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Sodium tungstate dihydrate: a redetermination

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Key indicators: single-crystal X-ray study; T = 291 K; mean σ(W–O) = 0.003 Å; R factor = 0.021; wR factor = 0.053; data-to-parameter ratio = 18.7.

There have been two previous structure determinations of the title compound, $Na_2WO_4 \cdot 2H_2O$: in 1969 [Mitra & Verma (1969). *Indian J. Chem.* **7**, 598–602] and in 1974 [Okada *et al.* (1974*a*). *Bull. Tokyo Inst. Technol.* **120**, 7–11]. However, both structures are incorrect according to their entries in the Inorganic Crystal Structure Database [(2007), URL: http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/index.html]. Despite the high absorption coefficient, the H-atom positions could be observed and refined in the present study. Owing to the accurate analytical absorption correction, all non-H atoms could be refined satisfactorily with anisotropic displacement parameters. There are hydrogen-bonding interactions between all H atoms and the O atoms of the tungstate dianion.

Related literature

For related literature, see: Mitra & Verma (1969); Okada *et al.* (1974*a*,*b*).

Experimental

Crystal data

$Na_2WO_4 \cdot 2H_2O$
M_r = 329.86
Orthorhombic, *Pbca*
a = 8.4797 (5) Å
b = 10.5930 (5) Å
c = 13.8527 (10) Å
V = 1244.33 (13) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 18.66 mm^{-1}
T = 291 (2) K
0.39 × 0.34 × 0.11 mm

Data collection

Enraf Nonius Turbo CAD-4 diffractometer
Absorption correction: analytical (de Meulenaer & Tompa, 1965; Alcock, 1970)
T_{min} = 0.021, T_{max} = 0.148
7543 measured reflections
1811 independent reflections
1664 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
6 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.053
S = 1.26
1811 reflections
97 parameters
4 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 2.75 e Å^{-3}
$\Delta\rho_{min}$ = −1.48 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O1^{i}	0.86 (3)	2.09 (4)	2.830 (4)	145 (6)
O5—H52···O4^{ii}	0.86 (3)	1.98 (3)	2.832 (4)	174 (6)
O5—H51···O3^{iii}	0.86 (3)	2.70 (6)	3.237 (4)	122 (5)
O6—H61···O1^{iv}	0.86 (3)	1.95 (3)	2.790 (4)	167 (6)
O6—H62···O4	0.86 (3)	2.02 (4)	2.837 (4)	159 (6)

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

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999) and *PLATON*(Spek, 2003).

The EPSRC is acknowledged for funding the purchase of an Enraf–Nonius CAD-4 diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2024).

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supplementary materials

Acta Cryst. (2007). E**63**, i142 [**doi:10.1107/S1600536807023355**]

Sodium tungstate dihydrate: a redetermination

L. J. Farrugia

Comment

The two previous crystal structure determinations on sodium tungstate dihydrate (I) were undertaken more than 30 years ago. The first report, by Mitra & Verma (1969), was based on photographic data using Cu radiation. The second report (Okada *et al.*, 1974*a*) was based on diffractometer data using Mo radiation, but both their entries in the Inorganic Crystal Structure Database (2007) indicate that there were problems with the deposited coordinates. In fact, the reported coordinates of Mitra & Verma (1969) are quite incorrect, while those of Okada *et al.*(1974*a*) have a single typographical error in the *z*-coordinate of O4 (which should read 0.5980). An anhydrous form of sodium tungstate has also been reported (Okada *et al.*, 1974*b*).

The intensity data set for (I) was originally collected as test data for the absorption corrections in the *WinGX* suite of programs (Farrugia, 1999). The compound has a large linear absorption coefficient, $\mu(\text{Mo—K}_\alpha)$ = 18.66 mm^{-1}, and was readily available in suitable crystalline form. We report here the refinement using the data corrected for absorption by the analytical method (de Meulenaar & Tompa, 1965), as implemented in *PLATON* (Spek, 2003). The parameters most seriously affected by absorption errors are the anisotropic displacement parameters (adp's). In severe cases, the eigenvalues of the adp tensors may become negative (*i.e.* non-positive definite), but in the current case they all have very reasonable values. The largest ratio of maximum:minimum mean square atomic displacements is 2.22 for atom O2.

An *ORTEP* view of the asymmetric unit of (I) is shown in Figure 1. A s expected, the $[WO_4]^{2-}$ dianion has very nearly exact tetrahedral geometry. The small deviations presumably arise from the differing chemical environments of the oxygen atoms in the crystal lattice. Despite the high sample absorption, all hydrogen atoms could be detected in difference maps and were successfully refined. All these atoms are involved in H-bonds with oxygen atoms of the tungstate dianion, see Table and Figure 2. The hydrogen atom H51 forms a bifurcated H-bond with the oxygen atoms of two separate $[WO_4]^{2-}$ anions, though one OH···O bond is relatively long. The other H-atoms are only involved in single classical H-bonds.

The Na^+ ions occur together with the water molecules in layers parallel to the *ac* plane. These layers are separated by the $[WO_4]^{2-}$ anions. The local coordination geometries of the two independent Na^+ ions are quite distinct, see Figs. 3 and 4. The atom Na1 is approximately octahedrally coordinated by the oxygen atoms of two water molecules and four $[WO_4]^{2-}$ anions, while Na2 is five-coordinate. The geometry is a very distorted trigonal bipyramid, with the atoms O1 and O5 occupying the axial positions, O1—Na2—O5 = 176.82 (13)°. However the O—W—O angles in the "equatorial" plane are very far from 120 °, and there is a relatively short non-bonded contact with a sixth oxygen atom, Na3···O5 = 3.607 (3) Å

Experimental

A commercial sample was used, and the crystals as received were adequate for the purpose.

Refinement

The initial hydrogen atom positions were obtained from difference Fourier maps. They were refined with a common restrained O—H distance of 0.086 (2) Å and with a common U_{iso} of 0.050 (9), through the use of free variables in *SHELXL* (Sheldrick, 1997). The highest peak in the final difference map is at 0.0065 0.7968 0.0393 [0.87 Å from W1], and the deepest trough at 0.0748 0.1777 0.0243 [0.78 Å from W1].

Figures

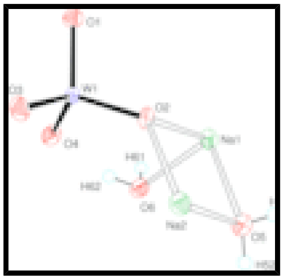


Fig. 1. An *ORTEP* view of the asymmetric unit of (1). Displacement ellipsoids are drawn at the 50% probability level.

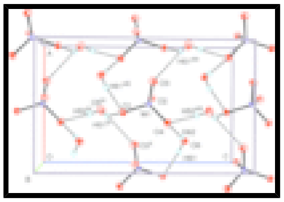


Fig. 2. An *ORTEP* view (50% probability ellipsoids) of the hydrogen bonding network between the $[WO_4]^{2-}$ anions and the water molecules, in the plane perpendicular to the *b* axis. H-bonding interactions are drawn as dashed lines, and Na^+ ions omitted for clarity. Symmetry codes: (viii) $1/2 + x, 3/2 - y, 1 - z$; (ix) $1 - x, 1 - y, 1 - z$; (x) $-1/2 + x, 3/2 - y, 1 - z$; (xiii) $1 - x, 1/2 + y, 3/2 - z$; (xiv) $3/2 - x, 1/2 + y, z$;

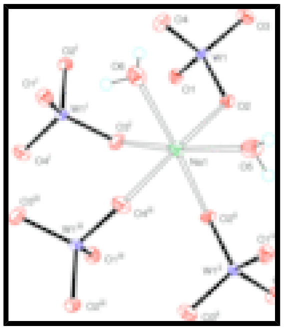


Fig. 3. An *ORTEP* view (50% probability ellipsoids)of the local geometry around the atom Na1. Symmetry codes: (i) $-1/2 + x, 3/2 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1/2 - x, -1/2 + y, z$;

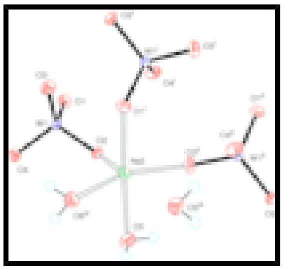


Fig. 4. An *ORTEP* view (50% probability ellipsoids) of the local geometry around the atom Na2 Symmetry codes: (i) $1/2 + x, 3/2 - y, 1 - z$; (ii) $3/2 - x, -1/2 + y, z$; (iii) $1/2 + x, y, 3/2 - z$;

(I)

Crystal data

$Na_2WO_4.2H_2O$

$D_x = 3.522$ Mg m^{-3}

M_r = 329.86

Orthorhombic, *Pbca*

a = 8.4797 (5) Å

b = 10.5930 (5) Å

c = 13.8527 (10) Å

V = 1244.33 (13) Å^3

Z = 8

F_{000} = 1184

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 21.1–24.9°

μ = 18.66 mm^{-1}

T = 291 (2) K

Plate, colourless

0.39 × 0.34 × 0.11 mm

Data collection

Enraf Nonius TurboCAD4 diffractometer

Monochromator: graphite

T = 291(2) K

non–profiled $\omega/2\theta$ scans

Absorption correction: analytical
(de Meulenaer & Tompa, 1965; Alcock, 1970)

$T_{\min}$ = 0.021, $T_{\max}$ = 0.148

7543 measured reflections

1811 independent reflections

1664 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.027

$\theta_{\max}$ = 30.0°

$\theta_{\min}$ = 2.9°

$h = -11 \rightarrow 11$

$k = -1 \rightarrow 14$

$l = -19 \rightarrow 19$

6 standard reflections

every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.021

$wR(F^2)$ = 0.053

S = 1.26

1811 reflections

97 parameters

4 restraints

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 2.0063P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max}$ = 2.75 e Å^{-3}

$\Delta\rho_{\min}$ = −1.48 e Å^{-3}

Extinction correction: SHELXL

Extinction coefficient: 0.00228 (11)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
W1	0.513897 (17)	0.801647 (13)	0.522950 (10)	0.01283 (7)
Na1	0.34357 (17)	0.49523 (14)	0.58520 (11)	0.0210 (3)
Na2	0.74189 (16)	0.54972 (15)	0.64750 (12)	0.0214 (3)
O1	0.4496 (3)	0.8227 (3)	0.4020 (2)	0.0199 (5)
O2	0.5570 (3)	0.6393 (2)	0.54181 (19)	0.0179 (5)
O3	0.6862 (3)	0.8921 (3)	0.5387 (2)	0.0239 (6)
O4	0.3692 (3)	0.8508 (3)	0.6089 (2)	0.0215 (5)
O5	0.5379 (4)	0.4088 (3)	0.6997 (2)	0.0273 (6)
O6	0.2280 (3)	0.6403 (3)	0.7015 (2)	0.0245 (6)
H51	0.584 (7)	0.349 (4)	0.669 (4)	0.050 (9)*
H52	0.572 (7)	0.395 (6)	0.757 (3)	0.050 (9)*
H61	0.136 (4)	0.644 (6)	0.676 (4)	0.050 (9)*
H62	0.255 (7)	0.715 (3)	0.684 (5)	0.050 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01363 (9)	0.01020 (10)	0.01466 (10)	0.00008 (4)	0.00046 (4)	0.00033 (4)
Na1	0.0215 (6)	0.0170 (7)	0.0245 (7)	−0.0023 (6)	0.0010 (5)	−0.0016 (7)
Na2	0.0212 (7)	0.0212 (7)	0.0217 (7)	−0.0016 (6)	0.0015 (5)	−0.0014 (6)
O1	0.0196 (11)	0.0215 (12)	0.0187 (13)	0.0024 (10)	−0.0019 (10)	0.0012 (10)
O2	0.0183 (11)	0.0111 (11)	0.0242 (12)	0.0000 (10)	0.0008 (10)	0.0013 (10)
O3	0.0231 (12)	0.0209 (13)	0.0276 (14)	−0.0075 (11)	−0.0018 (10)	−0.0029 (12)
O4	0.0224 (12)	0.0199 (12)	0.0221 (13)	0.0061 (10)	0.0039 (10)	0.0016 (11)
O5	0.0355 (14)	0.0209 (14)	0.0256 (14)	−0.0003 (12)	−0.0028 (12)	0.0025 (12)
O6	0.0241 (13)	0.0234 (14)	0.0258 (14)	−0.0027 (11)	−0.0052 (11)	0.0050 (12)

Geometric parameters (Å, °)

W1—O3	1.761 (3)	Na2—O2	2.346 (3)
W1—O1	1.776 (3)	Na2—O5	2.396 (4)
W1—O2	1.778 (3)	O1—Na2$^{\rm iii}$	2.323 (3)
W1—O4	1.787 (3)	O2—Na1$^{\rm ii}$	2.416 (3)
Na1—O4$^{\rm i}$	2.388 (3)	O3—Na2$^{\rm vii}$	2.331 (3)
Na1—O2$^{\rm ii}$	2.416 (3)	O3—Na1$^{\rm v}$	2.480 (3)
Na1—O6	2.433 (3)	O4—Na1$^{\rm viii}$	2.388 (3)
Na1—O2	2.442 (3)	O5—H51	0.86 (3)
Na1—O5	2.464 (4)	O5—H52	0.86 (3)
Na1—O3$^{\rm iii}$	2.480 (3)	O6—Na2$^{\rm ix}$	2.304 (3)
Na2—O6$^{\rm iv}$	2.304 (3)	O6—H61	0.86 (3)
Na2—O1$^{\rm v}$	2.323 (3)	O6—H62	0.86 (3)
Na2—O3$^{\rm vi}$	2.331 (3)		

O3—W1—O1	107.66 (13)
O3—W1—O2	109.73 (14)
O1—W1—O2	108.87 (12)
O3—W1—O4	109.17 (13)
O1—W1—O4	112.41 (12)
O2—W1—O4	108.97 (12)
O4^{i}—Na1—O2^{ii}	89.21 (10)
O4^{i}—Na1—O6	90.52 (11)
O2^{ii}—Na1—O6	174.56 (12)
O4^{i}—Na1—O2	173.66 (12)
O2^{ii}—Na1—O2	86.02 (10)
O6—Na1—O2	93.83 (10)
O4^{i}—Na1—O5	100.30 (11)
O2^{ii}—Na1—O5	90.93 (11)
O6—Na1—O5	94.47 (11)
O2—Na1—O5	83.98 (11)
O4^{i}—Na1—O3^{iii}	89.83 (11)
O2^{ii}—Na1—O3^{iii}	88.15 (10)
O6—Na1—O3^{iii}	86.42 (10)
O2—Na1—O3^{iii}	85.85 (10)
O5—Na1—O3^{iii}	169.82 (12)
O6^{iv}—Na2—O1^{v}	93.69 (11)
O6^{iv}—Na2—O3^{vi}	154.00 (13)
O1^{v}—Na2—O3^{vi}	91.58 (11)
O6^{iv}—Na2—O2	111.35 (11)
O1^{v}—Na2—O2	95.01 (11)
O3^{vi}—Na2—O2	93.50 (11)
O6^{iv}—Na2—O5	87.05 (12)
O1^{v}—Na2—O5	176.82 (13)
O3^{vi}—Na2—O5	86.42 (12)
O2—Na2—O5	87.59 (11)
W1—O1—Na2^{iii}	125.75 (14)
W1—O2—Na2	128.35 (14)
W1—O2—Na1^{ii}	122.37 (14)
Na2—O2—Na1^{ii}	89.01 (10)
W1—O2—Na1	119.24 (13)
Na2—O2—Na1	95.10 (10)
Na1^{ii}—O2—Na1	93.98 (10)
W1—O3—Na2^{vii}	133.39 (16)
W1—O3—Na1^{v}	128.51 (15)
Na2^{vii}—O3—Na1^{v}	87.82 (10)
W1—O4—Na1^{viii}	127.84 (15)
Na2—O5—Na1	93.26 (12)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O1^{ii}	0.86 (3)	2.09 (4)	2.830 (4)	145 (6)
O5—H52···O4^{x}	0.86 (3)	1.98 (3)	2.832 (4)	174 (6)
O5—H51···O3^{vi}	0.86 (3)	2.70 (6)	3.237 (4)	122 (5)
O6—H61···O1^{iii}	0.86 (3)	1.95 (3)	2.790 (4)	167 (6)
O6—H62···O4	0.86 (3)	2.02 (4)	2.837 (4)	159 (6)

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

Fig. 1

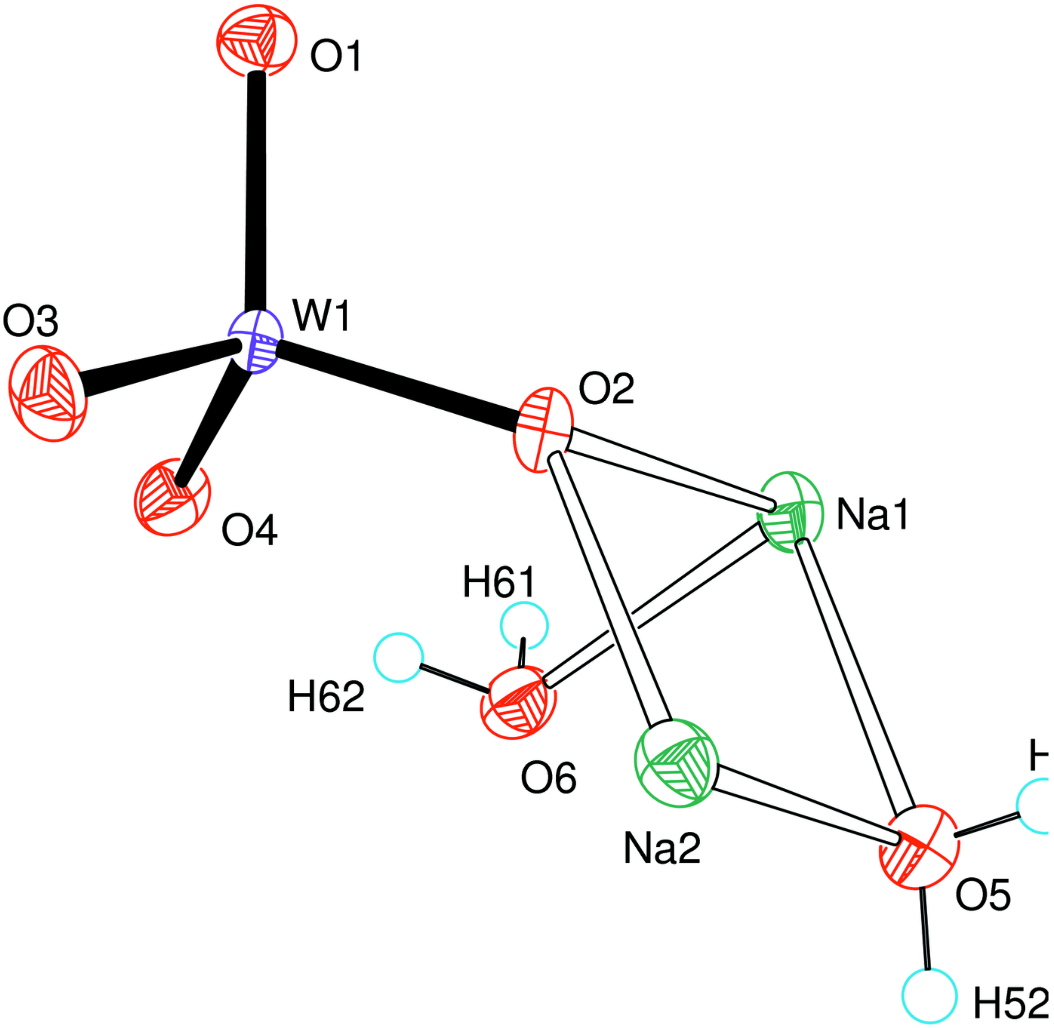
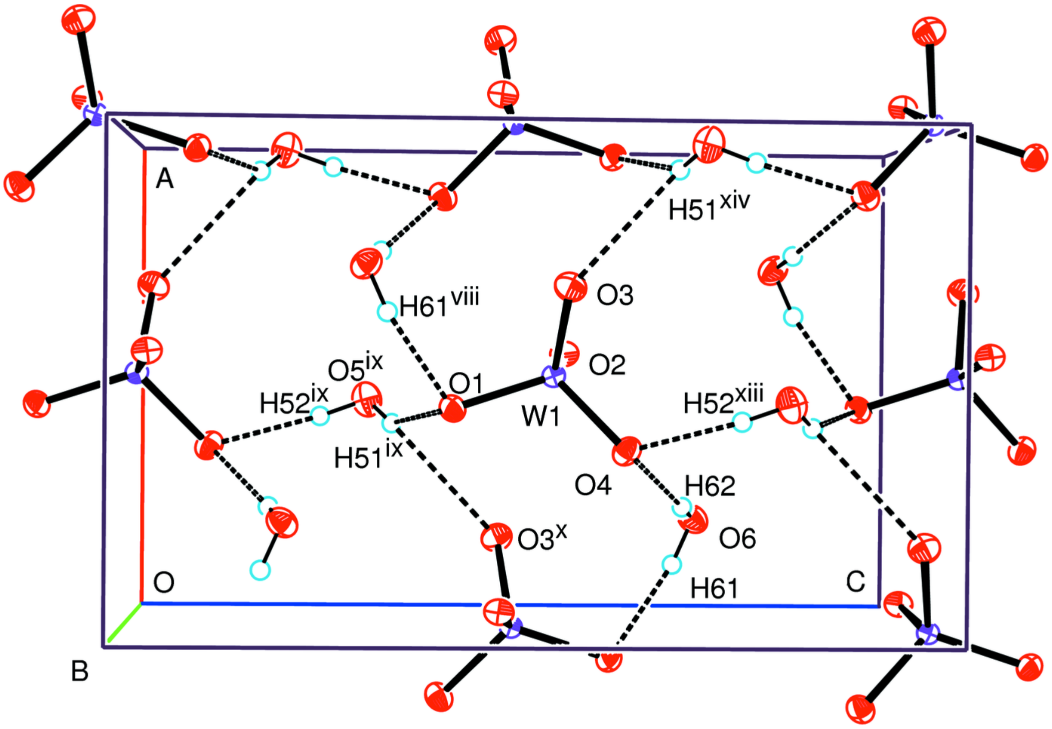


Fig. 2


A
H51^{xiv}
H61^{viii}
O3
O2
O5^{ix}
O1
W1
H52^{ix}
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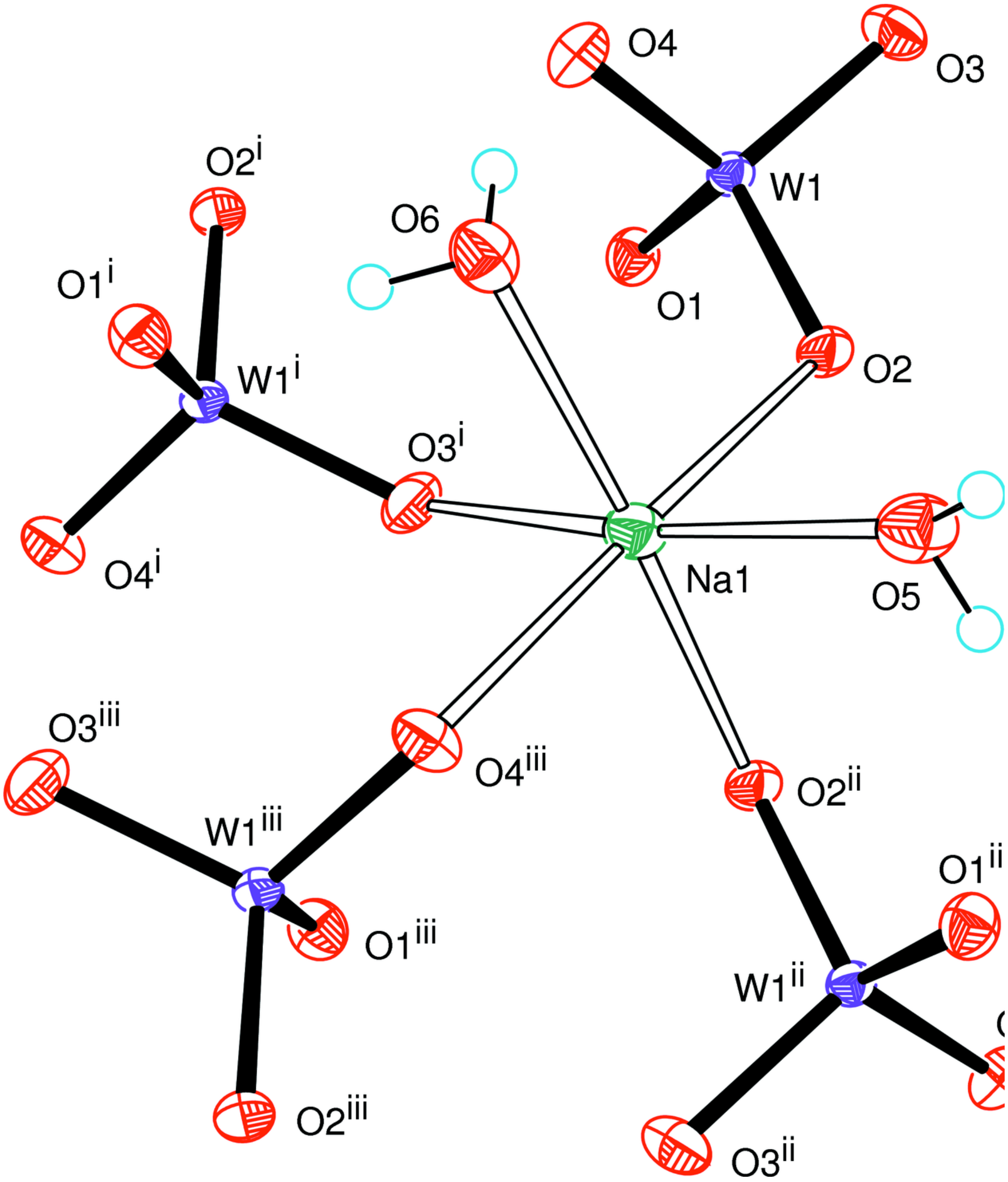
O4
H62
O6
O3^{x}
O
H61
C
B

Fig. 3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O3
O2i
W1
O6
O1
O1i
O2
W1i
O3i
O5
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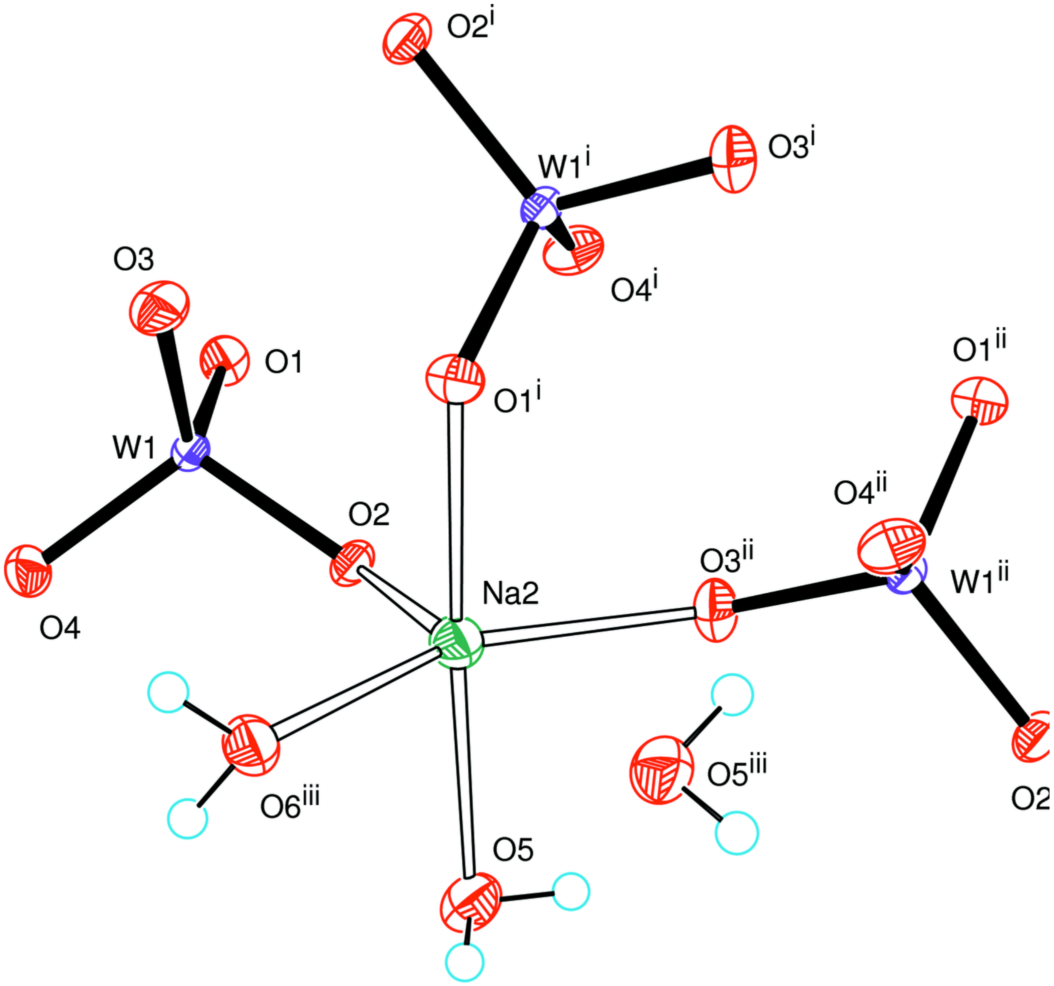
W1ii
O2iii
O3ii

Fig. 4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W1^{i}
O3^{i}
O4^{i}
O3
O1
O1^{i}
O1^{ii}
W1
O2
O4^{ii}
O3^{ii}
W1^{ii}
O4
Na2
O6^{iii}
O5^{iii}
O2
O5