inorganic compounds

Reinvestigation of trisodium dihydroxidotetraoxidoneptunate(VII)

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The title compound, $Na_3[NpO_4(OH)_2]$, contains complex $[NpO_4(OH)_2]^{3-}$ anions, having a distorted tetragonal bipyramidal form. The Np atom occupies a special position on a twofold axis. The Np—O distances are 1.8981 (13) and 1.9012 (12) Å in the NpO_4 group and 2.3145 (11) Å to the OH groups. The main distortion of the tetragonal bipyramid is a shift of the O atoms of the OH groups from ideal positions, the corresponding O—Np—O angle being 173.80 (7)°. The orientation of the OH groups differs significantly from the centrosymmetric arrangement found in other compounds with $[NpO_4(OH)_2]^{3-}$ anions.

Related literature

The structure of $Na_3[NpO_4(OH)_2]$ was investigated using the photographic technique with visual estimation of reflection intensities by Tomilin *et al.* (1981*a*). Several other Np^{VII} compounds containing $[NpO_4(OH)_2]^{3-}$ anions have been studied using the photographic technique: $Na_3[NpO_4(OH)_2]\cdot2H_2O$ (Tomilin *et al.*, 1981*b*), $Na_3[NpO_4(OH)_2]\cdot4H_2O$ (Tomilin *et al.*, 1981*c*) and $K_3[NpO_4(OH)_2]\cdot2H_2O$ (Tomilin *et al.*, 1983). Diffractometric structure determinations have been carried out for $[Co(NH_3)_6][NpO_4(OH)_2]\cdot2H_2O$ (Grigor'ev *et al.*, 1986), $Cs_3[NpO_4(OH)_2]\cdot3H_2O$ (Grigor'ev *et al.*, 1993) and $K_3[NpO_4(OH)_2]\cdot2H_2O$ (Charushnikova *et al.*, 2007).

Experimental

Crystal data

$Na_3[NpO_4(OH)_2]$	$V = 1220.04$ (7) Å^3
$M_r = 403.99$	$Z = 8$
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 20.0791$ (6) Å	$\mu = 17.21$ mm^{-1}
$b = 5.9534$ (2) Å	$T = 100$ (2) K
$c = 10.2062$ (3) Å	$0.20 \times 0.06 \times 0.04$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
	$T_{min} = 0.378$, $T_{max} = 0.546$ (expected range = 0.348–0.502)
21081 measured reflections	2442 independent reflections
	2258 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.012$	All H-atom parameters refined
$wR(F^2) = 0.022$	$\Delta\rho_{max} = 1.07$ e Å^{-3}
$S = 1.25$	$\Delta\rho_{min} = -1.49$ e Å^{-3}
2442 reflections	Absolute structure: Flack (1983), with 1136 Friedel pairs
52 parameters	Flack parameter: 0.039 (12)
2 restraints	

Table 1
Selected geometric parameters (Å, °).

Np1—O1	1.8981 (13)	Np1—O3	2.3145 (11)
Np1—O2	1.9012 (12)		
O1—Np1—O1^i	89.13 (9)	O1—Np1—O3^i	93.13 (5)
O1—Np1—O2^i	178.96 (7)	O1—Np1—O3	91.29 (5)
O1—Np1—O2	89.82 (5)	O2—Np1—O3	86.87 (5)
O2—Np1—O2^i	91.22 (8)	O3^i—Np1—O3	173.80 (7)

Symmetry code: (i) $-x + 1, -y + 1, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1^{ii}	0.800 (18)	2.25 (2)	3.0255 (17)	164 (4)

Symmetry code: (ii) $x - \frac{1}{4}, -y + \frac{5}{4}, z - \frac{1}{4}$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Reinvestigation of trisodium dihydroxidotetraoxidoneptunate(VII)

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Comment

The title compound, (I) (Fig. 1), contains complex anions $[NpO_4(OH)_2]^{3-}$, having a form of distorted tetragonal bipyramid. The main bond lengths and angles in this anion are given in Table 1. The Np atom occupies a special position on a twofold axis. The main distortion of the tetragonal bipyramid is a shift of O atoms of the OH groups from ideal positions, the corresponding O—Np—O angle being 173.80 (7)°. The orientaion of the OH groups differs significantly from centrosymmetric (Fig. 1) whereas in all other compounds with $[NpO_4(OH)_2]^{3-}$ anions (Tomilin *et al.*, 1981*b,c*, 1983; Grigor'ev *et al.*, 1986, 1993; Charushnikova *et al.*, 2007) these anions occupy centrosymmetric positions. Basing on diffractometrically studied structures of Np^{VII} compounds with alkaline cations, one can notice that the Np—O distances to the OH groups become longer in the sequence Na–K–Cs. The corresponding distances are 2.370 (5) Å for $K_3[NpO_4(OH)_2]·2H_2O$ (Charushnikova *et al.*, 2007) and 2.41 (1) Å for $Cs_3[NpO_4(OH)_2]·3H_2O$ (Grigor'ev *et al.*, 1993). The Np—O distances in the NpO_4 groups remain practically the same.

The Na1 atom occupies a special position on twofold axis and has a distorted octahedral oxygen environment. The Na2 atom is in general position with distorted tetrahedral oxygen environment.

The OH group acts as proton donor in a weak hydrogen bond with an O atom of NpO_4 group of a neighbouring anion (Table 2). The resulting hydrogen bond net in (I) is three-dimensional (Fig. 2).

Experimental

The starting solution for the synthesis of (I) was slightly acidic (pH ~3) 0.15 M $^{237}NpO_2(NO_3)_2$. The preparation of such solutions is described by Charushnikova *et al.* (2007). For the synthesis of (I), 0.2 ml of 0.15 M $NpO_2(NO_3)_2$ aqueous solution was taken into a bubble flask, 1 ml of 5 M LiOH solution was added, then ozonized oxygen (10% mass of O_3) was passed through the solution over a period of 2 h. An aliquots of 0.1 ml of the solution were put into plastic containers, 0.05, 0.1 or 0.2 ml of 16.7 M NaOH were added, and the containers were placed into a desiccator with granulated KOH (to absorb CO_2 and water vapour). After four days at room temperature almost all the Np^{VII} was crystallized as bulk black crystals.

Refinement

The H atom of the OH group was located on a difference Fourier-map and refined with O—H distance restrained to 0.82 (2) Å and individual isotropic displacement parameter.

Largest electron density peak on the final difference Fourier-synthesis is 1.071 e Å^{-3} (1.20 Å from O2), the deepest hole is −1.490 e Å^{-3} (1.67 Å from Na1).
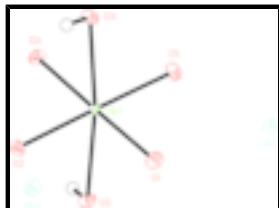
supplementary materials

Figures

Fig. 1. A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. [Symmetry code: (i) $1 - x$, $1 - y$, z.]
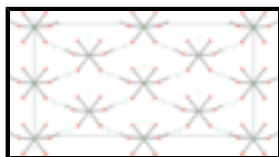

Fig. 2. The packing of (I) showing three-dimensional net of hydrogen bonds (dashed lines).

trisodium dihydroxidotetraoxidoneptunate(VII)

Crystal data

$Na_3[NpO_4(OH)_2]$	$F_{000} = 1408$
$M_r = 403.99$	$D_x = 4.399$ Mg m^{-3}
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: F 2 -2d	Cell parameters from 8824 reflections
$a = 20.0791$ (6) Å	$\theta = 4.1–45.0°$
$b = 5.9534$ (2) Å	$\mu = 17.21$ mm^{-1}
$c = 10.2062$ (3) Å	$T = 100$ (2) K
$V = 1220.04$ (7) Å^3	Plate, black
$Z = 8$	$0.20 \times 0.06 \times 0.04$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer	2442 independent reflections
Radiation source: fine-focus sealed tube	2258 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 100(2)$ K	$\theta_{max} = 45.0°$
ω and φ scans	$\theta_{min} = 4.1°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -39 \rightarrow 39$
$T_{min} = 0.378$, $T_{max} = 0.546$	$k = -11 \rightarrow 11$
21081 measured reflections	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.012$	$w = 1/[\sigma^2(F_o^2) + 2.58P]$

where $P = (F_o{}^2 + 2F_c{}^2)/3$

$wR(F^2) = 0.022$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.25$	$\Delta\rho_{max} = 1.07$ e Å^{-3}
2442 reflections	$\Delta\rho_{min} = -1.49$ e Å^{-3}
52 parameters	Extinction correction: none
2 restraints	Absolute structure: Flack (1983), with 1136 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.039 (12)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Np1	0.5000	0.5000	0.53211 (2)	0.00494 (1)
Na1	0.5000	0.5000	0.86871 (10)	0.00964 (14)
Na2	0.65942 (4)	0.75441 (14)	0.45853 (8)	0.01332 (11)
O1	0.55153 (7)	0.6409 (2)	0.66461 (14)	0.01161 (19)
O2	0.55254 (6)	0.6438 (2)	0.40181 (13)	0.00956 (17)
O3	0.42959 (5)	0.80708 (19)	0.51985 (14)	0.00980 (16)
H3	0.3955 (13)	0.777 (6)	0.483 (4)	0.025 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Np1	0.00478 (2)	0.00542 (2)	0.00464 (2)	−0.00093 (4)	0.000	0.000
Na1	0.0127 (3)	0.0077 (3)	0.0085 (4)	0.0009 (3)	0.000	0.000
Na2	0.0175 (3)	0.0125 (3)	0.0100 (3)	−0.0028 (3)	−0.0028 (2)	−0.0007 (2)
O1	0.0122 (4)	0.0120 (5)	0.0106 (5)	−0.0027 (4)	−0.0039 (4)	−0.0019 (4)
O2	0.0098 (4)	0.0091 (4)	0.0097 (4)	0.0009 (3)	0.0041 (3)	0.0017 (3)
O3	0.0087 (3)	0.0089 (3)	0.0118 (5)	0.0011 (3)	0.0007 (3)	−0.0018 (3)

Geometric parameters (Å, °)

Np1—O1	1.8981 (13)	Na1—O1	2.4725 (17)
Np1—O1^i	1.8981 (13)	Na2—O3^{iv}	2.2653 (16)

Np1—O2^{i}	1.9012 (12)	Na2—O2^{v}	2.2723 (15)
Np1—O2	1.9012 (12)	Na2—O2	2.3183 (15)
Np1—O3^{i}	2.3145 (11)	Na2—O1^{vi}	2.3451 (16)
Np1—O3	2.3145 (11)	O1—Na2^{v}	2.3451 (16)
Na1—O3^{ii}	2.3870 (14)	O2—Na2^{vi}	2.2723 (15)
Na1—O3^{iii}	2.3870 (14)	O2—Na1^{vii}	2.3924 (13)
Na1—O2^{ii}	2.3924 (13)	O3—Na2^{viii}	2.2653 (16)
Na1—O2^{iii}	2.3924 (13)	O3—Na1^{vii}	2.3870 (14)
Na1—O1^{i}	2.4725 (17)	O3—H3	0.800 (18)
O1—Np1—O1^{i}	89.13 (9)	O2^{ii}—Na1—O2^{iii}	163.77 (8)
O1—Np1—O2^{i}	178.96 (7)	O3^{ii}—Na1—O1^{i}	162.86 (5)
O1^{i}—Np1—O2^{i}	89.82 (5)	O3^{iii}—Na1—O1^{i}	97.66 (4)
O1—Np1—O2	89.82 (5)	O2^{ii}—Na1—O1^{i}	103.60 (5)
O1^{i}—Np1—O2	178.96 (7)	O2^{iii}—Na1—O1^{i}	90.16 (5)
O2—Np1—O2^{i}	91.22 (8)	O3^{ii}—Na1—O1	97.66 (4)
O1—Np1—O3^{i}	93.13 (5)	O3^{iii}—Na1—O1	162.86 (5)
O1^{i}—Np1—O3^{i}	91.29 (5)	O2^{ii}—Na1—O1	90.16 (5)
O2^{i}—Np1—O3^{i}	86.87 (5)	O2^{iii}—Na1—O1	103.60 (5)
O2—Np1—O3^{i}	88.79 (5)	O1^{i}—Na1—O1	65.19 (6)
O1—Np1—O3	91.29 (5)	O2^{ii}—Na1—Na2^{ii}	38.73 (3)
O1^{i}—Np1—O3	93.13 (5)	O2^{iii}—Na1—Na2^{ii}	135.15 (4)
O2^{i}—Np1—O3	88.79 (5)	O3^{iv}—Na2—O2^{v}	119.80 (6)
O2—Np1—O3	86.87 (5)	O3^{iv}—Na2—O2	95.39 (5)
O3^{i}—Np1—O3	173.80 (7)	O2^{v}—Na2—O2	129.18 (6)
O3^{ii}—Na1—O3^{iii}	99.48 (7)	O3^{iv}—Na2—O1^{vi}	103.59 (6)
O3^{ii}—Na1—O2^{ii}	75.13 (4)	O2^{v}—Na2—O1^{vi}	112.99 (6)
O3^{iii}—Na1—O2^{ii}	94.25 (5)	O2—Na2—O1^{vi}	89.98 (5)
O3^{ii}—Na1—O2^{iii}	94.25 (5)	Np1—O3—H3	112 (3)
O3^{iii}—Na1—O2^{iii}	75.13 (4)		

Symmetry codes: (i) −x+1, −y+1, z; (ii) −x+1, −y+3/2, z+1/2; (iii) x, y−1/2, z+1/2; (iv) x+1/4, −y+7/4, z−1/4; (v) −x+5/4, y+1/4, z+1/4; (vi) −x+5/4, y−1/4, z−1/4; (vii) x, y+1/2, z−1/2; (viii) x−1/4, −y+7/4, z+1/4.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O1^{ix}	0.800 (18)	2.25 (2)	3.0255 (17)	164 (4)

Symmetry codes: (ix) x−1/4, −y+5/4, z−1/4.

Fig. 1

Fig. 2