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Surprising Coordination for Plutonium in the First Plutonium(III) Borate

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S *Supporting Information*

ABSTRACT: The first plutonium(III) borate, $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$, has been prepared by reacting plutonium(III) with molten boric acid under strictly anaerobic conditions. This compound contains a three-dimensional polyborate network with triangular holes that house the plutonium(III) sites. The plutonium sites in this compound are 9- and 10-coordinate and display atypical geometries.

Structural intricacy and complexity are achieved at a remarkable level in lanthanide and actinide borates owing to the unsurpassed flexibility of the coordination chemistry of both rare-earth elements and boron. The former have coordination numbers ranging from 6 to 15 with a strong preference for seven-, eight-, and nine-coordinate geometries,[1] and the latter occurs as both BO_3 triangles and BO_4 tetrahedra that polymerize in a seemingly limitless variety of clusters, chains, sheets, and frameworks.[2−4] The structural chemistry of borates with trivalent cations has been well-developed over the past decade for the lanthanide series by using hydrothermal conditions and boric acid fluxes. High temperatures and pressures provide access to even more exotic borates.[5] The first of these studies yielded the hydrated gadolinium hexaborate $H_3GdB_6O_{12}$, which can be decomposed to the pentaborate GdB_5O_9.[6] In fact, the entire series of $H_3LnB_6O_{12}$ (Ln = Sm−Lu) can be decomposed to pentaborate phases.[7] Lanthanide borates yield extremely rich polyborate networks containing both BO_3 triangles and BO_4 tetrahedra, and phases such as $Ln[B_8O_{11}(OH)_5]$ (Ln = La−Nd) and $Ln[B_9O_{13}(OH)_4]\cdot H_2O$ have been prepared and structurally characterized and their luminescent properties elucidated.[8]

Interest in trivalent actinide [e.g., plutonium(III), americium(III), and curium(III)] borates does not stem from their potential applications as optical materials, as it does with lanthanide compounds,[9] but rather from their potential formation in the geological repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, NM. In this salt deposit, the concentration of borate species in intergranular brines can be as high as 166 ppm. There is not a single example of a well-characterized trivalent actinide borate in the literature, although studies of the complexation of neodymium(III) by borates in solution have been performed where the neodymium is serving as a surrogate for trivalent actinides.[10] We have recently undertaken the study of actinide borates starting with high oxidation states for the actinides,[11−19] but in this work, we demonstrate the first access to a low-oxidation-state actinide borate with the synthesis, structural characterization, and absorption spectroscopy of the plutonium(III) borate $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$.

Unlike trivalent lanthanides, americium(III), or curium(III), plutonium(III) is air-sensitive and is often oxidized to plutonium(IV) by oxygen, although it must be kept in mind that there are some systems (e.g., monazites) where plutonium(IV) is thermally reduced to plutonium(III) at high temperatures.[20] When plutonium(III) is reacted with molten boric acid at 200 °C or higher, it rapidly oxidizes to plutonium(IV) and plutonium(VI). In order to prevent this oxidation, strictly anaerobic conditions had to be maintained. It was found that, in the absence of oxygen, plutonium(III) (as the bromide salt) is retained in molten boric acid, and we were able to crystallize the first plutonium(III) borate, $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$, as thin navy blue/purple tablets.[21]

Single-crystal X-ray diffraction experiments on $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ proved to be very challenging for many reasons.[22] First, the crystals were small (ca. 30 μm). Second, the crystals had a tendency to stack on one another. Third, owing to the β angle being nearly 90°, all of the crystals were pseudomerohedrally twinned, and this twinning creates pseudoorthorhombic symmetry, leading one down the false path of trying to solve the structure in the orthorhombic space group *Pnn*2, where a suitable twin law does not exist. Even when the correct crystal system of monoclinic is selected, the centrosymmetric space group of $P2_1/n$ is suggested by the systematic absences. This space group requires a single crystallographically unique plutonium site, but, in fact, there are two distinct sites with different coordination environments. All of these features are only compatible with the noncentrosymmetric space group *Pn*, where a reasonable solution and refinement of the structure was finally achieved.[22]

Part of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ is shown in Figure 1. The structure consists of layers created by BO_3 triangles and BO_4 tetrahedra that extend in the [*ac*] plane. These sheets do not occur in the actinide borates that contain actinides in higher oxidation states and contain an unusual cluster of three BO_4 units that share a common corner. This type of polyborate network is also found in the lanthanide octaborates, $Ln[B_8O_{11}(OH)_5]$.[8] These sheets are linked together by interlayer BO_3 triangles to create a three-dimensional framework as shown in Figure 2. On the basis of the classification that we have recently developed for actinide borates, a 1 $L-1-0-0_{Pu\infty}$ structural descriptor can be used for the structure.[16]

The most remarkable feature of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ is coordination of the

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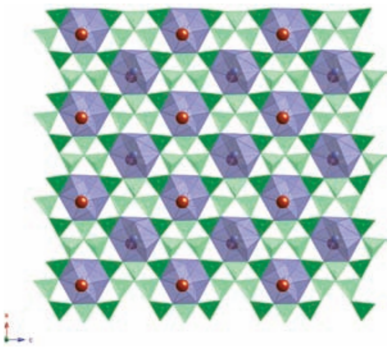

Figure 1. View of part of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ showing the polyborate framework that extends into the [*ac*] plane that has triangular holes that are filled with the plutonium(III) cations. Plutonium polyhedra are shown in blue-purple, BO_3 triangles in dark green, BO_4 tetrahedra in light green, and bromide anions in brown.

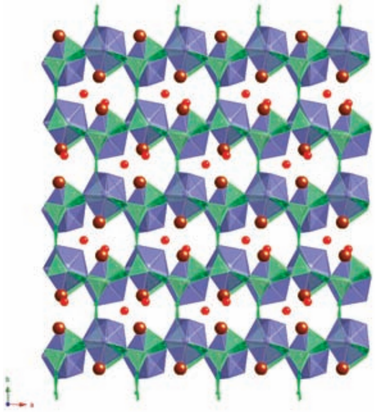

Figure 2. Depiction of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ showing the linking of the polyborate sheets by interlayer BO_3 triangles. Plutonium polyhedra are shown in blue-purple, BO_3 triangles in dark green, BO_4 tetrahedra in light green, bromide anions in brown, and unbound water in red.

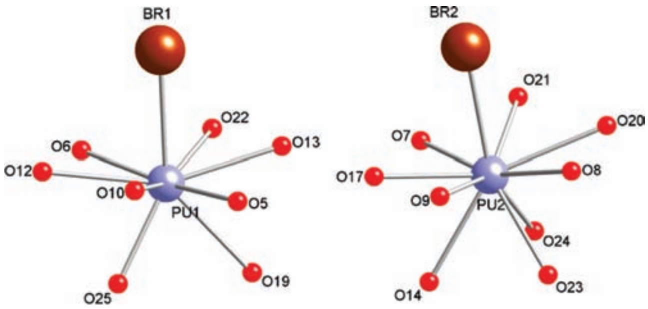

Figure 3. Views of the coordination environments for plutonium(III) in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ showing the 9- and 10-coordinate geometries.

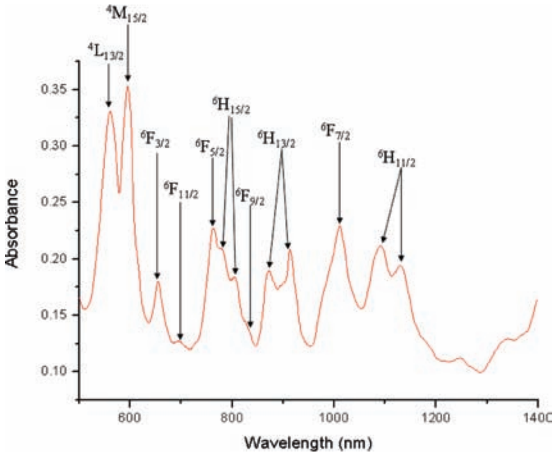

Figure 4. Absorption spectrum of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ showing f−f transitions that are diagnostic for plutonium(III).

plutonium(III) ion. As was previously mentioned, the plutonium ions reside in triangular holes in the polyborate sheets, and there are six oxygen donor atoms in these holes that bind the plutonium(III) cations. There are two crystallographically unique plutonium(III) sites. One of these, Pu1, is 9-coordinate, and the other, Pu2, is 10-coordinate, with the remaining donor atoms above and below the plane of the polyborate sheet. These two coordination environments are shown in Figure 3. Both sites are capped on one side by bromide anions. While the immediate thought would be that the low oxidation state is stabilized, in part, by having a soft donor in the inner-coordination sphere, this is, in fact, unnecessary for stabilizing plutonium(III). For Pu1, there are two water molecules opposite from the bromide anion, and for Pu2, there are three such water molecules. These coordination geometries are not typical for plutonium. The most prevalent coordination environment for 9-coordinate lanthanides and actinides is a tricapped trigonal prism. However, in this compound, six of the oxygen atoms are close to being in a plane. Therefore, this geometry is very different from a tricapped trigonal prism. Likewise, a 10-coordinate geometry was found for plutonium in the plutonium(IV) compound, $[Pu(NO_3)_3\{2\text{-}[(C_6H_5)_2P(O)CH_2]C_5H_4NO\}_2][Pu(NO_3)_6]_{0.5}$.[23] There are two idealized geometries for coordination number 10: the bicapped square antiprism and sphenocorona.[23] The Pu2 site in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ is neither of these. Having six nearly coplanar oxygen atoms distorts both Pu1 and Pu2 from having more typical coordination geometries. Ruiz-Martinez and Alvarez have substantially expanded recognized geometries for coordination number 10 and identified 19 ideal 10-vertex polyhedra.[24] This coordination number is actually reasonably common for La^{3+} but becomes less common as the lanthanide contraction occurs across the series.[24] A similar trend is found with the actinides. The 10-coordinate geometry of Pu2 is best described as a capped triangular cupola with C_{3v} symmetry.[24]

The bond distances around the plutonium sites are highly variable. The Pu−O bond distances to the borate donor oxygen atoms range from 2.502(6) to 2.721(6) Å. Pu−O bonds to the water molecules range from 2.304(8) to 2.546(6) Å. Finally, the Pu−Br bonds are long at 2.887(1) and 2.902(2) Å. These distances are similar to those found in other plutonium(III) bromide compounds.[25]

The absorption spectrum of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$ was obtained from a twinned crystal using a microspectrophotometer and is shown in Figure 4. The absorption spectrum of plutonium(III) is very rich and displays a series of weak Laporte-forbidden f−f transitions throughout the UV−vis−near-IR region of the spectrum. Plutonium(III) has a $^6H_{5/2}$ ground state, and its f−f transitions have been carefully assigned by Carnall and coworkers.[26] We have used Carnall's analysis of the absorption spectrum of plutonium(III) to assign the transitions for

$Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$, as shown in Figure 4. The most important transitions that distinguish plutonium(III) from plutonium(IV) are the $^6H_{5/2} \rightarrow {}^6H_{13/2}$ transitions near 900 nm. Fortunately, this region is barren for plutonium(IV). The $^4L_{13/2}$ and $^4M_{15/2}$ transitions are also used routinely to identify the presence of plutonium(III). The spectrum of this compound is very similar to the spectrum obtained from the triflate salt of $[Pu(H_2O)_9]^{3+}$.[27] It is important to note that, even with the substantially different geometries around plutonium(III), the absorption spectra are very similar.

In conclusion, we have successfully synthesized the first plutonium(III) borate by using boric acid as a reactive flux under strictly anaerobic conditions. The plutonium(III) sites in this compound display atypical geometries for actinides, and a rare 10-coordinate plutonium site is found in this compound. We continue to work on this system and plan to replace the bromide anions with smaller donor atoms such as chloride and oxide from nitrate. The synthesis and structures of the americium(III) and curium(III) borates will also be forthcoming.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic file in CIF format for $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) **Synthetic details:** A stock solution of ^{242}plutonium(VI) nitrate was prepare by first digesting PuO_2 in 8 M HNO_3 for 5 days at 200 °C (in an autoclave). The solution was ozonated for 1 h and reduced to a moist residue and redissolved in water forming a plutonium(VI) nitrate solution. UV−vis−near-IR spectroscopy indicates that only plutonium(VI) is present. An aliquot containing 5 mg of plutonium was taken from this solution and reduced to a residue. A total of 50 μL of concentrated HBr was added to this residue, resulting in the immediate formation of bromine gas and a red solution [the red color is from the dissolved bromine, which masks the color of plutonium(III)]. The red solution was reduced to a purple-black residue at 130 °C and then transferred into an argon-filled glovebox. The residue was redissolved in 30 μL of argon-sparged water, producing a navy blue/purple solution characteristic of plutonium(III). The droplet of plutonium(III) was then transferred to a poly(tetrafluoroethylene) (PTFE) autoclave liner that had been previously heated in the glovebox for 2 days at 200 °C to drive the oxygen out of the PTFE. The catalyst for the glovebox was then regenerated. A large excess of boric acid (63 mg) was then added directly to the droplet containing plutonium(III). The mixture was then sealed in an autoclave and heated at 240 °C for 7 days, followed by slow cooling to room temperature over a 2 day period. The furnace for heating the autoclave was also inside the glovebox to prevent oxygen from reentering the autoclave because oxygen is not excluded by PTFE. The autoclave was opened, and cold water was added to dissolve the excess boric acid, revealing navy blue/purple crystals with a platelike habit.

(22) Crystallographic data for $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$: navy blue/purple plate, 0.030 × 0.020 × 0.002 mm, monoclinic, Pn, $Z = 1$, $a = 8.0995(15)$ Å, $b = 14.635(3)$ Å, $c = 9.8248(18)$ Å, $\beta = 90.028(2)°$, $V = 1164.6(4)$ Å^3, $T = 100(2)$ K, $\mu = 91.55$ cm^{-1}, R1 = 0.0334, and wR2 = 0.0693. The occurrence of systematic absences that are consistent with $P2_1/n$ can be ascribed to the relationship between the two symmetrically independent plutonium atoms in the structure, which is responsible for the almost extinct $0k0$ reflections with k = odd. The y coordinates of both atoms differ by almost exactly $^1/_2$. $0k0$ reflections correspond to a projection of the structure onto b. Hence, in this projection, the plutonium atoms form a superstructure with $b/2$. Plutonium is by far the strongest X-ray scatterer in the structure. The remaining bromine, oxygen, and boron atoms are more or less randomly distributed in this projection, and their contributions tend to add up to something close to zero. Hence, plutonium scattering prevails, and $0k0$ odd are very weak, which mimics the extinction condition for a 2_1 screw.

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