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Redetermination of the crystal structure of NaTcO₄ at 100 and 296 K based on single-crystal X-ray data

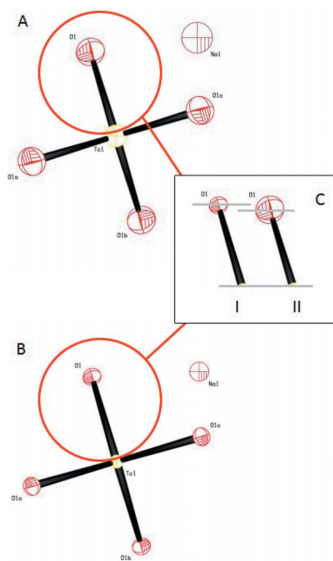
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The redetermination of the title compound, sodium pertechnetate, from single-crystal CCD data recorded both at 296 and 100 K confirms previous studies based on X-ray powder diffraction film data [Schwochau (1962). *Z. Naturforsch. Teil A*, **17**, 630; Keller & Kanellakopoulos (1963). *Radiochim. Acta*, **1**, 107–108] and neutron powder diffraction data using the Rietveld method [Weaver *et al.* (2017). *Inorg. Chem.* **12**, 677–681], but reveals a considerable improvement in precision. The standard uncertainties of the room-temperature structure determination are about seven times lower than those of the neutron diffraction structure determination and about 13 times lower at 100 K, due to the decrease in the amplitude of librations. The crystal expansion could be approximated linearly with a thermal volumic expansion coefficient of $1.19(12) \times 10^{-4} \text{ K}^{-1}$. NaTcO₄ adopts the scheelite (CaWO₄) structure type in space group type *I4₁/a* with Na and Tc atoms (both with site symmetry $\bar{4}$) replacing Ca and W atoms, respectively.

1. Chemical context

Sodium pertechnetate, NaTcO₄, refers to a group of *d*⁰-tetroxide anion salts. Since the inception of quantum chemistry, compounds of this type have been models (generally with respect to the MnO₄[−] anion) for which the validity of the proposed equations and approximations for the case of *d*-electrons are verified. It was believed that, owing to the *d*⁰ electronic state, they define the least complex class of compounds of *d*-elements. Such simplicity, due to the absence of *d*-electrons and their pseudospherical symmetry, does by far not imply that any of these compounds show no complex behavior under changing environmental conditions, *e.g.* by changing temperature and/or the strength of the crystal field, and publications on the discovery of a more complex behaviour and properties appeared periodically. For example, for sodium (German *et al.*, 1987b, 1993), potassium (German *et al.*, 1993; Gafurov & Aliev, 2005) and caesium (Tarasov *et al.*, 1991, 1992) tetraoxidotchnetates, the existence of phase transitions was noted at high temperatures, while for the rhenium analogue, caesium tetraoxidorhenate, the ability of laser-excited second harmonic generation has been observed (Stefanovich *et al.*, 1991). Differences for these systems are also observed in the crystal structures. Potassium permanganate crystallizes in the orthorhombic system (Palenik, 1967), whereas the pertechnetate and perrhenate of the same cation



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crystallize in the tetragonal system (Hoppe *et al.*, 1999; Schwochau, 1962). Next to the interest for the TcO_4^- anion in its sodium salt, sodium cations in general are worth being investigated in detail. For example, sodium salts are known to form hydrates with different hydration numbers and various coordination numbers for the sodium cation. The change in these numbers often occurs in the vitally important temperature range of 309–313 K (German *et al.*, 1987b; Tarasov *et al.*, 2015). Precise structural data of such systems are important for the analyses of transmutation rates in homogeneous systems as noted by Kuo *et al.* (2017) and in this respect, are more useful than the data of previously determined structures (Kuo *et al.*, 2017; Ackerman *et al.*, 2016; German *et al.*, 1987a; Spitsyn *et al.*, 1987; Tarasov *et al.*, 1983, 1991). Likewise, Ackerman *et al.* (2016) have shown that precise structural data are needed for the estimation of the incorporation possibility

Table 1
Selected geometric parameters (Å, °) at 100 K.

Tc1–O1	1.7208 (3)	Na1–O1 ⁱⁱ	2.5980 (4)
Na1–O1 ⁱ	2.5107 (4)		
O1 ⁱⁱⁱ –Tc1–O1	108.439 (12)	O1 ^{iv} –Tc1–O1	111.56 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x - 1, y, z$; (iii) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{1}{4}$; (iv) $-x + 1, -y + \frac{3}{2}, z$.

Table 2
Selected geometric parameters (Å, °) at 296 K.

Tc1–O1	1.7183 (6)	O1–Na1 ⁱⁱ	2.6304 (6)
O1–Na1 ⁱ	2.5357 (6)		
O1–Tc1–O1 ⁱⁱⁱ	111.53 (5)	O1–Tc1–O1 ^{iv}	108.45 (2)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y + \frac{3}{2}, z$; (iv) $y - \frac{1}{4}, -x + \frac{5}{4}, -z + \frac{1}{4}$.

for ^{99}Tc into stable scheelite matrices of different compositions. Another aspect for obtaining more precise structure data on pertechnetates is to clarify if pseudo-Jahn–Teller distortions of d^0 -tetraoxide anions really take place when compared with previous determinations (German *et al.*, 1987a; Spitsyn *et al.*, 1987; Tarasov *et al.*, 1983, 1991). In this context we have reinvestigated the crystal structure of NaTcO_4 that is known from powder diffraction data only, namely by inspection of its X-ray powder diffraction pattern (Schwochau, 1962; Keller & Kanellakopulos, 1963) and Rietveld refinement of neutron powder diffraction data (Weaver *et al.*, 2017).

2. Structural commentary

The structure of anhydrous NaTcO_4 , determined here on the basis of X-ray diffraction data of a single crystal recorded both at room and low temperature, belongs to the CaWO_4 structural type (space group type $I4_1/a$). The obtained bond lengths and angles are similar to those obtained from previous X-ray powder (Keller & Kanellakopulos, 1963; Schwochau, 1962) and neutron powder diffraction studies (Weaver *et al.*, 2017).

Lattice parameters determined here with the precision of 0.0002–0.0005 Å at 296 K (Table 1) are close to those of $a = 5.342$ (3) Å, $c = 11.874$ (6) Å given by Weaver *et al.* (2017). The lattice parameters at 100 K are $a = 5.2945$ (2) Å, $c = 11.7470$ (5) Å (single crystal measurement). These values represent the thermal volumic expansion coefficient of 1.19 (12) $\times 10^{-4} \text{ K}^{-1}$. The c/a ratio in this structure changes from 2.2187 (7) to 2.2223 (4) as a function of the temperature change from 100 to 296 K.

Our results confirm that NaTcO_4 is isostructural to KTcO_4 and RbTcO_4 (Keller & Kanellakopulos, 1963). The structure is composed of three atom types (Na, Tc, O). The Tc and Na atoms occupy special positions with $\bar{4}$ symmetry, Wyckoff positions $4b$ and $4a$, respectively. The configuration of the TeO_4^- anion is that of a slightly distorted tetrahedron both at 296 K and at 100 K (Tables 1 and 2). The Tc–O distances are 1.7183 (6) Å at 296 K and 1.7208 (3) Å at 100 K. These distances are in good agreement with values known for these ions from the literature (German *et al.*, 1987a; Tarasov *et al.*,

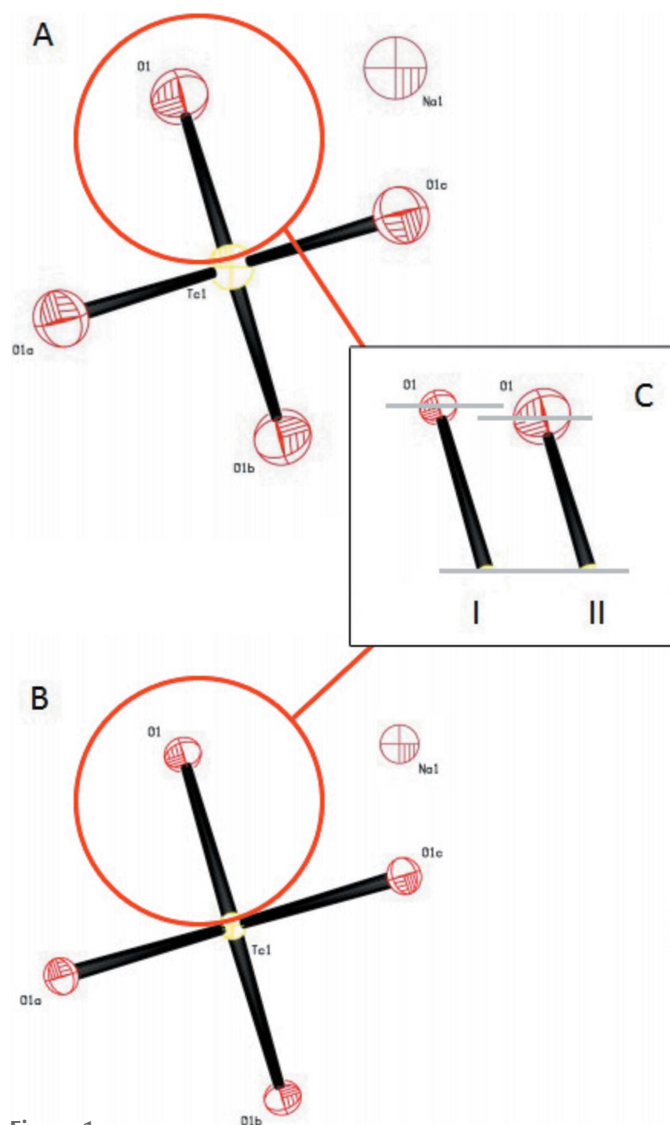


Figure 1
The elongation of bonds upon cooling from 296 K [(II), **A**] to 100 K [(I), **B**] is associated with a decrease in libration (**C**). All displacement ellipsoids are drawn at the 50% probability. [Symmetry codes: (a) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{1}{4}$; (b) $-x + 1, -y + \frac{3}{2}, z$; (c) $y + \frac{3}{2}, -x + \frac{1}{4}, z + \frac{3}{4}$]

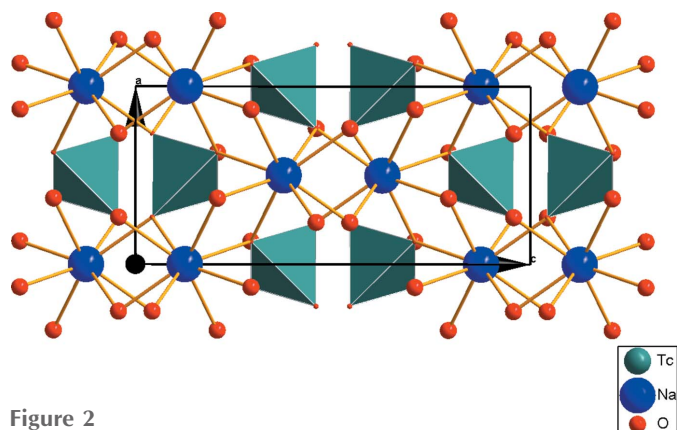


Figure 2
View of the crystal packing of the title compound.

1992; Kuo *et al.*, 2017; Ackerman *et al.*, 2016). The elongation of bonds (Fig. 1), while decreasing the temperature from 296 K to 100 K, can be attributed to a decrease in the libration effect (German *et al.*, 1987*a*). A similar phenomenon has previously been observed in the structure of anilinium pertechnetate (Maruk *et al.*, 2010).

The greatest distortion of the TcO_4^- anion from an ideal tetrahedral configuration reported by Weaver *et al.* (2017) is confirmed by our analysis of the O–Tc–O angles in the NaTcO_4 structure, but the difference is not as high as in the model from the neutron diffraction experiment (Weaver *et al.*, 2017). The maximum deviation values are 3.12° at 100 K and 3.08° at 296 K for the sodium salt and are larger in comparison with the potassium and rubidium salts, because the sodium cation has the smallest ionic radius compared to K^+ and Rb^+

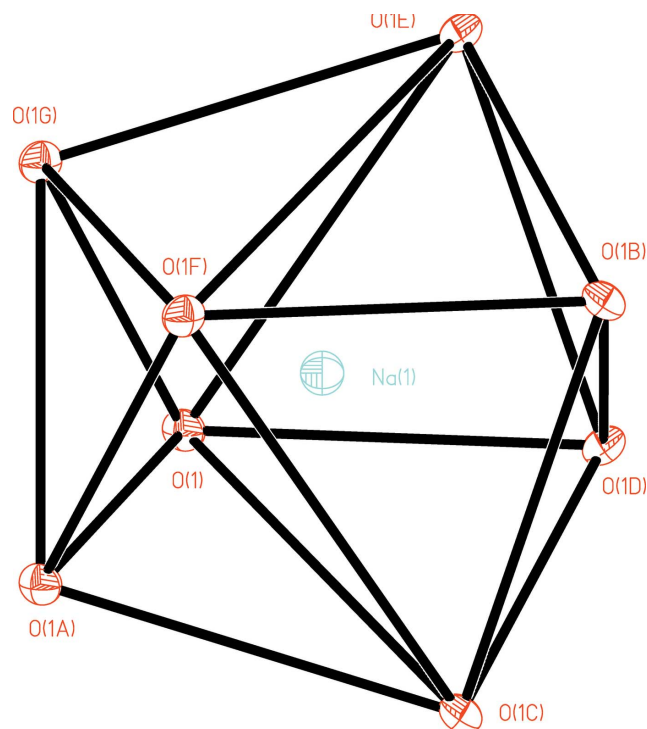


Figure 3
The coordination polyhedron of the sodium cation (data from 100 K measurement).

and hence has the highest polarizing ability. This distortion is insensitive to the temperature change from 100 K to 296 K.

The packing of Na^+ cations and TcO_4^- anions in the crystal is presented in Fig. 2. Each Na^+ cation is coordinated by eight

Table 3
Experimental details.

	100 K	296 K
Crystal data		
Chemical formula	NaTcO_4	NaTcO_4
M_r	185.9	185.9
Crystal system, space group	Tetragonal, $I4_1/a$	Tetragonal, $I4_1/a$
Temperature (K)	100	296
a, c (Å)	5.2945 (2), 11.7470 (5)	5.3325 (1), 11.8503 (3)
V (Å ³)	329.29 (3)	336.97 (2)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	4.33	4.23
Crystal size (mm)	0.34 × 0.28 × 0.20	0.28 × 0.26 × 0.20
Data collection		
Diffractometer	Bruker Kappa APEXII area-detector	Bruker Kappa APEXII area-detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.399, 0.478	0.386, 0.485
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6909, 678, 661	2371, 365, 350
R_{int}	0.018	0.016
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.995	0.805
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.009, 0.017, 1.31	0.008, 0.019, 1.16
No. of reflections	678	365
No. of parameters	15	15
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.26, -0.34	0.23, -0.33

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2008), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

oxygen atoms that are belonging to four TcO_4^- anions. The resulting coordination polyhedron can be described as a distorted dodecahedron (Fig. 3). The two dihedral angles between pairs of two triangular faces sharing an edge that connects two five-edged vertices of the dodecahedron are equal to 21.2 and 30.3°, respectively. The corresponding faces should form an angle of 29.5° for a dodecahedron and 0° for a square anti-prism according to the Aslanov–Porai-Koshits criterion (Porai-Koshits & Aslanov, 1972). Hence the coordination polyhedron of the sodium cation is closer to a dodecahedron than to a square anti-prism. Each of the four oxygen atoms of an individual TcO_4^- anion is in contact with two sodium cations, so that each TcO_4^- anion is directly contacted with eight sodium cations.

3. Synthesis and crystallization

The synthesis of the title compound was carried out based on neutralization of an aqueous solution of freshly prepared HTcO_4 with an equivalent quantity of 1 M aqueous solution of chemically pure sodium hydroxide. The HTcO_4 solution was made by dissolution of Tc_2O_7 sublimed from TcO_2 in an oxygen flow at 973 K.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Seven (six) reflections at room (and low) temperature were omitted from refinement due to large differences between observed and calculated intensities.

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Redetermination of the crystal structure of NaTcO₄ at 100 and 296 K based on single-crystal X-ray data

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE-Plus* (Bruker, 2008); data reduction: *SAINTE-Plus* (Bruker, 2008); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) Sodium pertechnetate

Crystal data

NaTcO₄

$M_r = 185.9$

Tetragonal, $I4_1/a$

$a = 5.2945$ (2) Å

$c = 11.7470$ (5) Å

$V = 329.29$ (3) Å³

$Z = 4$

$F(000) = 344$

$D_x = 3.750$ Mg m⁻³

Melting point < 1063 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5622 reflections

$\theta = 4.2\text{--}45.4^\circ$

$\mu = 4.33$ mm⁻¹

$T = 100$ K

Fragment, colourless

$0.34 \times 0.28 \times 0.20$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer

ω - and φ -scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2008)

$T_{\min} = 0.399$, $T_{\max} = 0.478$

6909 measured reflections

678 independent reflections

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

$R_{\text{int}} = 0.018$

$\theta_{\max} = 45.0^\circ$, $\theta_{\min} = 4.2^\circ$

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -22 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.009$

$wR(F^2) = 0.017$

$S = 1.31$

678 reflections

15 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0029P)^2 + 0.0769P]$

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

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

$\Delta\rho_{\max} = 0.26$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ e Å⁻³

Extinction correction: SHELXL2014

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0489 (10)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tc1	0.5000	0.7500	0.1250	0.00517 (2)
Na1	0.0000	0.2500	0.1250	0.00980 (7)
O1	0.73565 (6)	0.62081 (7)	0.04262 (3)	0.00879 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tc1	0.00489 (2)	0.00489 (2)	0.00574 (3)	0.000	0.000	0.000
Na1	0.00988 (10)	0.00988 (10)	0.00965 (16)	0.000	0.000	0.000
O1	0.00795 (11)	0.00901 (11)	0.00942 (11)	0.00054 (9)	0.00202 (10)	-0.00104 (10)

Geometric parameters (\AA , $^\circ$)

Tc1—O1 ⁱ	1.7208 (3)	Na1—O1 ^{viii}	2.5980 (4)
Tc1—O1 ⁱⁱ	1.7208 (3)	Na1—O1 ^{ix}	2.5980 (4)
Tc1—O1 ⁱⁱⁱ	1.7208 (3)	Na1—O1 ^x	2.5980 (4)
Tc1—O1	1.7208 (3)	Na1—Na1 ^{xi}	3.9538 (1)
Na1—O1 ^{iv}	2.5107 (4)	Na1—Na1 ^{xii}	3.9538 (1)
Na1—O1 ^v	2.5107 (4)	Na1—Na1 ^{xiii}	3.9538 (1)
Na1—O1 ^{vi}	2.5107 (4)	Na1—Na1 ^{xiv}	3.9538 (1)
Na1—O1 ^{vii}	2.5107 (4)	O1—Na1 ^{vii}	2.5107 (4)
Na1—O1 ⁱⁱⁱ	2.5980 (4)	O1—Na1 ^{xv}	2.5980 (4)
O1 ⁱ —Tc1—O1 ⁱⁱ	108.439 (12)	O1 ⁱⁱⁱ —Na1—Na1 ^{xi}	129.596 (8)
O1 ⁱ —Tc1—O1 ⁱⁱⁱ	111.56 (3)	O1 ^{viii} —Na1—Na1 ^{xi}	85.180 (8)
O1 ⁱⁱ —Tc1—O1 ⁱⁱⁱ	108.439 (12)	O1 ^{ix} —Na1—Na1 ^{xi}	38.498 (8)
O1 ⁱ —Tc1—O1	108.439 (12)	O1 ^x —Na1—Na1 ^{xi}	103.255 (8)
O1 ⁱⁱ —Tc1—O1	111.56 (3)	O1 ^{iv} —Na1—Na1 ^{xii}	162.891 (8)
O1 ⁱⁱⁱ —Tc1—O1	108.439 (12)	O1 ^v —Na1—Na1 ^{xii}	66.415 (8)
O1 ^{iv} —Na1—O1 ^v	127.954 (10)	O1 ^{vi} —Na1—Na1 ^{xii}	40.101 (8)
O1 ^{iv} —Na1—O1 ^{vi}	127.954 (10)	O1 ^{vii} —Na1—Na1 ^{xii}	102.079 (9)
O1 ^v —Na1—O1 ^{vi}	76.700 (17)	O1 ⁱⁱⁱ —Na1—Na1 ^{xii}	38.498 (8)
O1 ^{iv} —Na1—O1 ^{vii}	76.700 (17)	O1 ^{viii} —Na1—Na1 ^{xii}	103.255 (8)
O1 ^v —Na1—O1 ^{vii}	127.954 (10)	O1 ^{ix} —Na1—Na1 ^{xii}	85.180 (8)
O1 ^{vi} —Na1—O1 ^{vii}	127.954 (10)	O1 ^x —Na1—Na1 ^{xii}	129.596 (8)
O1 ^{iv} —Na1—O1 ⁱⁱⁱ	149.332 (14)	Na1 ^{xi} —Na1—Na1 ^{xii}	123.484 (2)
O1 ^v —Na1—O1 ⁱⁱⁱ	67.259 (8)	O1 ^{iv} —Na1—Na1 ^{xiii}	66.415 (8)
O1 ^{vi} —Na1—O1 ⁱⁱⁱ	78.599 (12)	O1 ^v —Na1—Na1 ^{xiii}	102.079 (9)
O1 ^{vii} —Na1—O1 ⁱⁱⁱ	73.985 (7)	O1 ^{vi} —Na1—Na1 ^{xiii}	162.891 (8)
O1 ^{iv} —Na1—O1 ^{viii}	73.985 (7)	O1 ^{vii} —Na1—Na1 ^{xiii}	40.101 (8)
O1 ^v —Na1—O1 ^{viii}	78.599 (12)	O1 ⁱⁱⁱ —Na1—Na1 ^{xiii}	85.180 (8)
O1 ^{vi} —Na1—O1 ^{viii}	67.259 (8)	O1 ^{viii} —Na1—Na1 ^{xiii}	129.596 (8)
O1 ^{vii} —Na1—O1 ^{viii}	149.332 (14)	O1 ^{ix} —Na1—Na1 ^{xiii}	103.255 (8)
O1 ⁱⁱⁱ —Na1—O1 ^{viii}	136.261 (16)	O1 ^x —Na1—Na1 ^{xiii}	38.498 (8)
O1 ^{iv} —Na1—O1 ^{ix}	78.599 (12)	Na1 ^{xi} —Na1—Na1 ^{xiii}	84.064 (3)

O1 ^v —Na1—O1 ^{ix}	149.332 (14)	Na1 ^{xii} —Na1—Na1 ^{xiii}	123.484 (2)
O1 ^{vi} —Na1—O1 ^{ix}	73.985 (7)	O1 ^{iv} —Na1—Na1 ^{xiv}	102.079 (9)
O1 ^{vii} —Na1—O1 ^{ix}	67.259 (8)	O1 ^v —Na1—Na1 ^{xiv}	40.101 (8)
O1 ⁱⁱⁱ —Na1—O1 ^{ix}	97.976 (6)	O1 ^{vi} —Na1—Na1 ^{xiv}	66.415 (8)
O1 ^{viii} —Na1—O1 ^{ix}	97.976 (6)	O1 ^{vii} —Na1—Na1 ^{xiv}	162.891 (8)
O1 ^{iv} —Na1—O1 ^x	67.259 (8)	O1 ⁱⁱⁱ —Na1—Na1 ^{xiv}	103.255 (8)
O1 ^v —Na1—O1 ^x	73.985 (7)	O1 ^{viii} —Na1—Na1 ^{xiv}	38.498 (8)
O1 ^{vi} —Na1—O1 ^x	149.332 (14)	O1 ^{ix} —Na1—Na1 ^{xiv}	129.596 (8)
O1 ^{vii} —Na1—O1 ^x	78.599 (12)	O1 ^x —Na1—Na1 ^{xiv}	85.180 (8)
O1 ⁱⁱⁱ —Na1—O1 ^x	97.976 (6)	Na1 ^{xi} —Na1—Na1 ^{xiv}	123.484 (2)
O1 ^{viii} —Na1—O1 ^x	97.976 (6)	Na1 ^{xii} —Na1—Na1 ^{xiv}	84.064 (4)
O1 ^{ix} —Na1—O1 ^x	136.261 (16)	Na1 ^{xiii} —Na1—Na1 ^{xiv}	123.484 (2)
O1 ^{iv} —Na1—Na1 ^{xi}	40.101 (8)	Tc1—O1—Na1 ^{vii}	137.472 (19)
O1 ^v —Na1—Na1 ^{xi}	162.891 (8)	Tc1—O1—Na1 ^{xv}	118.781 (18)
O1 ^{vi} —Na1—Na1 ^{xi}	102.079 (9)	Na1 ^{vii} —O1—Na1 ^{xv}	101.402 (12)
O1 ^{vii} —Na1—Na1 ^{xi}	66.415 (8)		

Symmetry codes: (i) $-y+5/4, x+1/4, -z+1/4$; (ii) $-x+1, -y+3/2, z$; (iii) $y-1/4, -x+5/4, -z+1/4$; (iv) $x-1, y-1/2, -z$; (v) $y-3/4, -x+5/4, z+1/4$; (vi) $-y+3/4, x-3/4, z+1/4$; (vii) $-x+1, -y+1, -z$; (viii) $-y+1/4, x-3/4, -z+1/4$; (ix) $-x+1, -y+1/2, z$; (x) $x-1, y, z$; (xi) $-x, -y, -z$; (xii) $-x+1/2, -y+1/2, -z+1/2$; (xiii) $-x, -y+1, -z$; (xiv) $-x-1/2, -y+1/2, -z+1/2$; (xv) $x+1, y, z$.

(II) Sodium tetraoxidotchnetate(VII)

Crystal data

O₄Tc·Na
M_r = 185.9
 Tetragonal, *I*₄/a
 Hall symbol: -I 4ad
a = 5.3325 (1) Å
c = 11.8503 (3) Å
V = 336.97 (2) Å³
Z = 4
F(000) = 344

D_x = 3.664 Mg m⁻³
 Melting point < 1063 K
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 2097 reflections
 θ = 4.2–35.2°
 μ = 4.23 mm⁻¹
T = 296 K
 Fragment, colourless
 0.28 × 0.26 × 0.20 mm

Data collection

Bruker Kappa APEX II area-detector
 diffractometer
 Graphite monochromator
 Detector resolution: 9.091 pixels mm⁻¹
 ω- and φ-scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2008)
T_{min} = 0.386, *T_{max}* = 0.485

2371 measured reflections
 365 independent reflections
 350 reflections with *I* > 2σ(*I*)
R_{int} = 0.016
 θ_{max} = 34.9°, θ_{min} = 4.2°
h = -8→7
k = -8→8
l = -18→18

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.008
wR(*F*²) = 0.019
S = 1.16
 365 reflections
 15 parameters
 0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0071P)^2 + 0.0846P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.23 e Å⁻³
 Δρ_{min} = -0.33 e Å⁻³
 Extinction correction: SHELXL,
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.136 (3)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tc1	0.5000	0.7500	0.1250	0.01434 (6)
Na1	0.0000	0.2500	0.1250	0.02546 (16)
O1	0.73494 (12)	0.62442 (11)	0.04342 (6)	0.02225 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tc1	0.01355 (6)	0.01355 (6)	0.01591 (7)	0.000	0.000	0.000
Na1	0.0261 (2)	0.0261 (2)	0.0242 (4)	0.000	0.000	0.000
O1	0.0200 (2)	0.0225 (2)	0.0242 (3)	0.0005 (2)	0.0050 (2)	-0.0030 (2)

Geometric parameters (\AA , $^\circ$)

Tc1—O1 ⁱ	1.7183 (6)	Na1—O1 ^{vii}	2.5357 (6)
Tc1—O1	1.7183 (6)	Na1—O1 ⁱⁱⁱ	2.6303 (6)
Tc1—O1 ⁱⁱ	1.7183 (6)	Na1—O1 ^{viii}	2.6303 (6)
Tc1—O1 ⁱⁱⁱ	1.7183 (6)	Na1—O1 ^{ix}	2.6303 (6)
Na1—O1 ^{iv}	2.5357 (6)	Na1—O1 ^x	2.6303 (6)
Na1—O1 ^v	2.5357 (6)	O1—Na1 ^{vii}	2.5357 (6)
Na1—O1 ^{vi}	2.5357 (6)	O1—Na1 ^{xi}	2.6304 (6)
O1 ⁱ —Tc1—O1	108.45 (2)	O1 ⁱⁱⁱ —Na1—Na1 ^{xii}	129.245 (14)
O1 ⁱ —Tc1—O1 ⁱⁱ	108.45 (2)	O1 ^{viii} —Na1—Na1 ^{xii}	85.049 (14)
O1—Tc1—O1 ⁱⁱ	111.53 (5)	O1 ^{ix} —Na1—Na1 ^{xii}	38.652 (13)
O1 ⁱ —Tc1—O1 ⁱⁱⁱ	111.53 (5)	O1 ^x —Na1—Na1 ^{xii}	103.569 (14)
O1—Tc1—O1 ⁱⁱⁱ	108.45 (2)	O1 ^{iv} —Na1—Na1 ^{xiii}	163.325 (14)
O1 ⁱⁱ —Tc1—O1 ⁱⁱⁱ	108.45 (2)	O1 ^v —Na1—Na1 ^{xiii}	65.896 (14)
O1 ^{iv} —Na1—O1 ^v	128.283 (18)	O1 ^{vi} —Na1—Na1 ^{xiii}	40.383 (14)
O1 ^{iv} —Na1—O1 ^{vi}	128.283 (18)	O1 ^{vii} —Na1—Na1 ^{xiii}	102.250 (15)
O1 ^v —Na1—O1 ^{vi}	76.17 (3)	O1 ⁱⁱⁱ —Na1—Na1 ^{xiii}	38.652 (13)
O1 ^{iv} —Na1—O1 ^{vii}	76.17 (3)	O1 ^{viii} —Na1—Na1 ^{xiii}	103.569 (14)
O1 ^v —Na1—O1 ^{vii}	128.283 (18)	O1 ^{ix} —Na1—Na1 ^{xiii}	85.049 (14)
O1 ^{vi} —Na1—O1 ^{vii}	128.283 (18)	O1 ^x —Na1—Na1 ^{xiii}	129.245 (14)
O1 ^{iv} —Na1—O1 ⁱⁱⁱ	148.68 (2)	Na1 ^{xii} —Na1—Na1 ^{xiii}	123.539 (1)
O1 ^v —Na1—O1 ⁱⁱⁱ	67.149 (15)	O1 ^{iv} —Na1—Na1 ^{xiv}	65.896 (14)
O1 ^{vi} —Na1—O1 ⁱⁱⁱ	79.04 (2)	O1 ^v —Na1—Na1 ^{xiv}	102.250 (15)
O1 ^{vii} —Na1—O1 ⁱⁱⁱ	73.993 (11)	O1 ^{vi} —Na1—Na1 ^{xiv}	163.325 (14)
O1 ^{iv} —Na1—O1 ^{viii}	73.993 (11)	O1 ^{vii} —Na1—Na1 ^{xiv}	40.383 (14)
O1 ^v —Na1—O1 ^{viii}	79.04 (2)	O1 ⁱⁱⁱ —Na1—Na1 ^{xiv}	85.049 (14)
O1 ^{vi} —Na1—O1 ^{viii}	67.149 (15)	O1 ^{viii} —Na1—Na1 ^{xiv}	129.245 (14)
O1 ^{vii} —Na1—O1 ^{viii}	148.68 (2)	O1 ^{ix} —Na1—Na1 ^{xiv}	103.569 (14)
O1 ⁱⁱⁱ —Na1—O1 ^{viii}	136.88 (3)	O1 ^x —Na1—Na1 ^{xiv}	38.652 (13)
O1 ^{iv} —Na1—O1 ^{ix}	79.04 (2)	Na1 ^{xii} —Na1—Na1 ^{xiv}	83.973 (2)
O1 ^v —Na1—O1 ^{ix}	148.68 (2)	Na1 ^{xiii} —Na1—Na1 ^{xiv}	123.539 (1)
O1 ^{vi} —Na1—O1 ^{ix}	73.993 (11)	O1 ^{iv} —Na1—Na1 ^{xv}	102.250 (15)

O1 ^{vii} —Na1—O1 ^{ix}	67.149 (15)	O1 ^v —Na1—Na1 ^{xv}	40.383 (14)
O1 ⁱⁱⁱ —Na1—O1 ^{ix}	97.762 (10)	O1 ^{vi} —Na1—Na1 ^{xv}	65.896 (14)
O1 ^{viii} —Na1—O1 ^{ix}	97.762 (10)	O1 ^{vii} —Na1—Na1 ^{xv}	163.325 (14)
O1 ^{iv} —Na1—O1 ^x	67.149 (15)	O1 ⁱⁱⁱ —Na1—Na1 ^{xv}	103.569 (14)
O1 ^v —Na1—O1 ^x	73.993 (11)	O1 ^{viii} —Na1—Na1 ^{xv}	38.652 (13)
O1 ^{vi} —Na1—O1 ^x	148.68 (2)	O1 ^{ix} —Na1—Na1 ^{xv}	129.245 (14)
O1 ^{vii} —Na1—O1 ^x	79.04 (2)	O1 ^x —Na1—Na1 ^{xv}	85.049 (14)
O1 ⁱⁱⁱ —Na1—O1 ^x	97.762 (10)	Na1 ^{xii} —Na1—Na1 ^{xv}	123.539 (1)
O1 ^{viii} —Na1—O1 ^x	97.762 (10)	Na1 ^{xiii} —Na1—Na1 ^{xv}	83.973 (2)
O1 ^{ix} —Na1—O1 ^x	136.88 (3)	Na1 ^{xiv} —Na1—Na1 ^{xv}	123.539 (1)
O1 ^{iv} —Na1—Na1 ^{xii}	40.383 (14)	Tc1—O1—Na1 ^{vii}	138.27 (3)
O1 ^v —Na1—Na1 ^{xii}	163.325 (14)	Tc1—O1—Na1 ^{xi}	118.74 (3)
O1 ^{vi} —Na1—Na1 ^{xii}	102.250 (15)	Na1 ^{vii} —O1—Na1 ^{xi}	100.96 (2)
O1 ^{vii} —Na1—Na1 ^{xii}	65.896 (14)		

Symmetry codes: (i) $-y+5/4, x+1/4, -z+1/4$; (ii) $-x+1, -y+3/2, z$; (iii) $y-1/4, -x+5/4, -z+1/4$; (iv) $x-1, y-1/2, -z$; (v) $y-3/4, -x+5/4, z+1/4$; (vi) $-y+3/4, x-3/4, z+1/4$; (vii) $-x+1, -y+1, -z$; (viii) $-y+1/4, x-3/4, -z+1/4$; (ix) $-x+1, -y+1/2, z$; (x) $x-1, y, z$; (xi) $x+1, y, z$; (xii) $-x, -y, -z$; (xiii) $-x+1/2, -y+1/2, -z+1/2$; (xiv) $-x, -y+1, -z$; (xv) $-x-1/2, -y+1/2, -z+1/2$.