Supporting Information

The Crystal Chemistry of Plutonium(IV) Borophosphate

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Table S1. Crystal parameters, data collection and structure refinement details for $Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$.

Crystal data	
Formula	$Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$
Formula weight (g mol^{-1})	628.53
Temperature (K)	273(2)
Cell setting	Hexagonal
Space group	*P*3 (No. 143)
a (Å)	7.8764(10)
c (Å)	5.5355(7)
V (Å^3)	297.40(8)
Z	1
Crystal size (mm)	0.020 × 0.020 × 0.025
Crystal form	blocky
Data collection	
Diffractometer	Bruker Apex II Quazar, CCD-detector
Radiation; λ	Mo K_α; 0.71073
Density (calculated, g/cm^3)	3.509
Absorption coefficient, μ (mm^{-1})	6.051
F (000)	285
Data range θ (º); *h*, *k*, *l*	2.99–29.15; –10<*h* <10, –10<*k*<10, –7<*l*<7
No. of measured reflections	3813
Refinement	
Refinement on	Full-matrix least squares on F^2
R_1, wR_2	0.0181, 0.0446
GOF (Goodness of fit)	1.085
Largest diff. peak and hole	1.35 / -1.36

Note: $R_1 = \sum||F_{obs}| - |F_{calc}|| / \sum|F_{obs}|$; $wR_2 = \{\sum[w(F_{obs}^2 - F_{calc}^2)^2] / \sum[w(F_{obs}^2)^2]\}^{1/2}$;

GOF = $\{\sum[w(F_{obs}^2 - F_{calc}^2)] / (n - p)\}^{1/2}$ where *n* is a number of reflections and *p* is a number of refined parameters.

Table S2. Fractional site coordinates (*xyz*), multiplicity (Mult.), site occupancy (*q*), and equivalent displacement parameters (U_{eq}, Å) for $Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$.

Site	*x*	*y*	*z*	Mult.	*q*	U_{eq}
Pu	1	1	0.208881(2)	1	1	0.00672(12)
P	0.6954(3)	1.0047(3)	0.7083(3)	3	1	0.0081(4)
B1	0.3333	0.6667	0.637(4)	1	1	0.015(3)
B2	0.6667	0.3333	0.646(5)	1	1	0.020(4)
O1	0.2615(10)	0.4697(9)	0.698(2)	3	1	0.046(2)
O2	0.8683(8)	0.4615(8)	0.7094(11)	3	1	0.0132(11)
O3	0.3333	0.6667	0.366(2)	1	1	0.029(3)
O4	0.6667	0.3333	0.377(3)	1	1	0.035(3)
O5	0.8092(12)	1.0392(11)	0.9359(13)	3	1	0.0321(17)
O6	0.0275(12)	0.3602(10)	0.2175(14)	3	1	0.0306(17)
O7	0.8117(13)	1.0447(11)	0.4806(13)	3	1	0.0334(17)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic atomic displacement parameters for $Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$.

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pu	0.00784(14)	0.00784(14)	0.00446(17)	0.00392(7)	0	0
P	0.0059(8)	0.0077(8)	0.0107(9)	0.0034(7)	0.0003(7)	0.0001(7)
B1	0.013(6)	0.013(6)	0.020(9)	0.006(3)	0	0
B2	0.013(6)	0.013(6)	0.035(12)	0.006(3)	0	0
O1	0.011(3)	0.006(3)	0.122(8)	0.005(3)	-0.002(4)	0.003(4)
O2	0.010(2)	0.007(3)	0.021(3)	0.003(2)	-0.002(2)	-0.003(2)
O3	0.023(4)	0.023(4)	0.040(7)	0.0116(18)	0	0
O4	0.030(4)	0.030(4)	0.045(8)	0.015(2)	0	0
O5	0.046(5)	0.034(4)	0.029(4)	0.029(4)	-0.026(3)	-0.012(3)
O6	0.030(4)	0.018(3)	0.034(4)	0.004(3)	-0.009(3)	-0.005(3)
O7	0.044(5)	0.040(4)	0.026(4)	0.028(4)	0.020(3)	0.008(3)

Table S4. Selected interatomic distances in $Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$.

Bond		Bond length, Å
Pu	O5	2.258(6) ×3
	O6	2.735(7) ×3
	O7	2.260(7) ×3
<Pu–O>		2.42
P	O1	1.525(7)
	O2	1.567(6)
	O5	1.491(7)
	O7	1.496(7)
<P–O>		1.52
B1	O1	1.402(9) ×3
	O3	1.50(3)
B2	O2	1.435(9) ×3
	O4	1.49(3)

Table S5. Bond valence calculations for $Pu(H_2O)_3[B_2(OH)(H_2O)(PO_4)_3]$. Bond-valence sum calculations were performed using the bond-valence parameters for Pu^{4+}–O (Diwu et al., 2010) and P^{5+}–O, B^{3+}–O (Brown and Altermatt, 1985). Bond-valence contribution of each cation has been weighted according to its site occupancy factor.

Site	O1	O2	O3	O4	O5	O6	O7	V_c
Pu					$0.610^{\times 3\rightarrow}$	$0.177^{\times 3\rightarrow}$	$0.607^{\times 3\rightarrow}$	4.182
P	1.275	1.139			1.398		1.379	5.191
B1	$0.920^{x3\rightarrow}$		0.706					3.466
B2		$0.841^{\times 3\rightarrow}$		0.725				3.248
V_a	2.195	1.98	0.706	0.725	2.008	0.531	1.986	

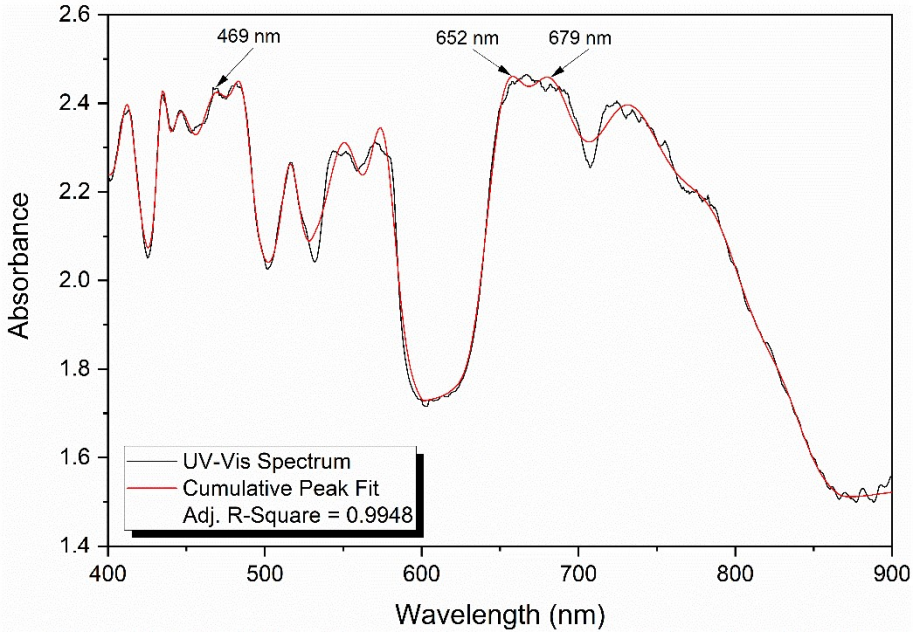

Figure S1. UV-vis-NIR absorption spectrum of plutonium borophosphate with a peak fit R^2 = 0.9948. Original data is shown in black and the cumulative peak fit is shown in red.

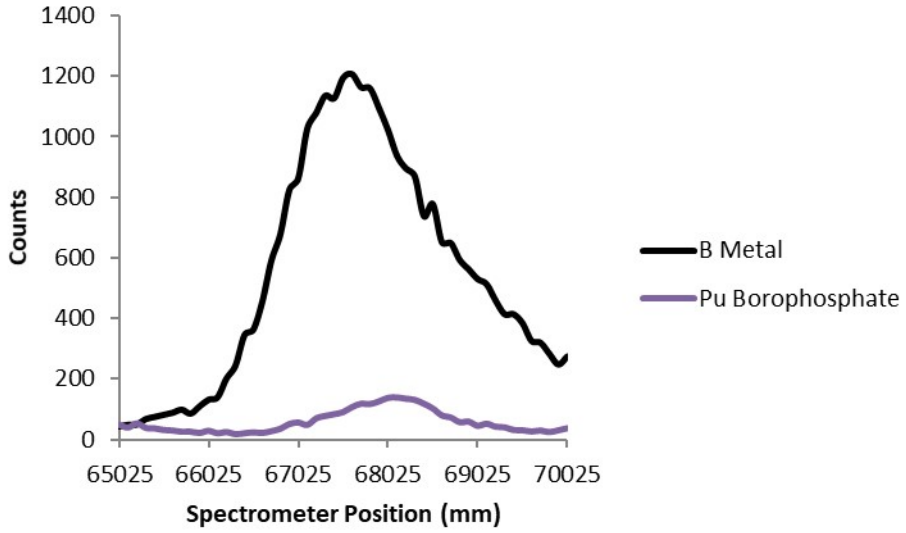

Figure S2. Comparison of electron microprobe signal for boron obtained from a B metal standard versus a crystal of plutonium borophosphate. The shift in peak maximum is attributed to the difference in chemical bonding of B in boron metal versus **1**.

REFERENCES

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Diwu, J.; Nelson, A.-G. D.; Wang, S.; Albrecht-Schmitt, T. E. Comparisons of Pu(IV) and Ce(IV) Diphosphonates. *Inorg. Chem.* **2010**, *49* (7), 3337-3342.