Actinides

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Bonding Changes in Plutonium(III) and Americium(III) Borates**

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Interest in trivalent actinide (e.g. Pu^{III}, Am^{III}, and Cm^{III}) borates stems from their potential formation in the geological repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, USA.[1] A similar repository is being considered in Germany. In this salt deposit the concentration of borate species in intergranular brines can be as high as 166 ppm.[1] Studies of the complexation of Nd^{III} by borates in solution have been performed indicating that borate is the primary complexant in WIPP for trivalent cations.[2] Furthermore, WIPP is self-sealing, and once closed will be saturated with hydrogen and methane, making it a highly reducing environment that will favor lower oxidation states for plutonium.

There are few systems that have been studied that extend between plutonium and americium for which detailed structural information is available. The differences in bonding between plutonium and americium in the same oxidation state (e.g. Pu^{III} and Am^{III}) is expected to be so small that the ligand set that binds these two cations has to be exquisitely sensitive to the differences in bonding between plutonium and americium to detect any divergence. In fact, the few systems where corresponding compounds are known such has the halides[3] and triflates[4] do not respond to the changes in bonding between plutonium and americium by exhibiting substantially different structures; although the actinide contraction is certainly found between these two elements.[5]

The formation of different polyborate networks is profoundly affected by numerous factors including minute changes in the pH value, reaction temperature, stoichiometry, cation size, and counterions. We have recently explored the syntheses, structures, spectroscopy, and stability of actinide borates from thorium to plutonium. These investigations have uncovered a pertechnetate-selective anion exchange material,[6,7] spectacularly complex acentric topologies in uranyl borates,[8–12,15,17] mixed-valency in neptunium borates,[12–15,17] and new coordination environments in plutonium borates.[12,15,16] It occurred to us that as these studies progressed that Pu^{III} and Am^{III} polyborates might be an ideal system for observing changes in bonding that occur across the actinide series when all other variables are held constant except for the identity of the actinides because the polyborate network should be hyper-responsive to subtle changes in the metal centers. Herein we report the syntheses, structures, coordination chemistry, and spectroscopy of new Pu^{III} and Am^{III} borates that achieve the goal of observing substantially different structures between these two elements.

The reactions of $PuCl_3$ and $AmCl_3$ with molten boric acid at 240 °C under strictly anaerobic conditions leads to the formation of $Pu[B_4O_6(OH)_2Cl]$ and $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and $Am[B_9O_{13}(OH)_4]\cdot H_2O$, respectively. $Pu[B_4O_6(OH)_2Cl]$ forms blue crystals that can exceed 1 mm in size. $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ forms smaller more lightly colored blue crystals. $Am[B_9O_{13}(OH)_4]\cdot H_2O$ is isolated as large pink tablets. Pictures of these crystals can be found in the Supporting Information. The crystals are not degraded by oxygen or water. Curiously the crystals of $Pu[B_4O_6(OH)_2Cl]$ are extremely hard and cannot be cut with steel tools. This might be a function of the multiple ways in which the structure is cross-linked. These crystals were used directly for structural and spectroscopic investigations.

Single-crystal X-ray diffraction experiments on all three compounds yielded models for the structures with low residuals.[18] There are very few single-crystal structures known for americium compounds.[3a,4b,19] Crystals of $Am[B_9O_{13}(OH)_4]\cdot H_2O$ are of remarkable quality, and the residuals for the model of the structure are the lowest reported for an americium compound, providing very precise metrics for the structure. All three compounds form dense, three-dimensional structures shown in Figure 1. $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ and $Am[B_9O_{13}(OH)_4]\cdot H_2O$ both contain similar polyborate sheets as shown in Figure 2 b,c. These sheets contain an unusual unit of three BO_4 tetrahedra that share a common corner. These clusters share corners with BO_3 triangles to create sheets with triangular holes where the An^{III} (An = Pu, Am) cations reside. For comparison, this sheet topology can be also found in the Ln^{III} borate systems, $Ln[B_8O_{11}(OH)_5]$ (Ln = La–Nd) and $Ln[B_9O_{13}(OH)_4]$ (Ln = Pr–Eu).[20] $Pu[B_4O_6(OH)_2Cl]$ possesses a very different sheet topology that lacks the clusters, and only contains corner-sharing BO_3 and BO_4 units (Figure 2 a). Once again there are triangular holes to house the Pu^{III} cations. These layers are

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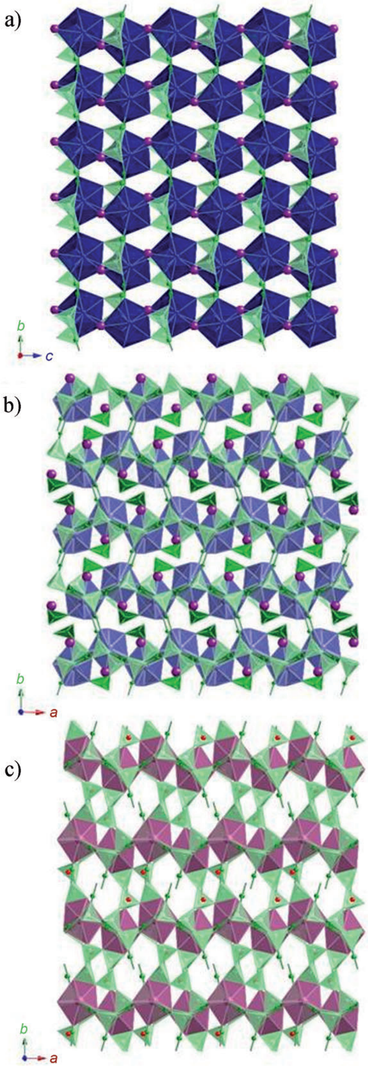

Figure 1. Three-dimensional framework structures of a) Pu-$[B_4O_6(OH)_2Cl]$, b) $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and c) Am-$[B_9O_{13}(OH)_4]\cdot H_2O$. Pu polyhedra are shown in blue (a) or light purple-blue (b), Am polyhedra in pink, BO_3 triangles in dark green, BO_4 tetrahedra in light green, chlorine atoms in purple, and unbound water in red. The color of the actinide polyhedra is similar to the color of the crystals.

very similar to those found with penta- and hexavalent actinides (e.g. U^{VI}, Np^{V}, Np^{VI}, and Pu^{VI}).[8–17] Both types of sheets are joined together by BO_3 or BO_4 units to create three-dimensional networks as shown in Figure 1.

The most remarkable features of the Pu^{III} and Am^{III} borates are the local coordination environments of the metal centers (see Figure 3). In all three compounds the polyborate layers provide six oxygen donors that are close to being co-planar. This environment forces the cations to have geometries that are not typically found for actinides in the trivalent oxidation state. $Pu[B_4O_6(OH)_2Cl]$ and $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ both contain ten-coordinate Pu^{III} in a geometry that is best described as a capped triangular cupola.[21] The capping group is a chloride anion, and the triangular base is created by either water molecules and

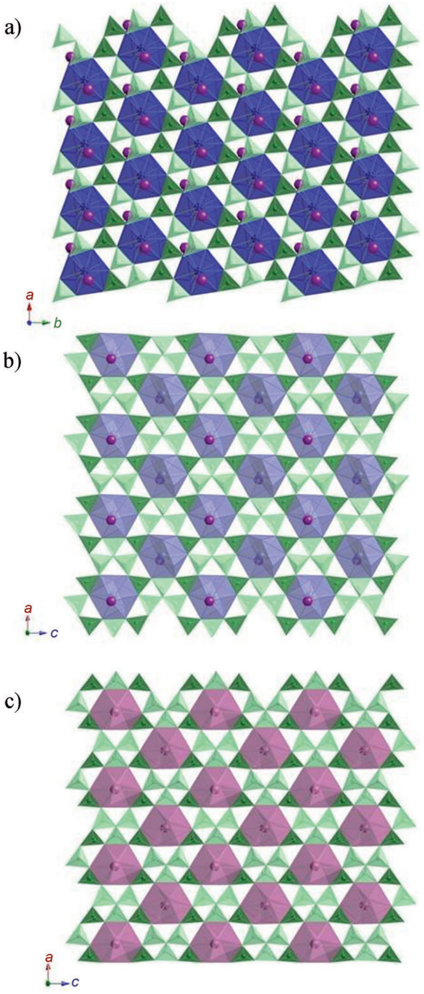

Figure 2. Sheet topologies of a) $Pu[B_4O_6(OH)_2Cl]$, b) Pu_2-$[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and c) $Am[B_9O_{13}(OH)_4]\cdot H_2O$. Pu polyhedra are shown in blue (a) or light purple-blue (b), Am polyhedra in pink, BO_3 triangles in dark green, BO_4 tetrahedra in light green, and chlorine atoms in purple.

borate anions in $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, or borate and an additional chloride anion in $Pu[B_4O_6(OH)_2Cl]$. Both chloride anions in $Pu[B_4O_6(OH)_2Cl]$ bridge between Pu^{III} centers, and these bridges span between the sheets. This type of connectivity is absent in all of the actinide borates that we have prepared and may be responsible for the hardness of the crystals. These bridges are lacking in $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and the chloride anion is terminal, much like the bromide anions in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5\,H_2O$.[16] As given by the formula, $Am[B_9O_{13}(OH)_4]\cdot H_2O$ lacks chloride entirely, and this is a significant departure from the reactivity of Pu^{III} halide starting materials for which we observe halides bound to Pu^{III} in the final products. The capping group where the halide would have been is instead occupied by a BO_3 unit that bridges to the next layer. The two sites beneath the borate layer are two oxo atoms from one chelating BO_4 unit. Therefore, the groups above and below the polyborate plane are different between Pu^{III} and Am^{III}. This is another point of distinction between the Pu^{III} borates herein and Am-

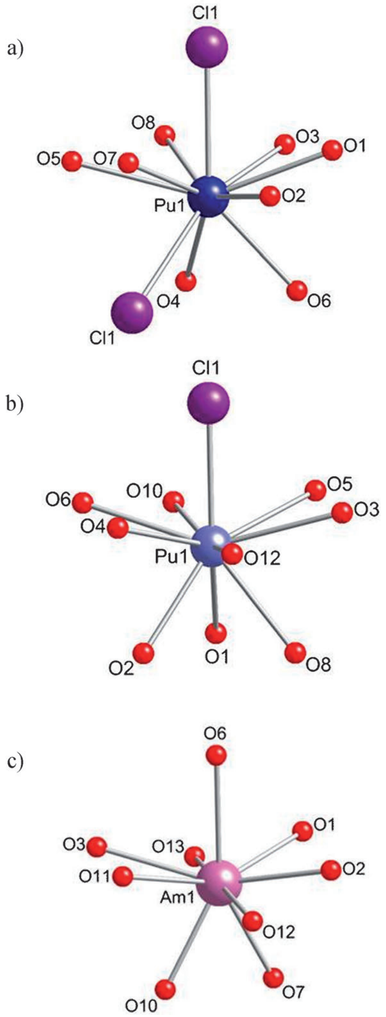

Figure 3. Coordination environments of actinide(III) sites in a) Pu-$[B_4O_6(OH)_2Cl]$, b) $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$, and c) Am-$[B_9O_{13}(OH)_4]\cdot H_2O$.

$[B_9O_{13}(OH)_4]\cdot H_2O$ because the Am^{III} is nine-coordinate instead of ten and has a hula-hoop-like geometry.[22]

The central question is why are the Pu^{III} and Am^{III} borates so different? There are several answers to this question. First, the actinide contraction between Pu^{III} and Am^{III} is larger than one might expect. Pu^{III} has an ionic radius of 1.00 Å, whereas Am^{III} has a radius of 0.975 Å (coordination number, CN = 6).[5] The typical change in the ionic radius between neighboring actinides in the same oxidation state with the same coordination number is approximately 0.01 Å,[5] and this is enough of a difference to induce structural changes.[23] Therefore, the formation of a different structure is not completely surprising based on this rather large change. Second, while exclusion of chloride from the inner coordination sphere is a bit more perplexing, it is also a reflection of the increased Pearson hardness of the Am^{III} versus the Pu^{III} cation.[24] Am^{III} shows a preference for all oxo donors. Finally, $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ does not have a lanthanide analog, whereas lanthanide borates with similar structures to $Am[B_9O_{13}(OH)_4]\cdot H_2O$ are known.[25] We suggest that this represents a sharp demarcation between the coordination chemistry of Pu^{III} and Am^{III}.

All oxo atoms that bind to the An^{III} centers in $Pu[B_4O_6(OH)_2Cl]$ and $Am[B_9O_{13}(OH)_4]\cdot H_2O$ are provided by the borate network; while one oxygen donor atom that binds to the Pu^{III} centers in $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ is from a water molecule, with a Pu–O_w distance of 2.524(18) Å. The Am–O bond distances in $Am[B_9O_{13}(OH)_4]\cdot H_2O$ range from 2.356(2) to 2.614(2) Å with an average of 2.497(2) Å. The Pu–O bond distances in $Pu[B_4O_6(OH)_2Cl]$ range from 2.445(5) to 2.722(5) Å with an average of 2.585(5) Å, and in $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ from 2.471(18) to 2.726(11) Å with an average of 2.609(18) Å. This large difference in the average An–O bond distances between Pu^{III} and Am^{III} is a consequence of different coordination environments and different structure types in Pu^{III} and Am^{III} borates, as well as the substantial change in the ionic radius.

In conclusion, the coordination chemistry of Pu^{III} and Am^{III} can be highly different even when synthetic parameters and crystallization conditions are held constant. Bond distances of Pu–O and Am–O are quite different, and the hope would be that future theory will be able to account for the differences in the bonding behavior.

Experimental Section

$Pu[B_4O_6(OH)_2Cl]$ and $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ were synthesized using weapons-grade (94% ^{239}Pu and 6% ^{240}Pu along with trace amounts of the other Pu isotopes and ^{241}Am) $PuCl_3$. Anhydrous $PuCl_3$ that results from the recycling and electrorefining of plutonium metal was used as received. $PuCl_3$ (10.6 mg) was placed in an autoclave and then transferred into an argon-filled glovebox. Argon-sparged water (30 μL) and boric acid (63 mg) 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 period of two days. The furnace for heating the autoclave was also inside the glovebox to prevent oxygen from re-entering the autoclave because oxygen is not excluded by PTFE. The resulting product was washed using cold water and consisted of large blue crystals of $Pu[B_4O_6(OH)_2Cl]$ (80%) and a few clusters of much smaller crystals of $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$ which are lighter in color and have an acicular habit (20%). Both compounds are not air-sensitive.

$Am[B_9O_{13}(OH)_4]\cdot H_2O$ was synthesized using $^{243}AmO_2$ as received. AmO_2 (6.6 mg) was dissolved in 5 M HCl (100 μL) in an autoclave. The solution was dried by heating at 130 °C, ending with a yellow solid of $AmCl_3$. The autoclave was then transferred into an argon-filled glovebox and the same procedure was followed forthwith as was done with $PuCl_3$. The resulting product consisted of large pink tablets of $Am[B_9O_{13}(OH)_4]\cdot H_2O$ as a pure phase.

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[18] Crystallographic data for $Pu[B_4O_6(OH)_2Cl]$: Blue block, $0.064 \times 0.056 \times 0.052$ mm, monoclinic, *Cc*, $Z = 4$, $a = 6.491(2)$ Å, $b = 11.184(4)$ Å, $c = 9.630(3)$ Å, $\beta = 105.175(9)^\circ$, $V = 674.7(4)$ Å^3 ($T = 100(2)$ K), $\mu = 101.76\ \mathrm{cm}^{-1}$, $R_1 = 0.0223$, $wR2 = 0.0408$. $Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3]$: Light purple-blue needle, $0.080 \times 0.010 \times 0.002$ mm, monoclinic, $P2_1/n$, $Z = 2$, $a = 8.0522(17)$ Å, $b = 14.568(3)$ Å, $c = 9.820(2)$ Å, $\beta = 90.120(2)^\circ$, $V = 1151.8(4)$ Å^3 ($T = 100(2)$ K), $\mu = 60.29\ \mathrm{cm}^{-1}$, $R_1 = 0.0547$, $wR2 = 0.1284$. $Am[B_9O_{13}(OH)_4]\cdot H_2O$: Pink tablet, $0.078 \times 0.061 \times 0.007$ mm, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.7030(15)$ Å, $b = 16.688(3)$ Å, $c = 9.872(2)$ Å, $\beta = 90.073(6)^\circ$, $V = 1269.1(4)$ Å^3 ($T = 100(2)$ K), $\mu = 61.60\ \mathrm{cm}^{-1}$, $R_1 = 0.0143$, $wR2 = 0.0370$. Further details on the crystal structure investigation 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 numbers CSD-423058, -423059, and -423060.

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