Synthesis and structural characterization of a molecular plutonium(IV) compound constructed from dimeric building blocks

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Single crystals of $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$, exhibiting bridging μ^2,η^2-O_2 ligands in unprecedented Pu(IV) dimeric units, were obtained at ambient temperature from an aqueous Pu(IV) peroxide carbonate solution.

Peroxide coordination was significant in early plutonium chemistry because of the ability of peroxide to control oxidation states and precipitate uranium and plutonium from acidic solutions for nuclear material separation.[1,2] More recently, radiolytic peroxide formation and secondary phase formation (*e.g.* studtite) have attracted interest due to their relevance to the corrosion of spent nuclear fuel.[3–5] To date, there are no structural details on plutonium peroxide compounds available.[1] However, several carbonate complexes have been proposed for tetravalent actinide ions, with the $An(CO_3)_5^{6-}$ (An = Th, U, Pu) anion identified as the limiting solution species under high carbonate concentrations. The Pu anion was crystallized as $[Na_6Pu(CO_3)_5]_2{\cdot}Na_2CO_3{\cdot}33H_2O$,[6] representing one of the very few molecular structures reported for plutonium. Surprisingly, the affinity of the O_2^{2-} ligand towards actinide ions is stronger than the hard O-donor ligands present in alkaline solutions (carbonate and hydroxide).[7] The scarcity of structurally characterized plutonium peroxide complexes has prompted us to attempt to replace carbonate ligands in $Pu(CO_3)_5^{6-}$ with peroxide to obtain single crystals of a discrete mononuclear Pu(IV) peroxide species. Expanding the coordination chemistry of plutonium, we report herein the synthesis and structural characterization of the first mixed peroxo-carbonato Pu(IV) compound, with a molecular architecture unprecedented among the 5f-elements.

Large olive-green crystals (up to 1.5 mm) of $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$ (**1**) were obtained in a methanol–carbonate–peroxide solution (Fig. 1), with greater than 95% yield.† Full single-crystal X-ray diffraction studies were performed revealing a dimeric Pu(IV) configuration.‡ Within about six weeks, these well-formed crystals decomposed under the intense radiation field of ^{239}Pu to a brown powder. The composition of the brown material is under investigation.

The title compound contains a complex network of discrete $Pu_2(O_2)_2(CO_3)_6^{8-}$ anions and Na^+ cations that are linked through shared interactions with carbonate ligands and H_2O molecules. The structural unit of ten-coordinate Pu atoms, with a Pu–Pu distance of 3.528 Å (Fig. 2), is very similar to the related $Ce_2(O_2)_2(CO_3)_6^{8-}$ anion found in $Na_8Ce_2(O_2)_2(CO_3)_6{\cdot}nH_2O$.[8,9] The Ce–Ce distance of 3.523 Å is very close to the Pu–Pu distance found in **1**, reflecting the similar ionic radii of Ce(IV) (0.97 Å, CN 8) and Pu(IV) (0.96 Å, CN 8).[10] The central Pu atoms are bound to six O atoms from three bidentate carbonato ligands and to four O atoms from two side-on coordinated peroxide ligands. Both peroxide ligands are shared between two Pu atoms, forming a distorted octahedral Pu_2O_4 arrangement with one Pu–O_{peroxo} bond distance of 2.33(1) Å and the second elongated to 2.36(1) Å. The O(10)–O(11) distance is 1.496(6) Å, which is significantly longer than that found in crystalline H_2O_2 (1.458 Å)[11] or in the $Ce_2(O_2)_2(CO_3)_6^{8-}$ anion (1.468(6) Å).[8,9] The six Pu–O_{carb} distances of the carbonate ligands range between 2.38 and 2.49 Å, which is similar to the average bond distance of 2.415(7) Å in $[Na_6Pu(CO_3)_5]_2{\cdot}Na_2CO_3{\cdot}33H_2O$.[6] The O(7) atom is the most separated from the central Pu_2O_4 cage, shielded by surrounding Pu–O_{carb} bonds. Thus, at 2.486(4) Å the Pu–O(7) bond is the longest among the Pu–O_{carb} bonds. Bond distances and angles associated with the carbonate ligands are all within the normal range found in other actinide carbonate compounds. A complex network of Na^+ cations and hydration waters surround the Pu dimers (Fig. 3). The latter are stacked along the *b* axis and linked

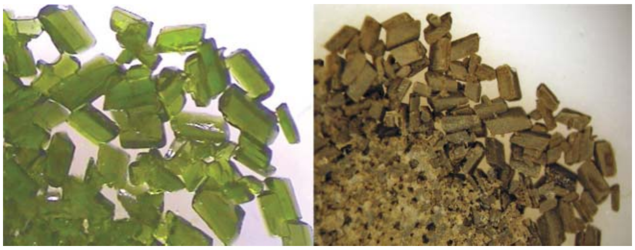

Fig. 1 Photograph of $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$ crystals (left) after 6 hours and (right) after 6 weeks of crystallization.

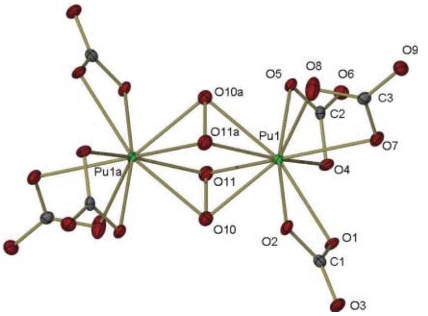

Fig. 2 Thermal ellipsoid plot (50% probability) of the $Pu_2(O_2)_2(CO_3)_6^{8-}$ anion present in $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$. A center of inversion symmetry lies at the midpoint between the two plutonium atom positions. The dimer occupies a site of inversion symmetry, *a*[2 − *x*, 1 − *y*, −*z*].

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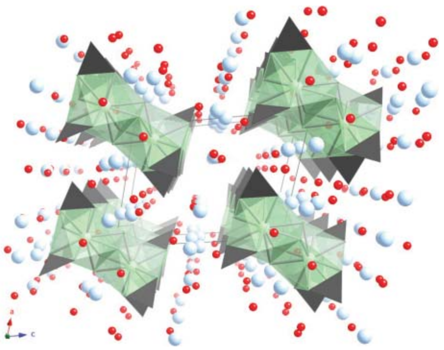

Fig. 3 Packing diagram of the dimeric Pu(IV) polyhedra in $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$ viewed down the crystallographic *b* axis.

by Na(3) and Na(4) polyhedra in the *ab* plane; while Na(1) and Na(2) polyhedra form chains in the *ab* plane that connect the Pu dimers along the *c* axis. All four crystallographically distinct Na atoms interact with six O atoms from hydration waters, carbonate and peroxide ligands to form pseudo-octahedral geometries with Na–O distances generally between 2.26 and 2.46 Å. One Na–O bond is elongated for three out of the four Na-octahedra: (Na(1)–O(13): 2.75(2), Na(2)–O(1): 2.766(5), and Na(4)–O(8): 2.691(6) Å). The O(13) atom is a μ^2-O_{water} atom shared between two adjacent Na(1) atoms; O(1) and O(8) are μ^3-O_{carb} atoms and are shared between one C, Pu, and Na(2) or Na(4) atom, respectively. While the Na(2) octahedra are not interconnected, the Na(1), (3) and (4) octahedra are internally linked to form discrete $[Na_2O_{10}]$ units with Na–Na distances of 4.174(6) Å for Na(1)–Na(1), 3.447(6) Å for Na(3)–Na(3), and 3.455(7) Å for Na(4)–Na(4).

Conventional UV-vis-NIR diffuse reflectance spectroscopy was used to verify the valency of the plutonium ion (Fig. 4). The electronic absorption spectrum of Pu(IV)(aq) shows several Laporte-forbidden f–f transition bands in the visible region (400–800 nm). The well-known electronic absorbance of the green $Pu(CO_3)_5^{6-}$(aq) complex in 2 M K_2CO_3 solution is dominated by its absorbance peak at 485.5 nm. This characteristic band is shifted to 495.5 nm upon addition of peroxide, indicating the formation of a new peroxy-carbonate mixed complex. The nature of this complex (*i.e.* mononuclear or dimeric) is the subject of current investigations. The diffuse reflectance spectrum of the corresponding solid phase exhibits remarkable agreement in peak positions and relative absorption strengths with the spectrum of the solution complex. The reflectance peak at 485.7 nm for the solid Pu(IV) pentacarbonate complex is again shifted to 495.8 nm for $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$, confirming not only the presence of tetravalent plutonium but also suggesting that the same dimeric chromophore is displayed both in solution and in the solid state.

The nature of Pu peroxo complexes under acidic conditions has been debated for over 50 years. Two dimeric Pu(IV) peroxo complexes containing bridging peroxo groups have been postulated to form with their main absorbance bands observed at about 495 nm and 510 nm.[12] The spectroscopic features of the reported complex at 495 nm absorbance are intriguingly similar to those of **1**, suggesting that peroxide is present in both acidic and alkaline complexes as a side-on, rather than end-on, bridging ligand. To date, the Pu(IV) dimeric complex in **1** is the first structurally characterized architecture of its kind among the transuranium complexes that offers new insights into the unresolved acidic Pu(IV) peroxo structures.

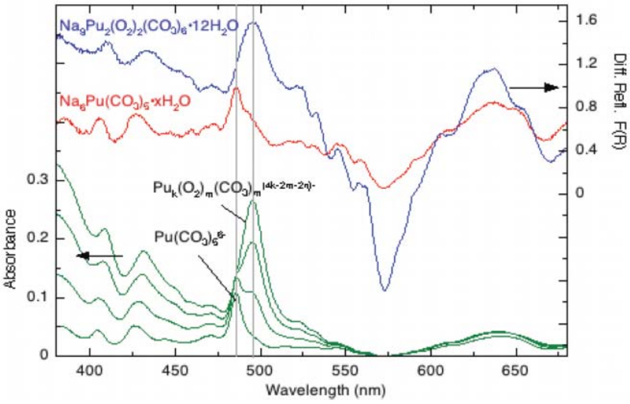

Fig. 4 Electronic transitions of the Pu(IV) chromophores in binary carbonato and ternary peroxo-carbonato complexes in solution (absorbance) and solid state (diffuse reflectance).

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Notes and references

† 50 μL of ^{239}Pu(IV) stock solution (0.12 M in 2 M HCl) was reacted with 2.2 M K_2CO_3 (2 mL) and 100 μL of 3.3% H_2O_2 at room temperature. Addition of 3 mL of methanol caused the formation of the title compound within 24 h.

‡ *Crystal data* for $Na_8Pu_2(O_2)_2(CO_3)_6{\cdot}12H_2O$: $Na_8Pu_2C_6H_{24}O_{34}$, M = 1308.17, triclinic, space group $P\bar{1}$, a = 8.861(8), b = 8.889(8), c = 11.511(10) Å, α = 69.45(1)°, β = 67.99(1)°, γ = 64.692(1)°, V = 739.9(11) Å^3, Z = 1, T = 141 K, μ = 4.665 mm^{-1}, R_{int} = 0.0324, $R1(I > 2\sigma(I))$ = 0.0304, and $wR2(I > 2\sigma(I))$ = 0.0818. The reflection data were collected on a Bruker D8/APEXII CCD using ϕ scans. The structure was solved using standard direct methods (SHELXS-97),[13] and refined using full-matrix least-squares based on F^2 (SHELXL-97).[14] All non-hydrogen atoms were refined anisotropically. CCDC 630066. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617878b

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