

Novel heptavalent actinide compounds: tetrasodium dihydroxidotetraoxido- neptunate(VII) hydroxide dihydrate and its plutonium analogue

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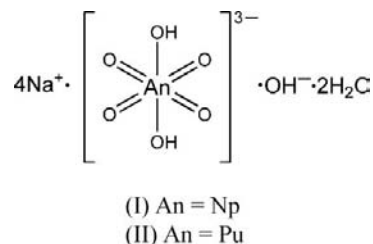
The title compounds, $\text{Na}_4[\text{NpO}_4(\text{OH})_2]\text{OH}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_4[\text{PuO}_4(\text{OH})_2]\text{OH}\cdot 2\text{H}_2\text{O}$, are isostructural and isomorphous, and contain complex $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions (Ac is an actinide) in the form of distorted tetragonal bipyramids, Na^+ cations, crystallization water molecules and outer-sphere OH groups. The complex $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions occupy general positions and the coordinated OH groups deviate significantly from a centrosymmetric relative orientation. The $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions exhibit anisotropic actinide contraction; the shortening of the An—O(hydroxide) bonds on going from Np to Pu is greater than that of the AnO_4 groups.

Comment

The majority of structural studies of An^{VII} compounds have been carried out on those containing $[\text{NpO}_4(\text{OH})_2]^{3-}$ anions and alkali cations (Tomilin *et al.*, 1981*a,b,c*, 1983; Grigoriev *et al.*, 1993; Charushnikova *et al.*, 2007; Grigoriev & Krot, 2007*b*, 2008). Recently, there have been two structure determinations of Pu^{VII} compounds, namely $\text{K}_3[\text{PuO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ (Charushnikova *et al.*, 2007) and $\text{Cs}_3[\text{PuO}_4(\text{OH})_2]\cdot 3\text{H}_2\text{O}$ (Grigoriev & Krot, 2007*a*). In all of these compounds, except for $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$, the $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions are centrosymmetric. In $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$, the $[\text{NpO}_4(\text{OH})_2]^{3-}$ anion occupies a special position on a twofold axis (Tomilin *et al.*, 1981*b*; Grigoriev & Krot, 2007*b*).

The title compounds, $\text{Na}_4[\text{NpO}_4(\text{OH})_2](\text{OH})\cdot 2\text{H}_2\text{O}$, (I), and $\text{Na}_4[\text{PuO}_4(\text{OH})_2](\text{OH})\cdot 2\text{H}_2\text{O}$, (II), are isostructural and isomorphous, and contain complex $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions, which are slightly distorted tetragonal bipyramids (the main distortions are different An—O distances for the O atoms of OH groups), Na^+ cations, crystallization water molecules and outer-sphere OH groups (Fig. 1). Selected bond lengths and angles in the anions are given in Tables 1 and 3. In contrast to the previously mentioned An^{VII} compounds, the complex $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions in (I) and (II) occupy general posi-

tions. The H5—O5··O6—H6 torsion angles are 149 (4) and 139 (3)° in (I) and (II), respectively, showing that the orientation of OH groups in the $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions is far from centrosymmetric.



The Na^+ cations have different structural roles. All have coordination number 6, but differ in the nature of their oxygen

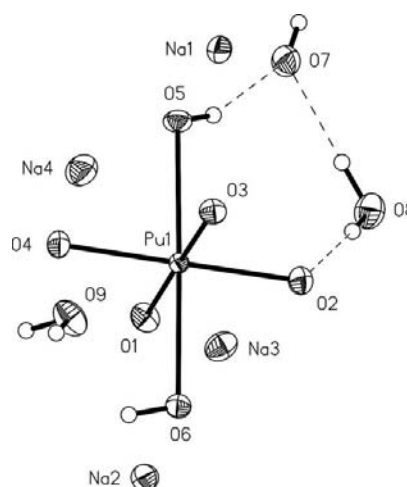


Figure 1

A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate hydrogen bonds.

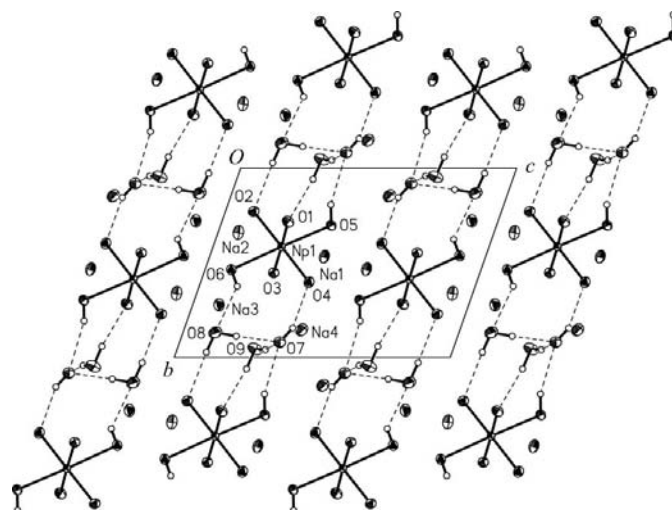


Figure 2

A view of (II), showing the layer structure with interlayer hydrogen bonds (dashed lines).

environments. It is possible to find in the structures electro-neutral $[\text{Na}_3[\text{AnO}_4(\text{OH})_2]]_n$, layers parallel to the (010) plane and formed by $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions and Na1, Na2 and Na3 cations. The environment of Na1 is formed only by O atoms of three complex anions of the same layer. The coordination polyhedra of Na1 (distorted octahedra) share edges to form zigzag chains in the [100] direction. The interlayer space is filled by Na4 cations, water molecules of crystallization and outer-sphere OH groups. The environments of Na2 and Na3 are formed by O atoms of one layer and interlayer water molecules of crystallization. Na4 atoms are also coordinated by bridging OH groups. The hydrogen bonds, in which the H-atom donors are OH groups of $[\text{AnO}_4(\text{OH})_2]^{3-}$ anions, crystallization water molecules and outer-sphere OH groups, link neighbouring layers (Tables 2 and 4, and Fig. 2).

The isomorphism of (I) and (II) once more demonstrates the chemical analogy between Np^{VII} and Pu^{VII} and permits a comparison of bond lengths in isostructural Np^{VII} and Pu^{VII} compounds. For Np and Pu, respectively, the average An—O distances are 1.894 and 1.889 Å in AnO_4 groups, and 2.338 and 2.317 Å to OH groups. The mean shortening of the An—O(hydroxide) bonds on changing from Np to Pu (0.021 Å) is greater than that for the AnO_4 groups (0.005 Å). Taking into account that the s.u. values of individual An—O distances in these structures are not greater than 0.002 Å, we can conclude that actinide contraction in the compounds under investigation is anisotropic. A similar behaviour was found for other isomorphous pairs of Np^{VII} and Pu^{VII} compounds (Charushnikova *et al.*, 2007; Grigoriev & Krot, 2007a).

Experimental

The starting solutions for the syntheses of (I) and (II) were 0.075 M $^{237}\text{Np}^{\text{VII}}$ and 0.06 M $^{239}\text{Pu}^{\text{VII}}$, respectively, in 2.5 M LiOH. The preparation of such solutions is described by Charushnikova *et al.* (2007). For the synthesis of (I), the relevant starting solution (0.1 ml) was placed in a plastic container, then 16.7 M NaOH (0.2 ml) was added and the container placed in a desiccator with granulated KOH (to absorb CO_2 and water vapour). After 3 d of evaporation at room temperature, crystalline hydroxides had been formed with inclusions of black crystals of (I). For the synthesis of (II), the corresponding starting solution (0.05 ml) was placed in a plastic container, then 16.7 M NaOH (0.2 ml) was added and the container placed in a desiccator with granulated KOH. After 1 d, a mixture of black plate-shaped crystals of (II) and small grey crystals of Pu^{VI} hydroxide was found. All attempts at the synthesis gave twinned crystals, both for Np and Pu.

Compound (I)

Crystal data

$\text{Na}_4[\text{NpO}_4(\text{OH})_2]\text{OH}\cdot 2\text{H}_2\text{O}$
 $M_r = 480.02$
 Triclinic, $P\bar{1}$
 $a = 5.9632(2)$ Å
 $b = 8.1157(2)$ Å
 $c = 10.9434(3)$ Å
 $\alpha = 105.007(2)^\circ$
 $\beta = 101.213(2)^\circ$
 $\gamma = 105.935(2)^\circ$
 $V = 471.36(2)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 7.33$ mm⁻¹
 $T = 293$ K
 $0.12 \times 0.06 \times 0.06$ mm

Table 1
Selected bond lengths (Å) for (I).

Np1—O1	1.891 (2)	Np1—O4	1.880 (2)
Np1—O2	1.888 (2)	Np1—O5	2.315 (2)
Np1—O3	1.917 (2)	Np1—O6	2.362 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
O5—H5 ⁱ ···O7	0.813 (19)	2.14 (2)	2.927 (3)	162 (5)
O6—H6 ⁱ ···O8 ⁱ	0.794 (19)	2.49 (3)	3.154 (4)	142 (4)
O7—H7 ⁱ ···O4 ⁱⁱ	0.788 (19)	2.31 (3)	3.039 (4)	154 (5)
O8—H8A ⁱ ···O7	0.849 (18)	1.755 (19)	2.603 (4)	178 (4)
O8—H8B ⁱ ···O2	0.847 (18)	2.03 (2)	2.876 (4)	175 (5)
O9—H9A ⁱ ···O1 ⁱⁱⁱ	0.849 (18)	1.937 (19)	2.781 (3)	173 (5)
O9—H9B ⁱ ···O7 ⁱ	0.828 (18)	1.87 (2)	2.676 (4)	165 (5)

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $x - 1, y - 1, z$; (iii) $x, y + 1, z$.

Data collection

Bruker Kappa APEXII area-detector diffractometer
 Absorption correction: multi-scan (TWINABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.451, T_{\text{max}} = 0.625$
 22639 measured reflections
 4029 independent reflections
 3812 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.054$
 $S = 1.10$
 4029 reflections
 149 parameters
 9 restraints
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 2.16$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.82$ e Å⁻³

Compound (II)

Crystal data

$\text{Na}_4[\text{PuO}_4(\text{OH})_2]\text{OH}\cdot 2\text{H}_2\text{O}$
 $M_r = 482.02$
 Triclinic, $P\bar{1}$
 $a = 5.9177(2)$ Å
 $b = 8.0736(2)$ Å
 $c = 10.8696(3)$ Å
 $\alpha = 105.007(2)^\circ$
 $\beta = 101.224(2)^\circ$
 $\gamma = 105.760(2)^\circ$
 $V = 462.72(2)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 7.79$ mm⁻¹
 $T = 100$ K
 $0.16 \times 0.06 \times 0.04$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
 Absorption correction: multi-scan (TWINABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.515, T_{\text{max}} = 0.758$
 31123 measured reflections
 5736 independent reflections
 4796 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.039$
 $S = 0.86$
 5736 reflections
 149 parameters
 9 restraints
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 2.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.99$ e Å⁻³

Both structures were solved with twinned crystals [the second domains are rotated from the first by 180° about the reciprocal axis (001)]. The refined twin parameters for the second domains are 0.4946 (4) and 0.4908 (2) for (I) and (II), respectively. The H atoms of

Table 3

Selected bond lengths (Å) for (II).

Pu1—O1	1.8824 (15)	Pu1—O4	1.8811 (19)
Pu1—O2	1.8805 (18)	Pu1—O5	2.2952 (19)
Pu1—O3	1.9109 (15)	Pu1—O6	2.339 (2)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O7	0.770 (16)	2.177 (18)	2.921 (3)	163 (3)
O6—H6 \cdots O8 ⁱ	0.760 (17)	2.59 (3)	3.152 (3)	132 (3)
O7—H7 \cdots O4 ⁱⁱ	0.745 (17)	2.281 (18)	3.013 (2)	167 (3)
O8—H8A \cdots O7	0.836 (16)	1.770 (17)	2.600 (3)	172 (3)
O8—H8B \cdots O2	0.793 (16)	2.076 (17)	2.865 (3)	174 (3)
O9—H9A \cdots O1 ⁱⁱⁱ	0.836 (16)	1.938 (16)	2.770 (2)	174 (3)
O9—H9B \cdots O7 ⁱ	0.866 (16)	1.812 (16)	2.667 (2)	169 (3)

Symmetry codes: (i) $x+1, y+1, z$; (ii) $x-1, y-1, z$; (iii) $x, y+1, z$.

the OH groups and crystallization water molecules were located in difference Fourier maps and refined with O—H distances restrained to 0.82 (2) and 0.85 (2) Å, respectively, for OH groups and water molecules. The respective displacement parameters of these H atoms were constrained to 1.2 and 1.5 times the U_{eq} of their parent atoms. The largest electron-density peak and deepest hole on the final difference Fourier synthesis for (I) are 0.68 and 0.62 Å, respectively, from Np1. The largest electron-density peak and deepest hole on the final difference Fourier synthesis for (II) are 0.69 and 0.42 Å, respectively, from Pu1.

For both compounds, data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick,

2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3208). Services for accessing these data are described at the back of the journal.

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