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Curium(III) Borate Shows Coordination Environments of Both Plutonium(III) and Americium(III) Borates[**]

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Curium is the heaviest element that is relevant to the nuclear fuel cycle produced by neutron capture of lighter actinides followed by a β decay in nuclear reactors. Separation of curium from americium is desirable during the reprocessing of used nuclear fuel. However, Am^{III} and Cm^{III} possess extraordinarily similar ionic radii that only differ by 0.005 Å, making the separation of these two elements challenging.[1] Curium is an underexplored element for a variety of reasons. First, for several decades after its discovery the one isotope available was ^{244}Cm. ^{244}Cm has a short half-life of 18 years and radiation damage in its compounds is very rapid. ^{242}Cm was also available, but is even shorter-lived with a half-life of 163 days.[2] The highly neutron-rich isotope, ^{248}Cm, became available in small quantities in the late 1970s. This isotope too has serious issues despite its long half-life of 3.48×10^5 years because 8.3 % of its decay is by spontaneous fission, and therefore even milligram amounts of ^{248}Cm release large fluxes of neutrons. The lack of availability of material combined with the hazards of working with the different isotopes of curium has greatly curtailed the development of a fundamental and applied chemistry of curium. Evidence for this is that $CmCl_3$,[3] $Cm(IO_3)_3$,[4] $Cm[M(CN)_2]_3\cdot3H_2O$ (M = Ag, Au),[5] and $[Cm(H_2O)_9][SO_3CF_3]_3$[6,7] are the sole inorganic compounds of curium for which single crystal structures are known. Like Gd^{III}, Cm^{III} has a half-filled f shell with seven unpaired electrons. However, the spin–orbit coupling is much stronger in Cm^{III} than in Gd^{III},[8] so its electronic properties are absolutely unique. Curium is the only f-block element, whose magnetic interactions can control its crystal structure.[9]

We have recently undertaken the study of the preparation of actinide borates with the aim of developing periodic trends that may aid in predicting the fate of actinides in nuclear waste repositories that are in salt deposits, such as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, USA.[10] A similar repository is being considered in Germany. These deposits contain borate in high concentrations in intergranular brines, and landmark work by Reed and co-workers has shown that borate, not carbonate, is the primarily complexant for trivalent cations in these repositories.[11]

We recently showed that Pu^{III} and Am^{III} borates possess substantially different compositions, structures, and local coordination environments at the metal centers.[12] Our prediction was that the chemistry of Cm^{III} would closely parallel that of Am^{III}, and that the borate compounds would be very similar given their nearly identical ionic radii and lack of redox activity. Herein, we show that this hypothesis is incorrect and that Cm^{III} borate simultaneously displays a coordination chemistry of both Pu^{III} and Am^{III} borates. Ln^{III} (Ln = La–Lu), Pu^{III}, and Am^{III} when reacted with boric acid do not yield a compound with the same composition as the Cm^{III} compounds reported herein.

Crystals of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ were isolated from the reaction of $^{248}CmCl_3$ with molten boric acid at 240 °C. The crystals take the form of small tablets (around 40 μm) with very pale yellow coloration. Single-crystal X-ray diffraction experiments on $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ pose a number of interesting challenges based on the fact that this compound combines one of the heaviest elements in the periodic table with some of the lightest elements. Clearly curium is responsible for the majority of the X-ray scattering. We have found in layered borates that the heavy elements can be arranged with higher symmetry than the rest of the extended network. For example, in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot0.5H_2O$, which has some structural similarities with $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$, the two different Pu^{III} centers appear to be crystallographically related, but in fact differ by one coordinating water molecule.[13] The relationship between the plutonium centers leads to the erroneous conclusion that the structure possesses higher symmetry than it actually does. We find a very similar phenomenon in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$, that is, there seem to be two different curium sites

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with different coordination environments in the low symmetry space groups $P2_1$ and Pn. However, unlike $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5\,H_2O$, the thermal parameters for some light atoms (B and O) as well as the B−O bond distances were unreasonable in these space groups. To achieve a suitable refinement, where both of the curium site(s) and the borate network possess reasonable metrics, the structure had to be solved and refined in $P2_1/n$, which forces the two Cm sites into a single site with mixed coordination environments. The induced disorder is easily accounted for, and the resulting model for the structure has low residuals, especially for a curium compound where spontaneous fission should induce rapid radiation damage.[14]

The crystal structure of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ contains a complicated 3D framework that is similar to several other An^{III} borates (Figure 1 a).[12,13] The framework is formed from a series of Cm^{III} borate sheets that extend in the [*ac*] plane bridged by additional BO_3 triangles and BO_4 tetrahedra that extend from the sheets. The Cm^{III} borate sheets adopt the same topology as those found in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5\,H_2O$, $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and $Am[B_9O_{13}(OH)_4]\cdot H_2O$ as shown in Figure 1 b. Within this sheet, a μ_3-oxo atom can be found in clusters formed by three corner-sharing BO_4 tetrahedra. These clusters share corners with BO_3 triangles to create sheets with triangular holes where the An^{III} (An = Pu, Am, Cm) cations reside.

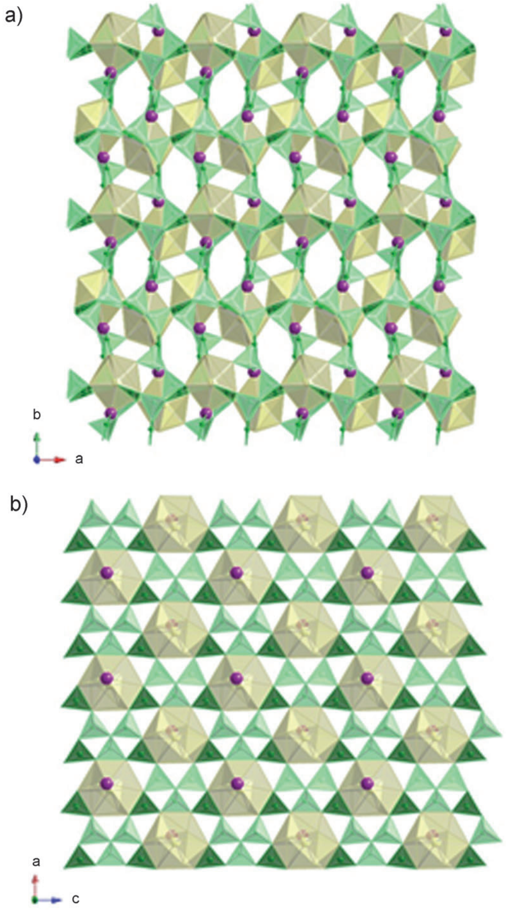

Figure 1. a) Three-dimensional framework structure of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$. b) Depiction of sheet topologies of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$. Cm polyhedra are shown in pale yellow, BO_3 triangles in dark green, BO_4 tetrahedra in light green, and chlorine atoms in purple. The chlorine positions are disordered with oxygen from BO_3 in this view.

Although the same sheet type implies the similarity of reactivity for Pu, Am, and Cm in the borate system, these Am^{III} borate compounds are all different as can be seen from their chemical formula. The structural differences among these compounds can be observed in the sheet-bridging units. In $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ and $Am[B_9O_{13}(OH)_4]\cdot H_2O$, both BO_3 triangles and BO_4 tetrahedra connect the sheets, whereas in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5\,H_2O$ and $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, only BO_3 triangles are found between the sheets. In addition, compared with $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$, the lack of the halide moiety in $Am[B_9O_{13}(OH)_4]\cdot H_2O$ results in more complicated bridging borate units. This can also be probed by the atomic ratio of Am:B in the formulas (1:9 for Am, 1:7 for Cm, and 1:6/1:6.5 for Pu). The polyborate network is found to be a powerful ligand that can be used to structurally probe small differences among actinides.[12]

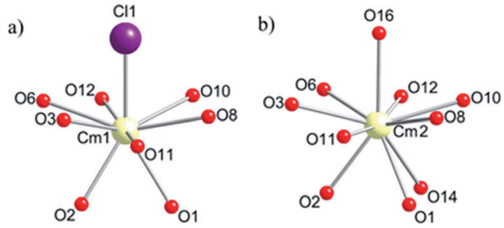

Figure 2. Views of two different coordination environments of Cm^{III} sites in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ with resolved disorder.

The local coordination environments of the Cm^{III} centers in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ are unusual. There are two different coordination environments for Cm^{III} in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ as shown in Figure 2. One is a nine-coordinated Cm^{III} polyhedron with six almost co-planar oxo atoms provided by the borate sheets and a capping chloride anion. This type of coordination environment can be referred to as the hula-hoop geometry[15] and can be also found in one of the Pu^{III} sites in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5\,H_2O$, which is bound by a capping bromide anion. Am^{III} centers in $Am[B_9O_{13}(OH)_4]\cdot H_2O$ also adopt this geometry, but lack the capping halide moiety.[12] The other is ten-coordinate Cm^{III} also with six almost co-planar oxo atoms. However, the capping group is an oxo atom from a bridging BO_3 triangle instead of the chloride anion. This change in the capping group is the disordered portion of the structure. The same coordination environment can only be found in $Ce[B_5O_8(OH)]NO_3\cdot 3\,H_2O$ and $Ln[B_8O_{11}(OH)_5]$ (Ln = La–Nd).[16] The geometry of this coordination environment is best described as a capped triangular cupola[17] and can also be found in most of the Pu^{III} centers in Pu^{III} borates with capping halide ions.[12,13] Therefore, Cm^{III} displays a bonding intermediate between that of Pu^{III} and Am^{III} not only with regard to the coordination numbers, but also with regard to the bonding interactions to the halide moieties.

Cm^{III} is known to produce intense orange luminescence when irradiated with blue light.[18] Owing to the fact that there are two different coordination environments with different ligand sets in this compound, spectroscopic studies should also indicate the presence to two distinct crystallographic sites. Laser-induced and time- and energy-resolved excitation and luminescence spectra were utilized to show the two sites of Cm^{3+} in the crystalline lattice of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$. There is clear evidence showing that Cm^{3+} has different local environments. However, the spectroscopic difference between Cm^{3+} at the two different sites is small, so our experiments had to be carried out at liquid helium temperature to eliminate thermal dynamics that obscure the energy levels of Cm^{3+} at different sites. The crystal field interaction of Cm^{3+} in $5f^7$ configuration is weak especially in the ground state and low-lying excited states.[8] The energy levels of these states are relatively insensitive to the lattice environment. Figure 3 shows the site-resolved fluorescence emission spectra of Cm^{3+} excited resonantly from the ground multiplet $^8S_{7/2}$ into the emitting state of $^6D_{7/2}$ mixed with $^6P_{5/2}$. Apparently, the two spectra are partially overlapped and with similar structures. They were recorded at 4 K with laser excitation at 601.4 and 602 nm, respectively, measuring the lowest level of the excited state for Site-A and Site-B. Four lines marked in both spectra measure the crystal field splitting of the ground state $^8S_{7/2}$. From the spectra, we know that the ground state splitting for the two Cm^{3+} sites have similar patterns with a total splitting of approximately 1.2 nm, and that the difference in the energy of the $^8S_{7/2}$–$^6D_{7/2}$ excitation between the two sites is only 0.6 nm. These characteristics are determined by the electronic properties of Cm^{3+}, and its interaction with the surrounding ligands as shown in Figure 2. However, there is no exclusive information obtained from the spectroscopic experiments to allow us to assign the spectra to the structures.

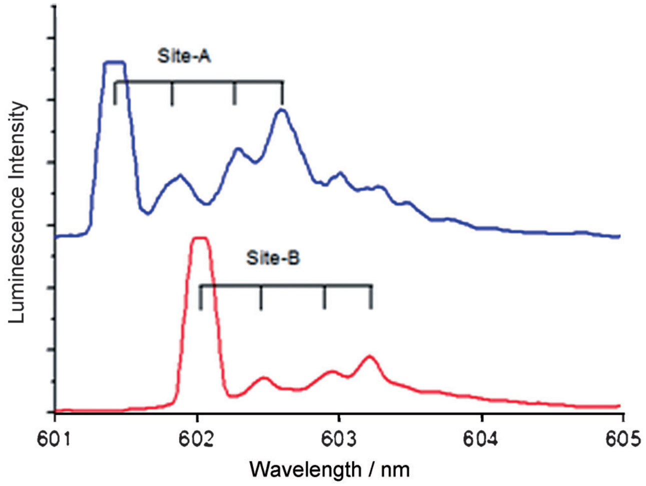

Figure 3. Luminescence spectra of Cm^{3+} at two different sites in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ recorded at 4 K in resonant excitation at 601.4 and 602 nm, respectively.

The two-site structure of Cm^{3+} and its dynamics are further investigated in luminescence decay measurements. At low temperature, when thermal population and phonon-assisted energy transfer are eliminated, excitation energy transfer occurs only from the donor sites at higher energies to the acceptor sites at lower energies.[19] As shown in Figure 4, in the system that we studied two very different fluorescence decay curves were recorded. When Site-A was excited, emission from both Site-A and Site-B was observed. Site-A luminescence which shows a nonexponential behavior has a much shorter decay time than that of Site-B luminescence. The Site-B luminescence has an initial rising before it approaches to an exponential decay. These results clearly indicate energy transfer from Site-A to Site-B and show that the relaxation of Site-A excitation is predominantly quenched through energy transfer. The effect of Site-A to Site-B energy transfer is seen also in the emission spectrum shown in Figure 3. When Site-A was excited at 601.4 nm, luminescence from Site-B was induced in addition to Site-A emission lines. The efficient energy transfer confirms the structure in which Cm^{3+} ions at Site-A and Site-B are paired with each other as shown in Figure 1.

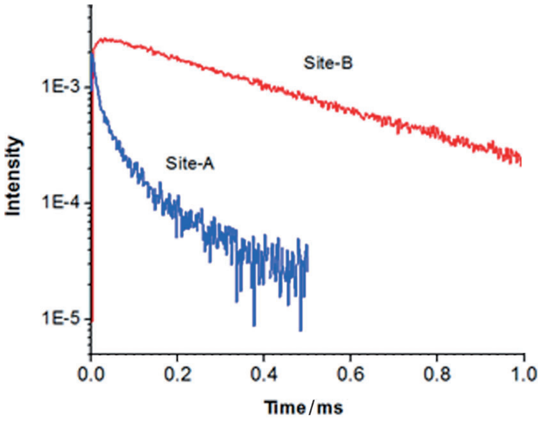

Figure 4. Luminescence decay curves of Cm^{3+} at Site-A and Site-B in $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ monitored at 601.5 and 602.3 nm, respectively. The decay curves were recorded at 4 K after laser excitation of Site-A.

In conclusion, crystallographic and spectroscopic studies provide complementary information about this complex Cm^{III} borate. Both confirm two distinct sites that are averaged in the crystal structure. The data that we have now gathered on Pu^{III}, Am^{III}, and Cm^{III} borates when combined with parallel studies on lanthanide borates show three key conclusions. First, lanthanide borates undergo systematic changes as a function of the size of the lanthanides. Second, Ln^{3+} and An^{3+} (An = Pu, Am, Cm) do not form the same compounds when reacted under the same conditions in boric acid. Gd^{III}, for instance, reacts with molten boric acid to form $Gd[B_6O_9(OH)_3]$. Third, trivalent actinide borates do not vary simply as a function of the ionic radius of the metal ion; the behavior is far more complex. Our current hypothesis is that actinide borate compounds yield such distinct chemistry among 5f elements because of the large polarizability of the BO_3 units. This yields unusual bonding with 5f orbitals that is absent in most other ligand systems. This supposition is currently being probed with high-level quantum theory.

Experimental Section

$Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ was synthesized using $^{248}CmCl_3$ (3% ^{246}Cm) as the starting material. 5 mg of $CmCl_3$ was placed in an autoclave and then transferred into an argon-filled glovebox. 30 μL of argon-sparged water and 63 mg of boric acid were added into the autoclave. The mixture was then sealed and heated at 240 °C for seven days followed by slow cooling to room temperature over a two day period. This is the same procedure used to synthesize Pu^{III} and Am^{III} borates. The resulting product was washed with boiling water and consisted of pale yellow tablets of $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$ as the sole product.

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[14] Crystallographic data for $Cm_2[B_{14}O_{20}(OH)_7(H_2O)_2Cl]$: Pale yellow tablet, 0.044 × 0.035 × 0.007 mm, monoclinic, $P2_1/n$, $Z = 2$, $a = 7.9561(17)$, $b = 14.212(3)$, $c = 9.836(2)$ Å, $\beta = 90.013(2)°$, $V = 1112.2(4)$ Å^3 ($T = 100(2)$ K), $\mu = 75.37\ \text{cm}^{-1}$, $R_1 = 0.0645$, $wR2 = 0.1452$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 49.42°$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, 0.5° ω scans, 10454 reflections measured, 1899 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption, the structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares on 184 parameters. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423777. EDS analysis confirms a 2:1 ratio of Cm:Cl.

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