

## Reinvestigation of trisodium dihydroxidotetraoxidoneptunate(VII) dihydrate

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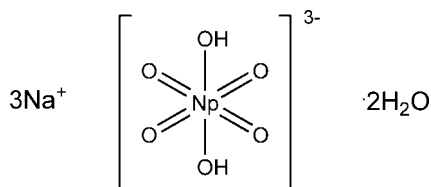
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{Np}-\text{O}) = 0.001$  Å;  $R$  factor = 0.010;  $wR$  factor = 0.021; data-to-parameter ratio = 33.7.

The title compound,  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ , contains distorted tetragonal-bipyramidal centrosymmetric  $[\text{NpO}_4(\text{OH})_2]^{3-}$  complex anions. The Np—O distances are 1.8975 (7) and 1.8891 (7) Å in the  $\text{NpO}_4$  group and 2.3451 (7) Å to the OH group. Both Na atoms (one in a general position, the second in a special position on an inversion centre) have a distorted octahedral oxygen environment.

### Related literature

The structure of  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  was investigated by photographic technique with visual estimation of reflection intensities by Tomilin *et al.* (1981*a*). Several other  $\text{Np}^{\text{VII}}$  compounds containing  $[\text{NpO}_4(\text{OH})_2]^{3-}$  anions have been studied by photographic techniques, *viz.*  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$  (Tomilin *et al.*, 1981*b*),  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]\cdot 4\text{H}_2\text{O}$  (Tomilin *et al.*, 1981*c*),  $\text{K}_3[\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  (Tomilin *et al.*, 1983). Diffractometric structure determinations have been made for  $[\text{Co}(\text{NH}_3)_6][\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  (Grigor'ev *et al.*, 1986),  $\text{Cs}_3[\text{NpO}_4(\text{OH})_2]\cdot 3\text{H}_2\text{O}$  (Grigor'ev *et al.*, 1993),  $\text{K}_3[\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  (Charushnikova *et al.*, 2007) and  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$  (Grigoriev & Krot, 2007).



### Experimental

#### Crystal data

$\text{Na}_3[\text{NpO}_4(\text{OH})_2]\cdot 2\text{H}_2\text{O}$   
 $M_r = 440.02$   
 Monoclinic,  $P2_1/c$   
 $a = 7.8166$  (3) Å  
 $b = 7.7703$  (2) Å  
 $c = 6.8211$  (2) Å  
 $\beta = 112.9139$  (14)°

$V = 381.60$  (2) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 13.79$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 $0.12 \times 0.08 \times 0.02$  mm

#### Data collection

Bruker Kappa APEXII area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)  
 $T_{\min} = 0.522$ ,  $T_{\max} = 0.770$

16264 measured reflections  
 2357 independent reflections  
 1920 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.010$   
 $wR(F^2) = 0.021$   
 $S = 1.04$   
 2357 reflections  
 70 parameters

3 restraints  
 All H-atom parameters refined  
 $\Delta\rho_{\text{max}} = 0.75$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.88$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Np—O1	1.8975 (7)	Np—O3	2.3451 (7)
Np—O2	1.8891 (7)		
O1—Np—O2	91.41 (3)	O2—Np—O3	94.67 (3)
O1—Np—O3	90.82 (3)		

**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 <sup>i</sup>	0.815 (15)	1.976 (16)	2.7866 (10)	173 (2)
O4—H4A $\cdots$ O3	0.856 (17)	1.799 (17)	2.6538 (12)	178 (2)
O4—H4B $\cdots$ O3 <sup>ii</sup>	0.840 (16)	1.931 (16)	2.7612 (12)	169 (2)

 Symmetry codes: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 2, -y + 1, -z + 1$ .

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: SHELXTL97 (Sheldrick, 1997*b*); software used to prepare material for publication: SHELXTL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2217).

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**supplementary materials**

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## Reinvestigation of trisodium dihydroxidotetraoxidoneptunate(VII) dihydrate

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### Comment

The title compound, (I) (Fig. 1), contains centrosymmetric complex anions  $[\text{NpO}_4(\text{OH})_2]^{3-}$  which are distorted tetragonal bipyramidal. The main bond lengths and angles in this anion are given in Table 1. The Np—O distances in the  $\text{NpO}_4$  group are close to the values 1.8981 (13) and 1.9012 (12) Å found in  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$  (Grigoriev & Krot, 2007). The Np—O distance to the OH group is a little longer than 2.3145 (11) Å in  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$ .

Principal features of structure are the same as described by Tomilin *et al.* (1981a).

The Na1 atom occupies a special position on an inversion centre and has a distorted octahedral oxygen environment formed by six O atoms of two  $[\text{NpO}_4(\text{OH})_2]^{3-}$  anions. The Na1 atoms and  $[\text{NpO}_4(\text{OH})_2]^{3-}$  anions form columns along the [001] direction, the layers of the columns are parallel to the (100) plane (Fig. 2). The Na2 atoms and crystallization water molecules occupy general positions between the layers. The Na2 atom has a distorted octahedral oxygen environment formed by O atoms of  $[\text{NpO}_4(\text{OH})_2]^{3-}$  anions and water molecules.

The OH group acts as proton donor in a hydrogen bond with an O atom of  $\text{NpO}_4$  group of a neighbouring anion (Table 2). This hydrogen bond is stronger than the bond formed by OH group in  $\text{Na}_3[\text{NpO}_4(\text{OH})_2]$  [the O...O distance 3.0255 (17)]. Such a difference can be one of the reasons for the elongation of the Np—O3 bond in (I). Water molecule makes two hydrogen bonds with O atoms of OH groups.

### Experimental

The starting solution for the synthesis of (I) was slightly acidic (pH ~3) 0.15 M  $^{237}\text{NpO}_2(\text{NO}_3)_2$ . The preparation of such solutions is described by Charushnikova *et al.* (2007). For the synthesis of (I), 1 ml of 0.15 M  $\text{NpO}_2(\text{NO}_3)_2$  aqueous solution was taken into a bubble flask, 1 ml of 5 M LiOH solution was added, then ozonized oxygen (10% mass of  $\text{O}_3$ ) was passed through the solution over a period of 2 h. 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 was added, and the containers were placed into a desiccator with granulated KOH (to absorb  $\text{CO}_2$  and water vapour). After four days at room temperature almost all the  $\text{Np}^{\text{VII}}$  was crystallized as bulk black crystals.

### Refinement

The H atoms of the OH-group and crystallization water molecule were located on a difference Fourier map and refined with individual displacement parameters and O—H distances restrained to 0.82 (2) and 0.85 (2) Å, respectively.

## Figures

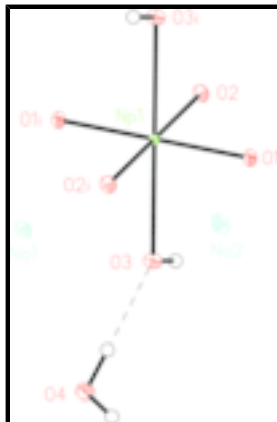


Fig. 1. A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed line indicates the hydrogen-bonding interaction. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]

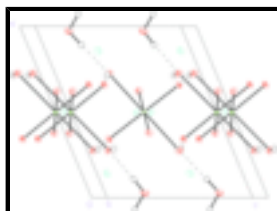


Fig. 2. The unit cell of (I).

## trisodium dihydroxidotetraoxidoneptunate(VII) dihydrate

### Crystal data

$\text{Na}_3[\text{NpO}_4(\text{OH})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 440.02$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 7.8166\ (3)\ \text{\AA}$

$b = 7.7703\ (2)\ \text{\AA}$

$c = 6.8211\ (2)\ \text{\AA}$

$\beta = 112.9139\ (14)^\circ$

$V = 381.60\ (2)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 392$

$D_x = 3.829\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5517 reflections

$\theta = 3.9\text{--}40.0^\circ$

$\mu = 13.79\ \text{mm}^{-1}$

$T = 100\ (2)\ \text{K}$

Plate, black

$0.12 \times 0.08 \times 0.02\ \text{mm}$

### Data collection

Bruker Kappa APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100\ (2)\ \text{K}$

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

2357 independent reflections

1920 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 40.0^\circ$

$\theta_{\text{min}} = 3.9^\circ$

$h = -14 \rightarrow 14$

$T_{\min} = 0.522$ ,  $T_{\max} = 0.770$   
16264 measured reflections

$k = -12 \rightarrow 14$   
 $l = -12 \rightarrow 12$

### Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.010$

$wR(F^2) = 0.021$

$S = 1.04$

2357 reflections

70 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0059P)^2 + 0.087P]$$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.88 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

### 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Np	0.5000	0.5000	0.5000	0.00406 (1)
Na1	0.5000	0.5000	0.0000	0.00859 (9)
Na2	0.85815 (7)	0.32123 (6)	0.90540 (8)	0.01157 (8)
O1	0.65824 (10)	0.56060 (10)	0.78208 (12)	0.00757 (11)
O2	0.37890 (10)	0.71543 (9)	0.45784 (12)	0.00792 (11)
O3	0.72436 (10)	0.59020 (9)	0.37305 (12)	0.00862 (11)
H3	0.715 (3)	0.693 (2)	0.349 (4)	0.031 (6)*
O4	0.97126 (12)	0.44316 (15)	0.24784 (14)	0.01657 (15)
H4A	0.892 (4)	0.493 (2)	0.286 (5)	0.021 (6)*
H4B	1.071 (2)	0.428 (3)	0.354 (3)	0.029 (5)*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Np	0.00487 (2)	0.00387 (2)	0.00377 (2)	0.00001 (2)	0.00205 (1)	-0.00008 (1)

## supplementary materials

Na1	0.0114 (2)	0.0080 (2)	0.0080 (2)	0.0013 (2)	0.0056 (2)	0.0006 (2)
Na2	0.01207 (18)	0.01314 (18)	0.00847 (17)	0.00321 (15)	0.00287 (14)	-0.00015 (15)
O1	0.0084 (3)	0.0080 (3)	0.0059 (3)	-0.0006 (2)	0.0023 (2)	-0.0011 (2)
O2	0.0097 (3)	0.0055 (2)	0.0086 (3)	0.0015 (2)	0.0037 (2)	0.0006 (2)
O3	0.0091 (3)	0.0075 (3)	0.0102 (3)	0.0010 (2)	0.0049 (2)	0.0020 (2)
O4	0.0077 (3)	0.0293 (4)	0.0106 (3)	0.0028 (3)	0.0013 (3)	-0.0068 (3)

### Geometric parameters (Å, °)

Np—O1	1.8975 (7)	Na2—O2 <sup>i</sup>	2.4655 (9)
Np—O2 <sup>i</sup>	1.8891 (7)	Na2—O2 <sup>vii</sup>	2.5150 (9)
Np—O2	1.8891 (7)	Na2—O4 <sup>viii</sup>	2.6263 (13)
Np—O1 <sup>i</sup>	1.8975 (7)	Na2—O4 <sup>ix</sup>	2.7033 (12)
Np—O3	2.3451 (7)	O1—Na1 <sup>vi</sup>	2.3223 (7)
Np—O3 <sup>i</sup>	2.3451 (7)	O2—Na1 <sup>x</sup>	2.3783 (7)
Na1—O1 <sup>ii</sup>	2.3223 (7)	O2—Na2 <sup>i</sup>	2.4655 (9)
Na1—O1 <sup>i</sup>	2.3223 (7)	O2—Na2 <sup>xi</sup>	2.5150 (9)
Na1—O2 <sup>iii</sup>	2.3783 (7)	O3—H3	0.815 (15)
Na1—O2 <sup>iv</sup>	2.3783 (7)	O4—Na2 <sup>ii</sup>	2.3510 (10)
Na1—O3	2.5626 (8)	O4—Na2 <sup>xii</sup>	2.6263 (13)
Na1—O3 <sup>v</sup>	2.5626 (8)	O4—Na2 <sup>ix</sup>	2.7033 (12)
Na2—O4 <sup>vi</sup>	2.3510 (10)	O4—H4A	0.856 (17)
Na2—O1	2.3633 (9)	O4—H4B	0.840 (16)
O1—Np—O2	91.41 (3)	O2 <sup>iii</sup> —Na1—O3	87.25 (2)
O1—Np—O3	90.82 (3)	O2 <sup>iv</sup> —Na1—O3	92.75 (2)
O2—Np—O3	94.67 (3)	O1 <sup>ii</sup> —Na1—O3 <sup>v</sup>	75.46 (2)
O2 <sup>i</sup> —Np—O2	180.0	O1 <sup>i</sup> —Na1—O3 <sup>v</sup>	104.54 (2)
O2 <sup>i</sup> —Np—O1	88.59 (3)	O2 <sup>iii</sup> —Na1—O3 <sup>v</sup>	92.75 (2)
O2 <sup>i</sup> —Np—O1 <sup>i</sup>	91.41 (3)	O2 <sup>iv</sup> —Na1—O3 <sup>v</sup>	87.25 (2)
O2—Np—O1 <sup>i</sup>	88.59 (3)	O3—Na1—O3 <sup>v</sup>	180.00 (3)
O1—Np—O1 <sup>i</sup>	180.0	O4 <sup>vi</sup> —Na2—O1	88.70 (4)
O2 <sup>i</sup> —Np—O3	85.33 (3)	O4 <sup>vi</sup> —Na2—O2 <sup>i</sup>	152.85 (4)
O1 <sup>i</sup> —Np—O3	89.18 (3)	O1—Na2—O2 <sup>i</sup>	66.37 (3)
O2 <sup>i</sup> —Np—O3 <sup>i</sup>	94.67 (3)	O4 <sup>vi</sup> —Na2—O2 <sup>vii</sup>	79.02 (3)
O2—Np—O3 <sup>i</sup>	85.33 (3)	O1—Na2—O2 <sup>vii</sup>	84.77 (3)
O1—Np—O3 <sup>i</sup>	89.18 (3)	O2 <sup>i</sup> —Na2—O2 <sup>vii</sup>	87.77 (3)
O1 <sup>i</sup> —Np—O3 <sup>i</sup>	90.82 (3)	O4 <sup>vi</sup> —Na2—O4 <sup>viii</sup>	131.72 (4)
O3—Np—O3 <sup>i</sup>	180.0	O1—Na2—O4 <sup>viii</sup>	138.70 (3)
O1 <sup>ii</sup> —Na1—O1 <sup>i</sup>	180.00 (2)	O2 <sup>i</sup> —Na2—O4 <sup>viii</sup>	74.89 (3)
O1 <sup>ii</sup> —Na1—O2 <sup>iii</sup>	91.16 (3)	O2 <sup>vii</sup> —Na2—O4 <sup>viii</sup>	108.07 (3)
O1 <sup>i</sup> —Na1—O2 <sup>iii</sup>	88.84 (3)	O4 <sup>vi</sup> —Na2—O4 <sup>ix</sup>	93.44 (4)
O1 <sup>ii</sup> —Na1—O2 <sup>iv</sup>	88.84 (3)	O1—Na2—O4 <sup>ix</sup>	71.74 (3)

O1 <sup>i</sup> —Na1—O2 <sup>iv</sup>	91.16 (3)	O2 <sup>i</sup> —Na2—O4 <sup>ix</sup>	88.88 (3)
O2 <sup>iii</sup> —Na1—O2 <sup>iv</sup>	180.0	O2 <sup>vii</sup> —Na2—O4 <sup>ix</sup>	155.55 (3)
O1 <sup>ii</sup> —Na1—O3	104.54 (2)	O4 <sup>viii</sup> —Na2—O4 <sup>ix</sup>	94.370 (16)
O1 <sup>i</sup> —Na1—O3	75.46 (2)	H4A—O4—H4B	110 (3)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, y, z-1$ ; (iii)  $x, -y+3/2, z-1/2$ ; (iv)  $-x+1, y-1/2, -z+1/2$ ; (v)  $-x+1, -y+1, -z$ ; (vi)  $x, y, z+1$ ; (vii)  $-x+1, y-1/2, -z+3/2$ ; (viii)  $x, -y+1/2, z+1/2$ ; (ix)  $-x+2, -y+1, -z+1$ ; (x)  $-x+1, y+1/2, -z+1/2$ ; (xi)  $-x+1, y+1/2, -z+3/2$ ; (xii)  $x, -y+1/2, z-1/2$ .

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O3—H3 $\cdots$ O1 <sup>iii</sup>	0.815 (15)	1.976 (16)	2.7866 (10)	173 (2)
O4—H4A $\cdots$ O3	0.856 (17)	1.799 (17)	2.6538 (12)	178 (2)
O4—H4B $\cdots$ O3 <sup>ix</sup>	0.840 (16)	1.931 (16)	2.7612 (12)	169 (2)

Symmetry codes: (iii)  $x, -y+3/2, z-1/2$ ; (ix)  $-x+2, -y+1, -z+1$ .

Fig. 1

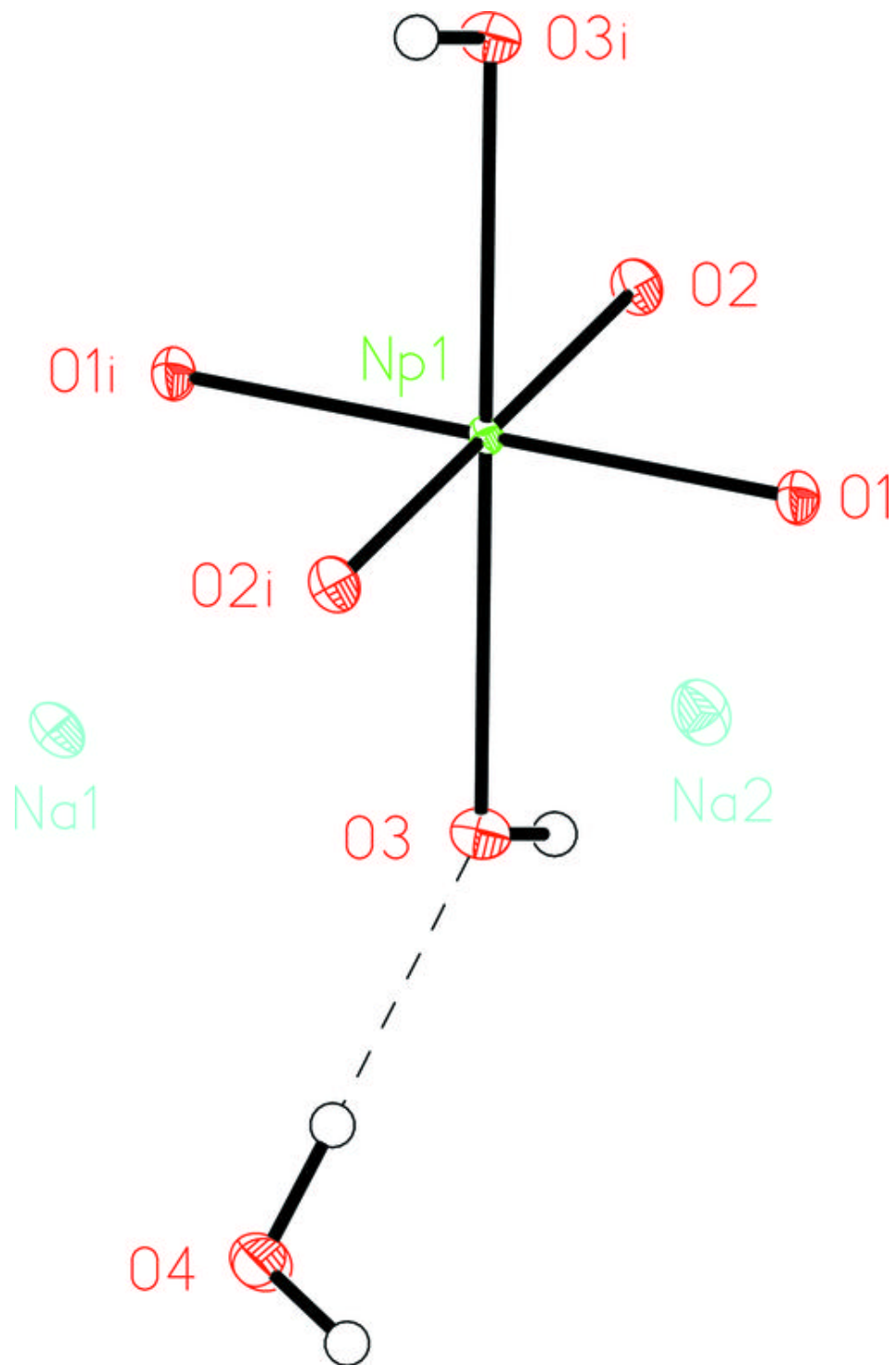




Fig. 2

