination environment in aqueous solution has yet to be undertaken. The results from such a study will underpin the assumptions behind the optical studies and provide a metrical understanding of Cm^{3+} aqua coordination that will support the basis upon which a predictive capability for the solution behavior of Cm under more complex and diverse conditions can be built.

A predictive knowledge of actinide solution coordination preferences and stabilities is important for several reasons, most notably those associated with the difficulties that are encountered in working with many of the transuranic isotopes, difficulties that result from both their limited availability and their chemical and radiological health risks. In addition, these man-made elements have no geochemical history available to guide the understanding of their behavior

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either in solution or in the solid state. There are very few published solid-state crystallographic studies of Cm-containing compounds available for use in assessing correlations between bond lengths and coordination environments, such as those used in the bond-valence formalism of Brown.[9] Only three of the structures have Cm with oxide coordination,[10-12] too few to provide a statistically meaningful foundation on which to base coordination number to distance correlations for water coordination in solution. Such knowledge of solution speciation also has practical applications in understanding how to optimize lanthanide/actinide separations or predict migration from contaminated sites in the environment.

The purpose of this study is to quantify the Cm^{3+} hydration sphere in solution, specifically the distances and numbers of waters in the first and second coordination spheres. Interesting in their own right, these data will be used to compare our experimental findings with recently published calculations.[2]

Experiments

$^{248}Cm^{3+}$ in perchloric acid (96% ^{248}Cm, 3.9% ^{246}Cm) solutions were assayed for Cm concentration by scintillation and UV spectroscopies. (***Caution**: ^{248}Cm is a radioactive isotope ($t_{1/2}$ = 3.5 × 10^5 year; 91.7% α; 8.3% SF) and should be handled only in designated hot-laboratory facilities.)*

Synthesis of $[Cm(H_2O)_9](CF_3SO_3)_3$. The Cm^{3+} nona-aqua triflate (trifluoromethanesulfonate) complex was prepared by an adaptation of the synthesis reported for $[Pu(H_2O)_9](CF_3SO_3)_3$.[13] A solution containing approximately 15 mg of ^{248}Cm in $HClO_4$ was reduced to near dryness by heating and was reconstituted with water several times. On the final volume reduction, 0.5 mL of water was added and the solution was transferred to a 2 mL centrifuge cone. Freshly prepared 5 M NaOH was added to precipitate the Cm^{3+}. The solid was centrifuged and washed with distilled water several times. After the solid was washed, 1 mL of 1.67 M triflic acid (trifluoromethanesulfonic acid) was added to dissolve the precipitate. This solution was heated to reduce the volume to approximately 0.5 mL. This solution was transferred to a watch glass where after 2 days at room temperature, light yellow to colorless needles had grown from solution.

X-ray Crystallography. The structure of $[Cm(H_2O)_9](CF_3SO_3)_3$ was determined using a Bruker AXS SMART diffractometer equipped with an APEX II CCD detector. Crystals were manipulated under oil and mounted on glass fibers using a quick-drying epoxy. Data were collected at 100 K under a stream of nitrogen. Corrections for absorption were performed using SADABS,[14] and data reduction and structural refinements were performed using SHELXTL.[15] Hydrogens were located from a difference-Fourier map and refined isotropically.

X-ray Scattering Studies. A 0.523 M $^{248}Cm^{3+}$ solution was prepared in 1 M perchloric acid. Samples containing perchloric acid, $LiClO_4$, or $Al(ClO_4)_3$ were prepared as standards to assess the effects of background subtraction. Except for the contributions from cation correlations, the spectra appeared similar, and consequently, the perchloric acid solution was chosen for background subtraction. Scattering experiments were conducted on the wiggler beamline 11-ID-C[16] at the Advanced Photon Source. Monochromatic 115 keV X-rays were employed, which are below the Cm K edge energy of 128.22 keV.[17] Samples were mounted in 3 mm glass capillaries that were further encapsulated with Kapton tape. The capillaries were mounted with their long axes perpendicular to both the incident beam and detector travel.[18] The experiment was performed in transmission geometry, which provides a constant path length as a function of scattering angle. The X-ray absorption is about 8% at the X-ray energy employed in this experiment. Data were collected covering the momentum transfer range of Q from about 0.3 to 30 $Å^{-1}$ and corrected for detector dead time, background (with empty sample holder), polarization, and tangential detector movement. The data were normalized to a cross section per formula unit and subtracted from background solutions containing perchloric acid, following previously published procedures.[19] The resultant structure factor data, $S(Q)$, were used as the basis for data treatment.[20,21]

X-ray Absorption Spectroscopy. The same Cm sample used for the scattering experiment was also used for the extended X-ray absorption fine structure (EXAFS) measurements. The Cm L_3 edge X-ray absorption spectroscopy experiments were performed on beamline 12-BM-B, which is equipped with a Si⟨111⟩ double-crystal monochromator and a Rh focusing mirror that also serves to filter harmonics.[22] The monochromator calibration was referenced to the inflection point energy of Nb foil XANES at 18.986 keV. The Cm^{3+} L_3 edge was determined to be 18.973 keV, in agreement with previous measurements.[11,12] Data were collected in the transmission mode using an Ar-filled ion chamber. Data were analyzed following normal procedures using EXAFSPAK software[23] and FEFF8.0.1[24,25] for the Cm−O phase and oxygen backscattering amplitude with the scale factor of S_0^2 fixed to 1.

Results

X-ray Diffraction. $[Cm(H_2O)_9](CF_3SO_3)_3$ is isostructural with the previously reported lanthanide series[26] and with the Pu analogue.[13] The structure of the complex is shown in Figure 1, and the Cm−O bond distances are provided in Table 1. The structure contains one crystallographically

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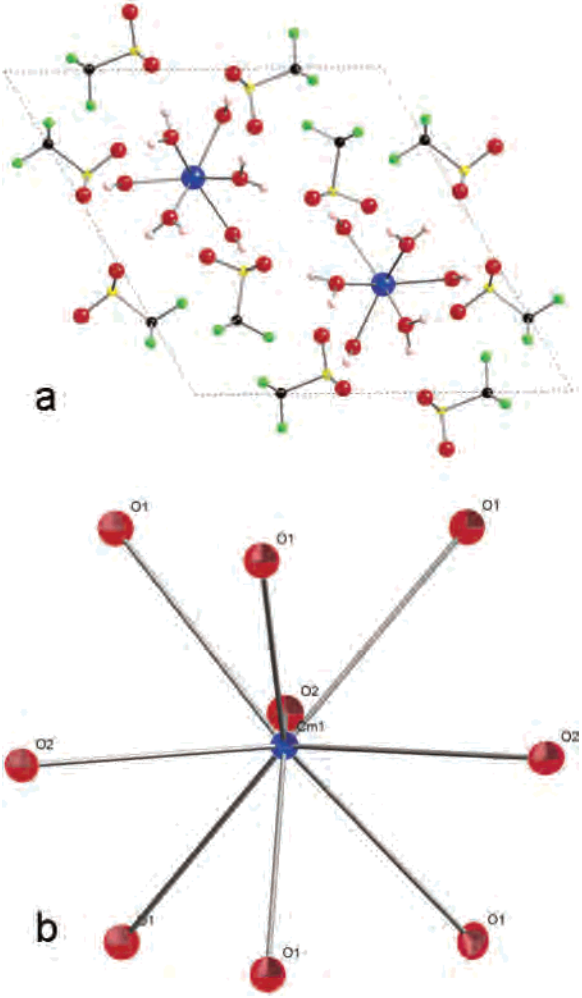

Figure 1. (a) Molecular packing of $[Cm(H_2O)_9](CF_3SO_3)_3$ in the unit cell, *c*-axis into the page. (b) Thermal ellipsoid plot (50% probability) showing the prismatic water O(1) and capping water O(2) at Cm−O distances of 2.4528(10) and 2.5452(14) Å, respectively. The corresponding Cm−H distances number six at 2.94(2) Å, six at 2.95(3) Å, and six at 3.11(2) Å. The protons are omitted for clarity.

Table 1. Crystallographic and Structural Details for $[Cm(H_2O)_9](CF_3SO_3)_3$

Crystallographic Details	
$[Cm(H_2O)_9](CF_3SO_3)_3$	M_r 857.35 g·mol^{-1}
$a = b = 13.860(2)$ Å	hexagonal $P6_3/m$ (No. 176)
$c = 7.330(2)$ Å	$T = -173$ °C
$\alpha = \beta = 90°$	$\lambda = 0.71073$ Å (Mo Kα)
$\gamma = 120°$	$\rho_{calc} = 2.335$ g·cm^{-3}
$V = 1219.4$ Å^3	$\mu = 3.78$ mm^{-1}
$Z = 2$	$R(F_o)$, $R_w(F_o^2)^a = 0.012, 0.029$

Bond Distances (Å)	
Cm−O(1)$_{prism}$	2.4528(10)
Cm−O(2)$_{cap}$	2.5452(14)
Cm−H(1)$_{prism}$	2.94(2)
Cm−H(2)$_{prism}$	2.95(3)
Cm−H(3)$_{cap}$	3.11(2)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $R_w^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, F on all data, $w = 1/[\sigma^2(F_o^2) + (0.0100P)^2 + 0.9033P]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

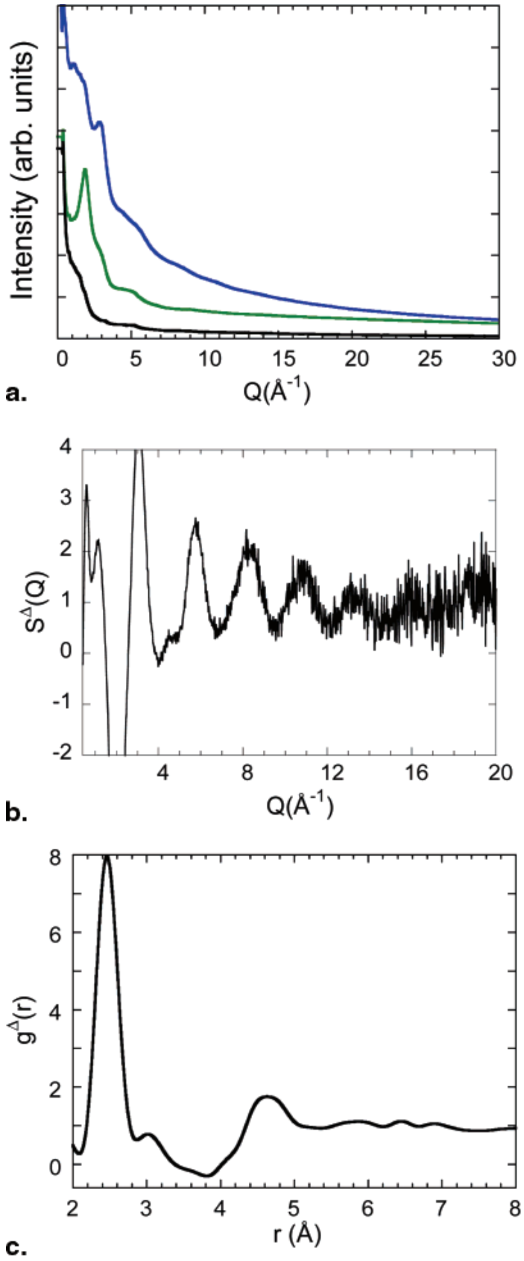

Figure 2. (a) Experimental HEXS intensities. (Top line) Sample (a solution containing 0.523 M Cm^{3+} and 2.57 M ClO_4^-). (Middle line) Perchloric acid solution, 2.57 M. (Bottom line) Empty sample holder. (b) The difference-structure factor $S^\Delta(Q)$, obtained from the background-subtracted data and used for the Fourier transform (FT). The predominant features involve Cm correlations. (c) The FT of $S^\Delta(Q)$ using data out to $Q = 19.5$ Å^{-1}.

unique Cm on a $\bar{6}$ site (2*d*) with nine waters in its inner coordination sphere. These water molecules are arranged in a tricapped-trigonal-prismatic coordination, with six waters on a general position (12*i*) at a Cm−O distance of 2.453(1) Å and three waters on an *m* site (6*h*) at a Cm−O distance of 2.545(1) Å. The corresponding Cm−H distances number six at 2.94(2) Å, six at 2.95(3) Å, and six at 3.11(2) Å. The difference in the two Cm−O distances is 0.092(2) Å and represents the splitting between the two subshells that comprise the first coordination sphere. The second coordination sphere of Cm is comprised of six equidistant oxygens that belong to the triflate anion at a Cm−O distance of 4.612(2) Å.

High-Energy X-ray Scattering (HEXS). The scattering data for the 0.5 M Cm solution in 1 M $HClO_4$, plotted as intensity versus momentum transfer, are shown in Figure 2a, together with the spectra of the empty-holder and of a perchloric acid solution in the absence of Cm. The scattering data contain correlations between all of the atoms in solution. We are interested in contributions to the scattering intensities from ions in the environment of the Cm. By subtracting data from a perchloric acid solution, correlations are removed to first order between H_2O itself, H_2O and perchlorate, and perchlorate itself.[27] Errors arising from this procedure, which does not correct for small differences in the scattering that results from changes in the solvent structure due to the presence of Cm, are estimated to be less than 5%. Included in Figure 2b are the background-subtracted and normalized data, plotted as a difference-structure function $S^{\Delta}(Q)$ vs Q ($Å^{-1}$).[28] The Fourier transform (FT) of the $S^{\Delta}(Q)$ data, obtained over the Q range of 0.4−19.5 $Å^{-1}$, is shown in Figure 2c. The FT plot thus derived represents correlations present in the 0.5 M Cm in perchlorate solution that are not present in the perchlorate solution alone. There are peaks observed corresponding to correlations at distances of 2.48(1), 3.05(1), 4.65(1), 5.9(4), and 6.7(4) Å. These peaks are all assumed to involve a Cm−ligand correlation because of the large contribution that Cm^{3+}, with 93 electrons, makes to the total scattering.

The first peak in the FT at 2.48(1) Å is attributed to contributions from oxygen in the form of coordinating H_2O. Although ClO_4^- is present in our samples, it is expected to be a noncoordinating ligand in acidic solution.[29,30] In addition, if perchlorate is a coordinating ligand, published structural studies of rare-earth perchlorates $R(ClO_4)_3$[31] indicate that there should be a Cm−Cl correlation at 3.6−3.8 Å. Since there is no indication of a peak in this region, we assume that water correlations dominate the first coordination sphere of Cm. An integration of the intensity in the $g^{\Delta}(r)$ vs r data, as shown in Figure 3, over the range of 2−4.0 Å is used to determine that there are 92(3) electrons associated with correlations in this region,[18,19] which corresponds to 9 coordinating waters (10 electrons per H_2O). The resolution of the data is not sufficient to determine whether the tricapped-trigonal-prismatic coordination found for Cm in the solid state is preserved in solution, as seen in the HEXS spectrum, also included in the figure, which is calculated from the known crystal structure in the solid state. Although the calculated peak at 2.48 Å is slightly narrow relative to experiment, any subshell fitting is not resolvable. Gaussian fits to the peaks in the region of interest are compared with the data in Figure 3. The metrical parameters determined from the best fit correspond to 8.8(3) O atoms at 2.48(1) Å and 23(4) H atoms at a distance of 3.05(1) Å, for a total of 93(4) electrons, consistent with the total number of electrons determined by integration.

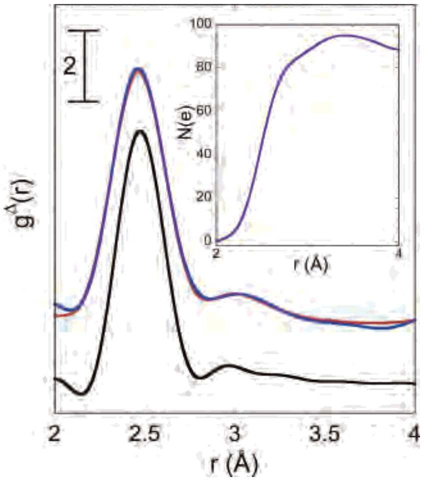

Figure 3. (Top curve) A comparison of the fit (red line) with the FT of the HEXS data (blue line). (Bottom curve) A calculated spectrum of Cm−$(H_2O)_9$ correlations based on atomic positions determined from the Cm triflate single-crystal structure. Consistent with the calculated spectrum, the peak centered at 2.48(1) Å is attributed to a Cm correlated to 8.8(3) oxygens whereas the peak centered at 3.05 Å is attributed to a Cm correlated to 23(4) hydrogens. Overall, the fit shows 93(4) electrons, which corresponds to nine waters in the first coordination sphere of Cm^{3+}. The inset shows the integration of scattered X-ray intensity from 2 to 4 Å, which corresponds to 92(3) electrons or nine water molecules in the first coordination sphere.

The data seen in Figure 2c also show a significant correlation peaking between 4 and 5 Å that is assigned to a second sphere of coordinating waters. The longer distance of this correlation means that there is a larger contribution from the average number density that represents the increasing integration volume.[19,20] Therefore, fitting this longer r peak requires an assumption about the form of the local number density over the integration range of interest. For the purpose of the limited r fit, the number density is treated as an arctangent function, a convolution of the step function expected for a gaseous sample and the Gaussian functions expected for a crystalline sample.[32] The use of this function contributes significantly to the error associated with the fit. The best fit to the correlation itself yields 13(4) oxygens at a distance of 4.65(10) Å.

There are two additional peaks, at approximately 5.9 and 6.7 Å, that are visible in the data. Peaks in HEXS data at even longer distances have previously been shown to represent real correlations, as exemplified in Th−dimer solutions.[33] Unfortunately, expected errors in background subtraction and low statistics vitiate attempts to assign any species or coordination number to the weak correlations seen in the Cm data. It is not possible to ascertain from the data whether the peaks are the result of Cm−Cm interactions or whether they result from correlated perchlorate or additional waters.

EXAFS Spectroscopy. The Cm L_3 edge EXAFS spectrum, obtained from the same solution that was used for the

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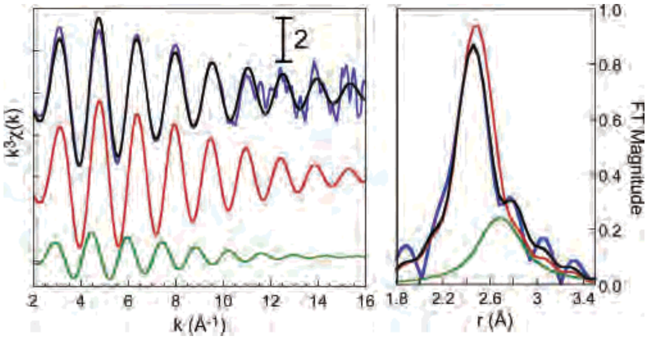

Figure 4. (Left panel) The Cm L_3 edge experimental $k^3\chi(k)$ EXAFS data (blue line) compared with the best fit (top black line) as described in the text. The components of the fit are shown as the Cm−O_n contribution at 2.470(6) Å (middle line) and the Cm−O_m contribution at 2.63(2) Å (bottom line). Note the two oxygen contributions are significantly out-of-phase over much of the *k* range shown. (Right panel) The *corresponding phase-shift-corrected* FTs. The experimentally determined peak (blue line) is compared with its first (red) and second (green) oxygen subshell components. Included in the Supporting Information is a comparative fit of the EXAFS data using a one-shell model as outlined in the text. The FT is extended to a longer *r* to better represent the noise level.

HEXS data collection, is shown, together with its FT, in Figure 4. The long data set yields 18 degrees of freedom, conservatively calculated from $2\Delta k\Delta R/\pi$, assuming data lengths of $\Delta k = 14$ Å^{-1} and $\Delta R = 2$ Å, in reciprocal and real space, respectively.[34] In addition, the long data set provides a resolution in the FT peaks of 0.11 Å, which is sufficient to observe any splitting of the first shell coordinating waters with a similar magnitude to that determined in the crystal structure. Indeed, the FT of the data reveals two peaks, with an intensity ratio of approximately 1/0.3. Assuming a splitting of the first coordination sphere that persists from the solid state, the EXAFS data were fit by fixing the coordination numbers of $N_n = 6$ and $N_m = 3$, the values obtained from the single-crystal structural refinement. Fixing $S_0{}^2 = 1$, the spectrum can be fit by varying the Cm−O distances for the two subshells as well as the Debye−Waller factors for the two subshells. With this approach, the best fit with five variable parameters results in two Cm−O distances of 2.470(6) and 2.63(2) Å with Debye−Waller factors of 0.0053(6) and 0.009(2) Å^2, respectively. Thus, the oxygen-subshell splitting that occurs in solution is 0.16(2) Å, somewhat larger than the 0.092 Å seen in the solid state. Fitting details are presented in Table 2. For purposes of comparison, the best fit obtained assuming only a single Cm−O distance in the first coordination sphere and four variable parameters is also included in the table and is compared with the data as Figure S1 in Supporting Information.

Table 2. Parameters Obtained from Fitting the $k^3\chi(k)$ EXAFS Data over the *k* Range of 2−16 Å^{-1} [a]

model	correlation	N^b	R (Å)^c	σ^2 (Å^2)^d	ΔE_0 (eV)^e	F^f
two-shell fit	Cm−O_n	*6*	2.470(6)	0.0053(2)	0.7(7)	70
	Cm−O_m	*3*	2.63(2)	0.009(2)		
single-shell fit	Cm−O	7.0(4)	2.469(7)	0.0071(8)	−2.0(9)	85

[a] Parameters fixed in the fit are italicized; details are outlined in the text. Fitted parameters have their usual notation except for the goodness-of-fit (GOF) parameter, *F*. Estimated uncertainties (3σ) are shown in parentheses. [b] Number of coordinating O ions. [c] Distance to coordinating O ion. [d] Debye−Waller factor for the correlation. [e] Energy shift with respect to the E_0 of 18.979 keV. [f] GOF, defined as the sum of the squares of the differences between experimental and calculated data, as minimized by the Marquardt algorithm in EXAFSPAK, http://www-ssrl.slac.stanford.edu/exafspak.html.

Discussion

The determination of the structure of $[Cm(H_2O)_9](CF_3SO_3)_3$ using single-crystal diffraction provides a solid-state model for Cm^{3+} ligated solely to water in its first coordination sphere. The preference for a trigonal prismatic coordination of six short and three longer Cm−O distances in the solid state is the same as seen in its isostructural series of trivalent lanthanide structures, published for La−Lu[26,35] and the isotypic actinide Pu.[13] The location of the H atoms associated with the waters coordinated to the Cm also agrees very well with those previously reported for the Pu triflate.[13] The weighted average of 2.48 Å for the Cm−O distances in the first coordination sphere is the same as that found for the Nd nona-aqua triflate at room temperature. The 0.092(2) Å splitting of the Cm first coordination sphere seen in the solid is slightly smaller than the 0.098(2) Å splitting seen in the Pu analogue.[13] Although this result is inconsistent with the trend to a larger subshell splitting with decreasing ionic radius,[35] it should be noted that the Cm data were obtained at 100 K whereas the Pu data were obtained at 218 K, thus complicating any detailed comparison. Overall, the difference between the Cm−O distances for the prismatic and equatorial oxgyens in the first coordination sphere or subshell splitting of both the actinide structures appears smaller than the 0.12 Å observed for Nd, which has a larger ionic radius. Following the trend established for the lanthanides in the triflate structures, Cm would be expected to have a splitting of about 0.13 Å, similar to that observed for Sm but with a splitting slightly smaller than that observed at room temperature for La.

The second coordination sphere of Cm in the solid is comprised of triflate anion contributions, with six O atoms at a Cm−O distance of 4.612(2) Å, three F atoms at a distance of 4.635(3) Å, and six O atoms at a distance of 4.700(2) Å. The Cm−O distance seen for the second coordination sphere of O from the triflate, 4.612 Å, is only slightly shorter than the second coordination sphere seen in solution at 4.65 Å, where it is attributed to a second solvation sphere. The distance between oxygens in the first and second coordination spheres of Cm is short, 2.74−2.81 Å, pointing to strong hydrogen bonding between the coordinating waters and the triflate ion, which is consistent with the apparent stability of this series of compounds. A comprehensive discussion on the H bonding in these structures is presented in detail elsewhere.[13]

There are very few solid-state structures previously reported for Cm, none of which have only water in their first coordination sphere. There are three compounds reported that have only oxygen coordinating Cm^{3+}, one of which is

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Cm_2CuO_4,[11] in which the Cm sits at a site with tetrahedral symmetry and has four O atoms at 2.316 Å and four more distant O atoms at 2.667 Å, for an average Cm−O distance of 2.491 Å. This distance is remarkably similar to the weighted distance determined in our triflate compound, despite the difference in overall coordination number. The structure has also been reported for $Pr_2Sr_2CmCu_3O_8$,[12] which has eight O atoms at a Cm−O distance of 2.426(24) Å. $Cm(IO_3)_3$[36] also has eight coordinating O atoms, in a site with low symmetry, and an average Cm−O distance of 2.431 Å.

The HEXS and EXAFS data provide an overall comparison of the coordination environment of Cm^{3+} in solution. The HEXS data confirm that the nine coordinating H_2O molecules about the Cm ion are preserved in solution. The peak centered at 2.48 Å in Figure 3 is attributable to nine coordinating oxygens and the smaller peak at 3.05 Å is consistent with the hydrogen associated with the waters, as seen in the solid-state triflate structure. A direct comparison of the correlations observed in solution with those calculated from the structure is included in Figure 3. The calculated spectrum for the first coordination sphere of Cm includes a peak centered at 2.97 Å that results from Cm−H correlations in addition to the peak at 2.48 Å arising from the Cm−O interactions. Although the Cm−H peak is evident in the experimental data, there is a slight difference between the calculated and best fit data in both the refined distance and the total number of H responsible for the correlation. This difference may result, at least in part, by the superposition of O−O interactions at the same distance. The O−O interactions arise from two different sources, the interactions between the solvent water molecules themselves, which are subtracted during background correction, and interactions between the water molecules coordinated to Cm. The latter interactions are estimated to contribute about 40% to the peak intensity relative to the Cm−H interaction and are not separable without making several assumptions. The data as presented in the figure has had the total water scattering removed as background. This approach slightly underestimates the background subtraction in the neighborhood of the Cm−H peaks, as evidenced by the determination of 23 H atoms at that position. The inclusion of the O−O interactions from the Cm coordinated waters would overestimate their contribution. Notwithstanding this error, the Cm−H interactions are observed both in the single-crystal data and in the HEXS solution scattering data.

The EXAFS data confirm that the first coordination shell of waters is split into two independent subshells, as demonstrated by the FT shown in Figure 4. The splitting of the Cm first coordination sphere, 0.16(2) Å, is larger than that seen in the solid-state structure and cannot be accounted for by the difference in the temperature at which the data were obtained. The difference in splitting is accounted for by the lengthening of the tricapping oxygen distance, whereas the prismatic−oxygen distance remains similar to that seen in the solid state. The observation of a lengthening of the Cm to tricapping oxygen distance in solution may provide insight into a possible mechanism for the reported change in lanthanide coordination number from nine to eight with decreasing ionic radius that is reported to occur in solution[8] but not in the solid state.[35] This coordination number change occurs between Sm and Tb, which have been shown to exhibit evidence of intermediate coordination numbers in solution.[8] If the ionic radius of the central ion is the principal driving force for the change across the lanthanides, and if the actinides follow a similar behavior, then Cm, with a radius slightly larger than Sm, is expected to be just large enough to stabilize nine coordination. Indeed, it has been suggested that the hydration number changes from nine to eight between Cm^{3+} and Fm^{3+}.[37,38] There are no reported solid-state aqua structures with which to compare. However, independent support for this suggestion comes from a temperature-dependent study of the hydration of Cm using time-resolved laser fluorescence spectroscopy[39] that interprets a shift in the Cm^{3+} emission band to lower energy with increasing temperature as resulting from a change in the number of waters coordinating Cm, from 90% nine coordinate at ambient temperature to only 40% at 200 °C. A simple explanation for the change in solution coordination with increasing temperature can be expressed in terms of more loosely bound waters, as evidenced by their longer Cm−O bond distance. In another study, in situ EXAFS spectroelectrochemistry experiments on the redox properties of Bk in 1 M $HClO_4$ solution showed a change in hydration number, from nine to eight, upon oxidation of Bk^{3+}.[40] This same change does not occur for Np^{3+}, which is a considerably larger ion.[41]

Cm−O distances and coordination numbers can be compared with other selected studies of An^{3+} (An = actinide) solution speciation, as presented in Table 3. All experimentally determined metrical information is obtained from solution EXAFS data.[42] Overall, it can be seen that coordination numbers in the range of 8.5−10.3 H_2O molecules are determined in a variety of solutions, with distances in the range of 2.45−2.56 Å for the lighter actinides and 2.42−2.43 Å for the heavier actinides, consistent with the actinide contraction. These published numbers are consistent with the results determined herein, although our errors are much smaller.

Aqua coordination of Cm^{3+} in solution has been the subject of a recent systematic theoretical study in which quantum mechanical and molecular dynamics methods were used to calculate the solvation environment.[2] DFT calculations

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Table 3. Previously Published Coordination Numbers and An−O Bond Distances of Selected Solution An^{3+} Aqua Complexes as Determined by EXAFS Spectroscopy[a]

ion	An solution concentration	solvent	N^b	R (Å)[c]	reference
U^{3+}	ns[d]	1 M HCl	8.7(9)	2.56(1)	46
Np^{3+}	4.7 mM	1 M $HClO_4$	9(1)	2.48(2)	41
Pu^{3+}	10 mM	0.1 M LiCl	9(1)	2.510(6)	47
Am^{3+}	10 mM	0.25 M HCl	10(1)	2.480(6)	47
Cm^{3+}	10 mM	0.25 M HCl	10(1)	2.450(6)	47
Bk^{3+}	0.47 mM	1 M $HClO_4$	9(1)	2.43(2)	40
Cf^{3+}	7 mM	1 M HCl	8.5(15)	2.42(2)	48

[a] Estimated uncertainties are shown in parentheses. Uncertainties may have been recalculated to represent 3σ. [b] Number of coordinating ions. [c] An^{3+}−O distance. [d] Not specified.

determined that Cm^{3+} is coordinated to nine waters in the first coordination shell. These waters are arranged in a tricapped-trigonal-prismatic configuration with six waters at 2.47 Å and the three tricapping waters at 2.48 Å. These calculated values are in good agreement with our experimental results, although the splitting of the first coordination sphere into two subshells is less pronounced than that observed even from our diffraction results. The calculations also determined a second hydration sphere of 21 water molecules at 4.65 Å, which can be compared to the HEXS results of 13(4) waters at a distance of 4.65(10) Å. Overall, the calculations agree remarkably well with our experimental findings. A previously published relativistic DFT study of the Pu^{3+} aqua ion, optimized with the D_{3h} structure, also determined nine waters in two subshells, with Pu−O distances of 2.491 and 2.585 Å.[43] Although the difference in coordinating distances of the two subshells, 0.094 Å, more closely matches the splitting determined herein for Cm^{3+} than do the calculations on Cm^{3+}, the shorter distance in the case of the Pu^{3+} calculations corresponds to the three-H_2O subshell, whereas the six-H_2O subshell is at the longer distance, reversed from our experimental findings.

The HEXS and EXAFS results presented herein on Cm−water coordination, taken together with the Cm nonaaquatriflate single-crystal structure and previously published crystal structures that include waters coordinating to the lighter lanthanides[6,26,35] and trivalent Pu,[13] constitute a growing consensus that these f-ions prefer nona-aqua coordination with tricapped-trigonal-prismatic geometry, and that preference extends into solution. The magnitude of the subshell splitting for Cm in solution is 0.16(2) Å, significantly larger than the splitting observed for either Cm or Pu[13] in the solid state. The single-crystal structural studies of the triflates have included the trivalent La, Gd, Y, and Lu[26,35] ions that, like Cm^{3+} to a first approximation,[44] are S-state ions and as such have spherically symmetric electronic ground states in the Russell−Saunders coupling scheme. As a result, any structural distortion would not provide significant electronic stabilization energy, suggesting that the distortion of H_2O coordination into two subshells is driven by electrostatics arising from crowding within the coordinating environment. Such a steric driver would require that the distortion be correlated with the ionic radius of the central ion and become more pronounced as the ionic radius becomes smaller. Such a correlation has been previously observed[35] where its origin has been attributed to higher-order polarization of the electron distribution.[45] Although the magnitude of our bond lengths in solution differ from those determined by single-crystal X-ray diffraction, which were obtained at a lower temperature, the difference in the bond lengths between the equatorial and tricapping bonds in solution is approximately the same as that found in the Dy[35] analogue of $[Ln(H_2O)_9](CF_3SO_3)_3$ in the solid state, again suggesting that the ionic radius of the metal ion may be the predominant factor governing the split subshell. The differences seen between coordination numbers and bond distances in solution and in the solid-state reflect the complex intra- and intermolecular forces exerted by the medium in which the Cm aqua ion is embedded. Further study is necessary to probe this detail, which could be of interest in studies seeking to improve lanthanide/actinide separations.

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Supporting Information Available: Detailed information about the single-crystal structure refinement for $[Cm(H_2O)_9](CF_3SO_3)_3$ is available in CIF format; Cm L_3 EXAFS best-fit data using a single-shell model to fit the data available in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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