Acta Cryst C STRUCTURAL CHEMISTRY

ISSN 2053-2296

Iron(II) and copper(II) paratungstates B: a single-crystal X-ray diffraction study

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Received 17 May 2018
Accepted 11 July 2018

Edited by J. R. Galán-Mascarós, Institute of Chemical Research of Catalonia (ICIQ), Spain

Keywords: polyoxometalate; POM; isopolytungstate; three-dimensional structure; crystal structure; dodecatungstate; IPOT.

CCDC references: 1843518; 1843519

Supporting information: this article has supporting information at journals.iucr.org/c

Paratungstate B is a common isopolytungstate (IPOT) built of the $[W_{12}O_{40}(OH)_2]^{10-}$ anion and exhibits a cluster-like construction of 12 W-centred distorted octahedra. Due to a high surface charge density, the paratungstate anion acts as a multidentate ligand forming high-dimensional extended structures, which exhibit unique catalytic and magnetic properties. Two new paradodecatungstate B compounds decorated by iron(II) or copper(II), namely $Na_5Fe_{2.5}[W_{12}O_{40}(OH)_2]\cdot 36H_2O$ (**$Na_5Fe_{2.5}$paraB**) and $Na_4Cu_3[W_{12}O_{40}(OH)_2]\cdot 28H_2O$ (**Na_4Cu_3paraB**), have been synthesized by a convenient aqueous solution method, and structurally characterized by single-crystal and powder X-ray diffraction, IR spectroscopy, elemental analysis and thermogravimetric analysis. Both compounds crystallize in the triclinic $P\overline{1}$ space group. In both compounds, the $[W_{12}O_{40}(OH)_2]^{10-}$ polyanion acts as a multidentate ligand that links transition-metal and sodium cations, forming a three-dimensional framework.

1. Introduction

The structural diversity of polyoxometalates (Pope, 1983) and their proven applications in catalysis (Wang & Yang, 2015), nanotechnology (Yamase & Pope, 2002), electrochemistry (Sadakane & Steckhan, 1998), materials science (Proust *et al.*, 2008), molecular magnetism (Clemente-Juan *et al.*, 2012), macromolecular crystallography (Bijelic & Rompel, 2015, 2017; Molitor *et al.*, 2017) and medicine (Fu *et al.*, 2015; Bijelic *et al.*, 2018*a*,*b*) have encouraged the synthesis of novel polyanions with promising properties. One of the most common isopolytungstates (IPOTs) is paratungstate B, built of the $[W_{12}O_{40}(OH)_2]^{10-}$ anion that is stable in aqueous acidic solution and exhibits a cluster-like construction of 12 W-centred distorted octahedra (Evans & Rollins, 1976; Pope, 1983). Due to a high surface charge density, the paratungstate anion acts as a multidentate ligand, which can coordinate alkaline (Peresypkina *et al.*, 2014) and transition-metal cations (Radio *et al.*, 2010, 2011; Gumerova *et al.*, 2015), and also act as a precursor (Sokolov *et al.*, 2012). By coordinating transition-metal cations, paratungstates can form high-dimensional extended structures, which exhibit unique catalytic (He *et al.*, 2008; Chen *et al.*, 2017) and magnetic properties (Li *et al.*, 2008, 2009). So far, three paratungstates B with Fe^{II} and nine with Cu^{II} as counter-cations have been successfully synthesized and characterized by X-ray diffraction (Table 1). We present herein two novel paratungstates B, one with Fe^{II} and one with Cu^{II}, namely the double sodium–iron(II) paratungstate $Na_5Fe_{2.5}[W_{12}O_{40}(OH)_2]\cdot 36H_2O$ (denoted **$Na_5Fe_{2.5}$paraB**) and the double sodium–copper(II) paratungstate $Na_4Cu_3[W_{12}O_{40}(OH)_2]\cdot 28H_2O$ (denoted **Na_4Cu_3paraB**),

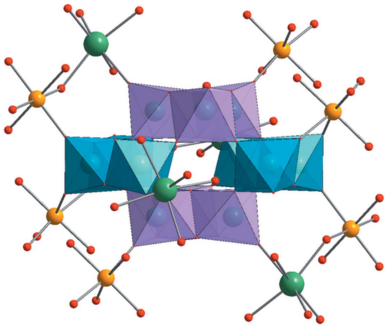

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Table 1
Fe^{II}- and Cu^{II}-containing paratungstates B [based on the Inorganic Crystal Structure Database (FIZ, Karlsruhe; http://www.fiz-informationsdienste.de/DB/icsd/www-recherche.html) and the Cambridge Structural Database (CSD; Groom *et al.*, 2016)].

Compounds	Unit-cell parameters *a*, *b* and *c* (Å), and α, β and γ (°)	Volume (Å^3), *Z* and space group	Synthesis details (source of W; W:M^{II} ratio, with *M* = Fe, Cu; pH)	Reference
Fe^{II}				
$K_6[\{Fe(H_2O)_4\}_2(H_2W_{12}O_{42})]\cdot15H_2O$	14.9967 (5), 10.3872 (3), 18.8237 (6); 90, 93.407 (1), 90	2927.1 (2), 2, $P2_1/n$	K_2WO_4; 12:1.4; –	Yang *et al.* (2003)
$(H_3O)_2[\{Fe(H_2O)_4Fe(H_2O)_3\}_2(H_2W_{12}O_{42})]\cdot20H_2O$	12.1794 (4), 22.4938 (4), 11.6941 (3); 90, 105.731 (2), 90	3083.7 (1), 2, $P2_1/c$	Li_2WO_4; 12:1.4; –	Yang *et al.* (2003)
$Na_5[\{Fe(H_2O)_3\}_2[Fe(H_2O)_4]_{0.5}(H_2W_{12}O_{42})]\cdot30H_2O$	12.121 (2), 12.426 (3), 13.247 (3); 68.33 (3), 71.33 (3), 71.44 (3)	1710.7 (6), 1, $P\overline{1}$	Na_2WO_4; 12:1.4; –	Yang *et al.* (2003)
Cu^{II}				
$Na_8[Cu(H_2O)_2(H_2W_{12}O_{42})]\cdot30H_2O$	13.081 (4), 13.160 (6), 20.127 (6); 78.294 (12), 78.524 (11), 72.593 (11)	3201.7 (17), 2, $P\overline{1}$	Na_2WO_4; 12:2.4; 4.8	Li *et al.* (2008)
$KNa_3[Cu(H_2O)_2\{Cu(H_2O)_3\}_2(H_2W_{12}O_{42})]\cdot16H_2O$	10.799 (2), 11.914 (2), 13.377 (3); 70.18 (3), 68.07 (3), 64.80 (3)	1410.9 (5), 1, $P\overline{1}$	$Na_2[W_{12}O_{40}(OH)_2]$; 12:2; 3.5	Li *et al.* (2009)
$[\{Na_2(\mu\text{-}H_2O)_2(H_2O)_6\}\{Cu(H_2O)_2\}\{Cu(H_2O)_4\}_2\text{-}\{Cu_2(\mu\text{-}OH)_2(H_2O)_6\}(H_2W_{12}O_{42})]\cdot10H_2O$	10.697 (5), 12.921 (5), 13.653 (5); 73.608 (5), 75.671 (5), 67.748 (5)	1654.4 (12), 1, $P\overline{1}$	$(NH_4)_6[W_{12}O_{40}]$; 12:0.4; 6.2	Kong *et al.* (2010)
$[\{Na(H_2O)_4\}_2\{Cu_{0.5}(H_2O)\}_4\{Cu_{0.5}(H_2O)_{1.5}\}_2\text{-}(H_4W_{12}O_{42})]\cdot3H_2O$	10.7060 (11), 12.7124 (14), 13.1664 (14); 113.7600 (10), 90.8230 (10), 111.8290 (10)	1493.8 (3), 1, $P\overline{1}$	Na_2WO_4; 12:3; 6.5	Gao *et al.* (2011)
$[Na_2(H_2O)_{10}][Cu_4(H_2O)_{12}(H_2W_{12}O_{42})]\cdot15H_2O$	10.1535 (2), 13.2118 (3), 13.7049 (5); 112.692 (3), 94.771 (3), 102.969 (2)	1623.15 (8), 1, $P\overline{1}$	Na_2WO_4; 12:36; 4	Qu *et al.* (2012)
$Cu_3(H_2O)_8[H_6W_{12}O_{42}]$	10.6753 (5), 12.7814 (5), 13.0976 (5); 113.737 (4), 90.433 (3), 112.560 (4)	1482.73 (12), 2, $P\overline{1}$	$(NH_4)_6[W_{12}O_{40}]$; 12:36; –	Chen *et al.* (2017)
$(NH_4)_8[Cu(H_2O)_2H_2W_{12}O_{42}]\cdot10H_2O$	14.278 (5), 15.435 (5), 24.881 (5); 90, 90, 90	5483 (3), 2, *Pbcn*	$(NH_4)_6[W_{12}O_{40}]$; 12:2.5; 4.8	Zhang (2012)
$Na_2Cu_3(CuOH)_2[W_{12}O_{40}(OH)_2]\cdot32H_2O$	10.6836 (4), 12.9066 (6), 13.6475 (5); 73.561 (4), 75.685 (3), 67.666 (4)	1648.68 (12), 1, $P\overline{1}$	Na_2WO_4; 12:7.5; –	Radio *et al.* (2014)
$Na_2Cu_5(H_2O)_{24}(OH)_2[H_2W_{12}O_{42}]\cdot10H_2O$	10.7140 (8), 12.9476 (9), 13.6696 (10); 73.56, 75.73, 67.69	1661.8 (2), 1, $P\overline{1}$	Na_2WO_4; 12:20; 3.8	Qu *et al.* (2015)

Table 2
Experimental details.

	Na_4Cu_3paraBM	**$Na_5Fe_{2.5}$paraB**
Crystal data		
Chemical formula	$Na_4Cu_3[W_{12}O_{40}(OH)_2]\cdot28H_2O$	$Na_5Fe_{2.5}[W_{12}O_{40}(OH)_2]\cdot36H_2O$
M_r	3621.13	3771.27
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	100	100
a, *b*, *c* (Å)	10.6516 (5), 12.7532 (6), 13.0730 (5)	12.3758 (6), 14.7752 (7), 18.8919 (8)
α, β, γ (°)	113.771 (1), 90.443 (1), 112.502 (1)	92.9341 (14), 100.6938 (14), 94.1698 (15)
V (Å^3)	1473.65 (11)	3378.1 (3)
Z	1	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	24.53	21.02
Crystal size (mm)	0.13 × 0.07 × 0.02	0.37 × 0.07 × 0.04
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.004, 0.023	0.012, 0.044
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11292, 5321, 4720	38068, 12318, 10876
R_{int}	0.048	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.602
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.098, 1.05	0.022, 0.058, 1.09
No. of reflections	5321	12318
No. of parameters	463	980
No. of restraints	100	405
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.15, −1.63	1.57, −1.25

Computer programs: *APEX3* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXS97* (Sheldrick, 2008), *shelXle* (Hübschle *et al.*, 2011), *SHELXL2014* (Sheldrick, 2015), *SHELXL2016* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *DIAMOND* (Brandenburg, 2006).

which were synthesized by a convenient aqueous solution method.

2. Experimental

2.1. Synthesis and crystallization

The reagents were used as purchased from Sigma–Aldrich without further purification.

2.1.1. Synthesis of $Na_5Fe_{2.5}$paraB. Iron powder (0.112 g, 2 mmol) was added to a solution (15 ml) of $Na_2WO_4{\cdot}2H_2O$ (3.96 g, 12 mmol), which was acidified to pH = 2.5 with HCl (1 *M*). The mixture was stirred in an ultrasonic bath, giving a deep-blue solution, which was left to stand closed at room temperature. The pale-red–brown crystals which grew on the beaker walls were collected after three weeks (yield ∼2 g, ∼53%, based on W). Elemental analysis found (calculated) for $Fe_{2.5}H_{74}Na_5O_{78}W_{12}$ (%): Na 3.13 (3.03), Fe 3.71 (3.69), W 56.8 (58.32).

2.1.2. Synthesis of Na_4Cu_3paraB. Sodium orthotungstate $Na_2WO_4{\cdot}2H_2O$ (5.5 g, 16.7 mmol) was dissolved in water (25 ml) and the pH was adjusted to 8 by adding dilute HNO_3 (1 *M*). An aqueous solution (10 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.5 g, 2.1 mmol) was then added dropwise, while the pH was maintained between 3.0 and 4.5 with HNO_3 (1 *M*). The final mixture was filtered (pH = 4.2) and allowed to stand closed at room temperature. Light-blue crystals formed within two months (yield ∼3.5 g, 69% based on W). Elemental analysis found (calculated) for $Cu_3H_{58}Na_4O_{70}W_{12}$ (%): Na 2.62 (2.51), Cu 5.13 (5.20), W 59.1 (60.16).

2.2. IR spectroscopy

The title compounds were identified by IR measurements on a Bruker Vertex70 IR Spectrometer equipped with a single-reflection diamond-ATR unit (ATR is attenuated total reflectance) in the range 4000–400 cm^{-1}.

2.3. TGA measurements

Thermogravimetric analysis (TGA) was performed on a Mettler SDTA851e Thermogravimetric Analyzer under a

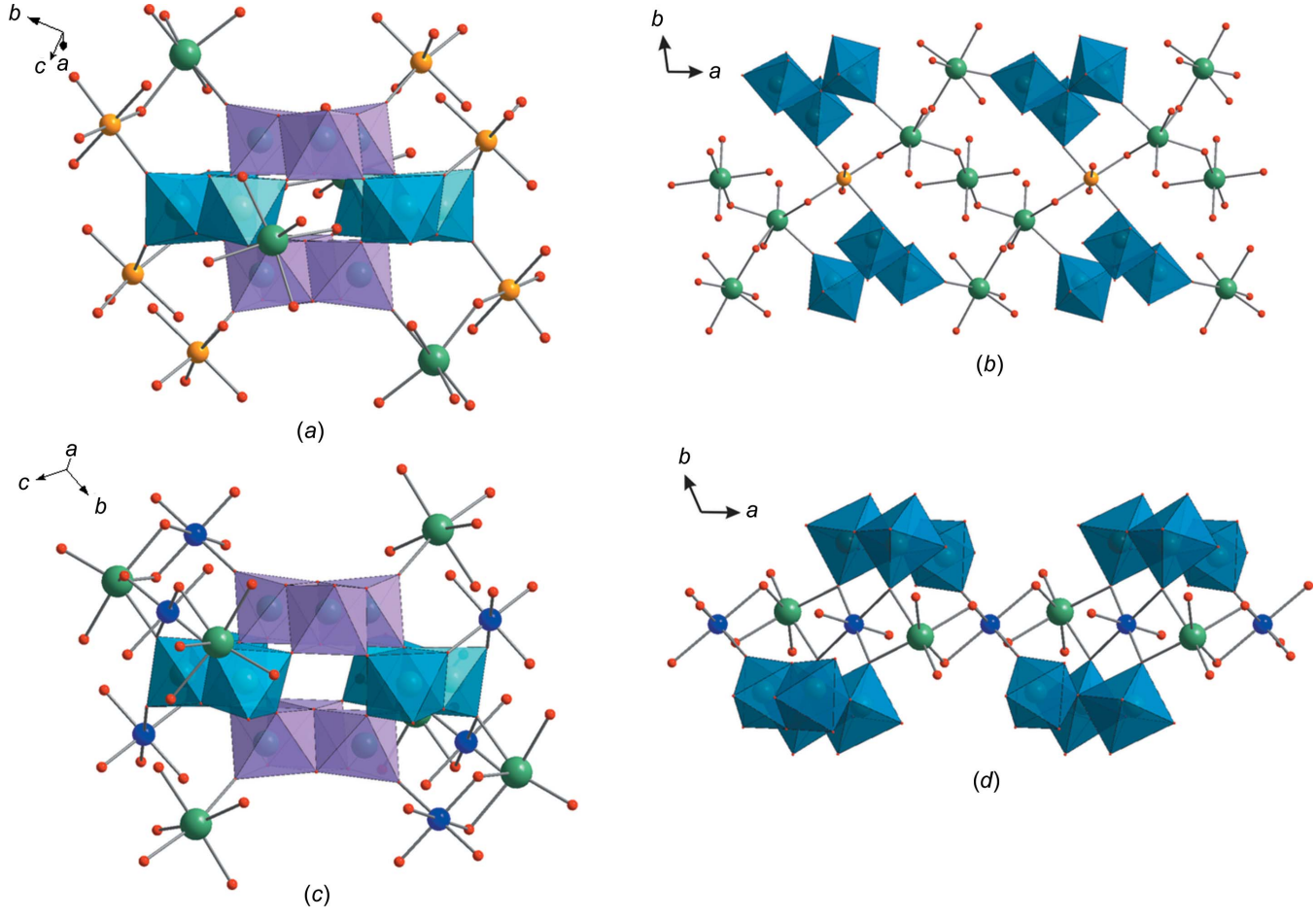

Figure 1
Structural elements in **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB**. (*a*) The $[W_{12}O_{40}(OH)_2]^{10-}$ anion in **$Na_5Fe_{2.5}$paraB** connected to four Na^+ and six Fe^{2+} ions *via* terminal O atoms. (*b*) A fragment of the infinite 1D chain in **$Na_5Fe_{2.5}$paraB** consisting of Na and Fe polyhedra. (*c*) The $[W_{12}O_{40}(OH)_2]^{10-}$ anion in **Na_4Cu_3paraB** connected to six Na^+ and six Cu^{2+} ions *via* terminal O atoms. (*d*) A fragment of the infinite 1D chain in **Na_4Cu_3paraB** consisting of Na and Cu polyhedra. Colour code: {WO_6} are light-blue or violet octahedra, {W_3O_{14}} are blue octahedra and {W_3O_{13}} are violet octahedra, and Na atoms are green, Fe orange, Cu blue and O red.

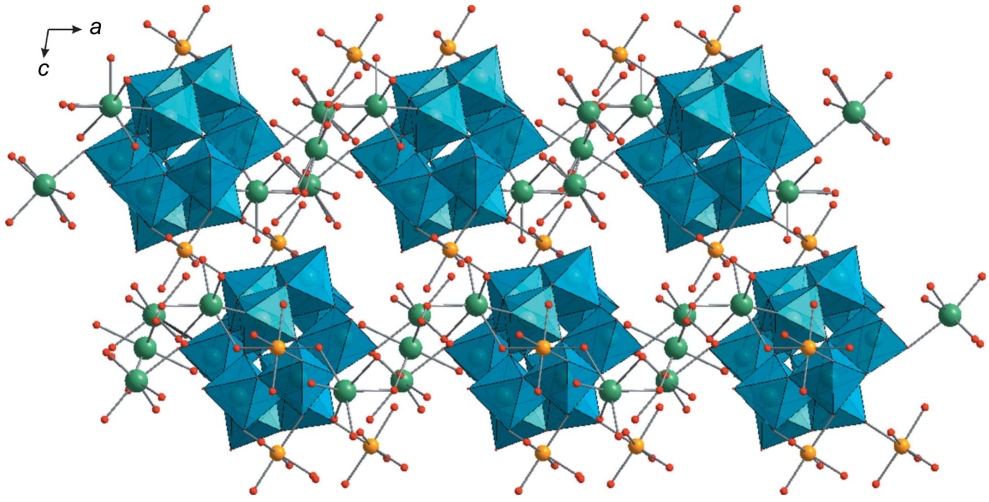

Figure 2
The crystal packing of **$Na_5Fe_{2.5}$paraB**, viewed along the *b* axis. Colour code: {WO_6} are light-blue octahedra and Na atoms are green, Fe yellow and O red.

nitrogen flow with a heating rate of 5 K min^{-1} in the region from 298 to 973 K.

2.4. Elemental analysis

Elemental analysis was conducted using inductive-coupled plasma–mass spectrometry (PerkinElmer Elan 6000 ICP MS) and atomic absorption spectroscopy (PerkinElmer 1100 Flame AAS) in aqueous solutions containing 2% HNO_3. Standards were prepared from single-element standard solutions of concentration 1000 mg l^{-1} (from Merck, Ultra Scientific and Analytika Prague).

2.5. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer, with Cu $K\alpha$ radiation (λ = 1.54056 Å), a Lynxeye silicon strip detector, a SolX energy dispersive detector and a variable slit aperture of 12 mm. The 2θ range was 8–50°.

2.6. Refinement

In Table 2, the crystallographic characteristics of the two new paratungstates B and the experimental conditions of the data collection and refinement are reported. The positions of the independent H atoms were obtained by difference Fourier techniques and were refined with free isotropic displacement parameters.

Fixed isotropic displacement parameters for all H atoms with a value equal to 1.5U_{eq} of the corresponding O—H group atom were assigned. Restrained distances for D—H bonds were applied to avoid short D—H···H—D interactions. To force correct bonds, specified bonds were added to or removed from the connectivity list.

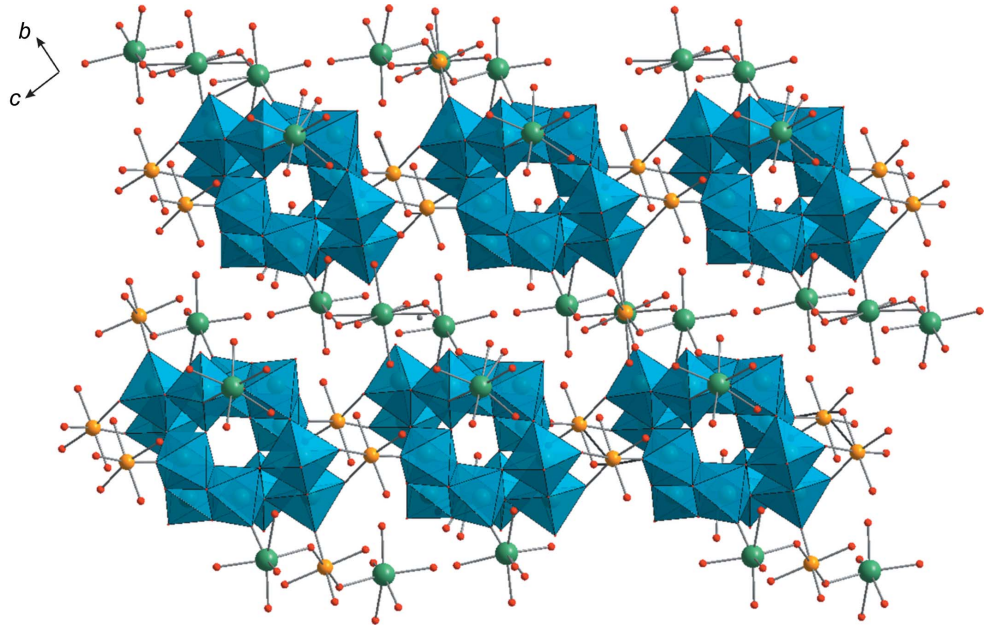

Figure 3
The crystal packing of **$Na_5Fe_{2.5}$paraB**, viewed along the *a* axis. Colour code: {WO_6} are light-blue octahedra and Na atoms are green, Fe yellow and O red.

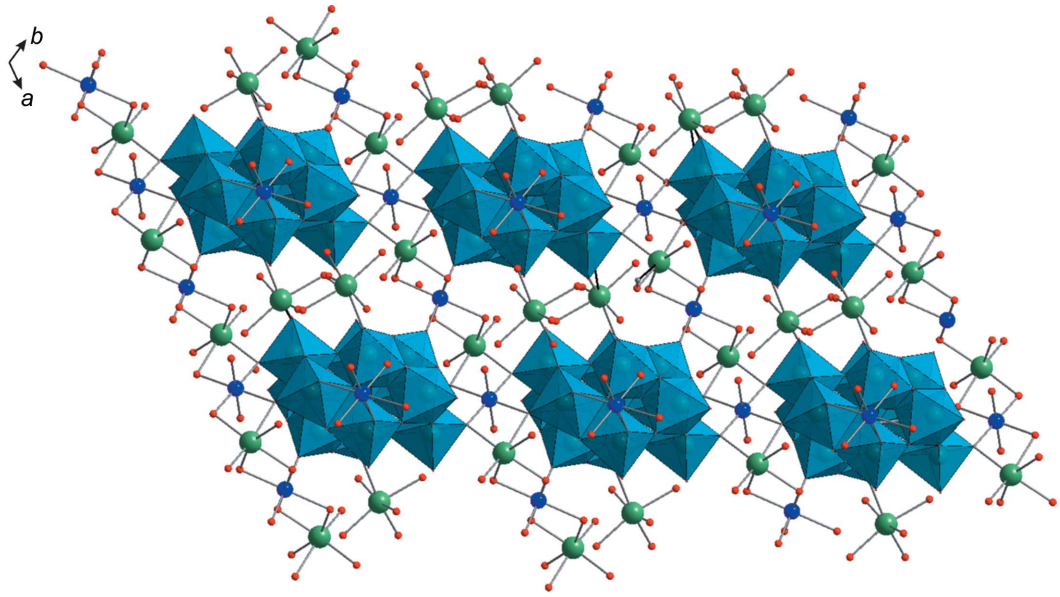

Figure 4
The crystal packing of **Na_4Cu_3paraB**, viewed along the *c* axis. Colour code: {WO_6} are light-blue octahedra and Na atoms are green, Cu blue and O red.

The disordered water molecules in the coordination spheres of atom Na1 in **Na_4Cu_3paraB** and of atoms Na4 and Na5 in **$Na_5Fe_{2.5}$paraB** were refined with two positions with fixed occupancy factors of 0.5.

In **Na_4Cu_3paraB**, part of the disordered water molecules were not modelled and the disordered density was considered using the *OLEX2* (Dolomanov *et al.*, 2009) implementation of *BYPASS* (a.k.a. SQUEEZE; Spek, 2015). The modelled electron density is consistent with approximately four water molecules per unit cell.

The structures have been deposited with the Inorganic Crystal Structure Database (ICSD) (http://www2.fiz-karlsruhe.de/icsd_home.html) under collection numbers 434558 and 434559.

3. Results and discussion

The syntheses of **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB** were carried out with W^{VI}-to-M^{II} ratios of W:Fe = 12:2 and W:Cu = 12:1.5, and a pH of 2.5 for **$Na_5Fe_{2.5}$paraB** and 4.2 for **Na_4Cu_3paraB**, which are different from previously reported conditions (Table 1) and made it possible to obtain compounds with new Fe–Na and Cu–Na compositions. The presence of Na^I as counter-cation in paratungstates B, together with Cu^{II} or Fe^{II}, have been observed previously both in excess and in deficiency of the transition-metal ion in the reaction mixture, which had a pH in the range 3.5–6.5 (Table 1). This allows one to conclude that crystallization of paratungstates B as double-alkali–transition-metal salts is more preferable than crystallization of pure transition-metal paratungstates B, regardless of the starting molar ratios of the components and the pH of the reaction system.

The main structural elements of **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB** are shown in Fig. 1. Both compounds consist of paradodecatungstate B $[W_{12}O_{40}(OH)_2]^{10-}$ polyanions (Evans & Rollins, 1976; Pope, 1983), sodium and transition-metal cations, and additional water molecules (Fig. 1). The paratungstate B units observed in **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB** are structurally identical to previously reported units (Table 1).

In **Na_4Cu_3paraB**, there is one-half unit of the POM, which lies on an inversion centre, in the asymmetric unit. For **$Na_5Fe_{2.5}$paraB**, there are two independent half-POM units in the asymmetric unit.

The centrosymmetric $[W_{12}O_{40}(OH)_2]^{10-}$ anion consists of four corner-sharing groups: two {W_3O_{13}} (violet octahedra in Figs. 1*a* and 1*c*) and two {W_3O_{14}} (blue octahedra in Figs. 1*a* and 1*c*) units. Each {W_3O_{13}} fragment is formed by three edge-sharing {WO_6} octahedra with a common O atom, while in the {W_3O_{14}} triads, the three edge-sharing {WO_6} octahedra are linearly connected with no common O atom to the three W atoms. In the {W_3O_{13}} groups, each octahedron has one terminal O atom, while in the {W_3O_{14}} units, each octahedron has two unshared O atoms (Figs. 1*a* and 1*c*). The O atoms

Table 3
Selected bond length and angles (Å, °) in **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB**.

	$Na_5Fe_{2.5}$paraB	**Na_4Cu_3paraB**
W═O_t	1.719 (4)–1.797 (4)	1.710 (8)–1.780 (7)
W—O_{db1}	1.888 (4)–2.050 (2)	1.872 (7)–2.103 (7)
W—O_{db2}	1.826 (3)–2.166 (3)	1.805 (7)–2.098 (7)
W—O_{tb1}	2.201 (3)–2.297 (3)	2.207 (7)–2.273 (7)
W—O_{tb2}	1.895 (4)–2.259 (4)	1.882 (8)–2.287 (7)
W···W (between corner-sharing WO_6)	3.649 (4)–3.878 (5)	3.377 (4)–3.688 (2)
W···W (between edge-sharing WO_6)	3.273 (4)–3.352 (4)	3.306 (2)–3.377 (3)
M^{II}—O (M = Fe or Cu)	2.087 (4)–2.169 (4)	1.918 (7)–2.366 (8)
Na^I—O	2.302 (11)–2.606 (11)	2.345 (9)–2.519 (13)
O—W—O	70.73 (14)–104.38 (17) 70.2 (3)–105.6 (3)	154.94 (15)–177.56 (16) 152.8 (3)–178.1 (3)

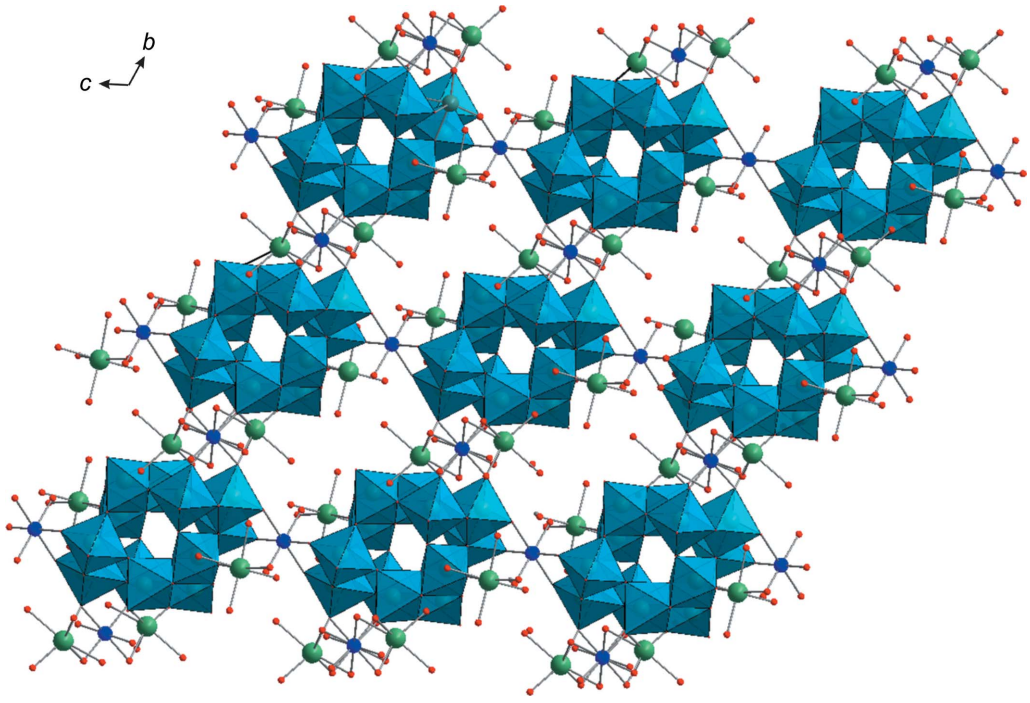

Figure 5
The crystal packing of **Na_4Cu_3paraB**, viewed along the *a* axis. Colour code: {WO_6} are light-blue octahedra and Na atoms are green, Cu blue and O red.

connected to the W centres can be classified into three groups. The first group is comprised of terminal O atoms (O_t), each bonded to one W atom. The second group consists of bridging O atoms (O_{db}), each connected to two W atoms. There are two types of O_{db}, one bridges two W atoms within the same {W_3O_{13}} or {W_3O_{14}} fragment (O_{db1}), while the other bridges two W atoms between the different {W_3O_{13}} and {W_3O_{14}} units (O_{db2}). The third group contains triply bridging O atoms, linked by three W atoms. The triply bridging O atoms exclusively from {W_3O_{13}} are labelled O_{tb1}, whereas the O atoms bridging three W atoms between {W_3O_{13}} and {W_3O_{14}} units are labelled as O_{tb2}.

The exact positions of the two protons in $[W_{12}O_{40}(OH)_2]^{10-}$ were located previously on triply bridging O atoms of {W_3O_{13}} by neutron diffraction (Evans & Prince, 1983). Selected bond lengths and angles are presented in Table 3. All the W atoms in $[W_{12}O_{40}(OH)_2]^{10-}$ exhibit the +VI oxidation state, when applying the bond valence sum (BVS) calculations of Brown & Altermatt (1985). For **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB**, we got average values of 6.01 and 6.09, respectively. BVS calculations for Fe and Cu sites show that both ions exhibit the +II oxidation state, with a value of 2.12 for Fe and 2.08 for Cu.

In the crystal structure of **$Na_5Fe_{2.5}$paraB**, the paratungstate anions act as decadentate ligands, which are linked *via* terminal O atoms to six Fe^{2+} and four Na^+ cations. There are two crystallographically unique iron centres with different coordination modes (Figs. 1*a* and 1*b*). The coordination sphere of one type of Fe^{2+} atom (Fe2) is formed by two O_t from the belt unit {W_3O_{14}} of one $[W_{12}O_{40}(OH)_2]^{10-}$, one O_t from the capping {W_3O_{13}} group of a neighbouring polyanion and

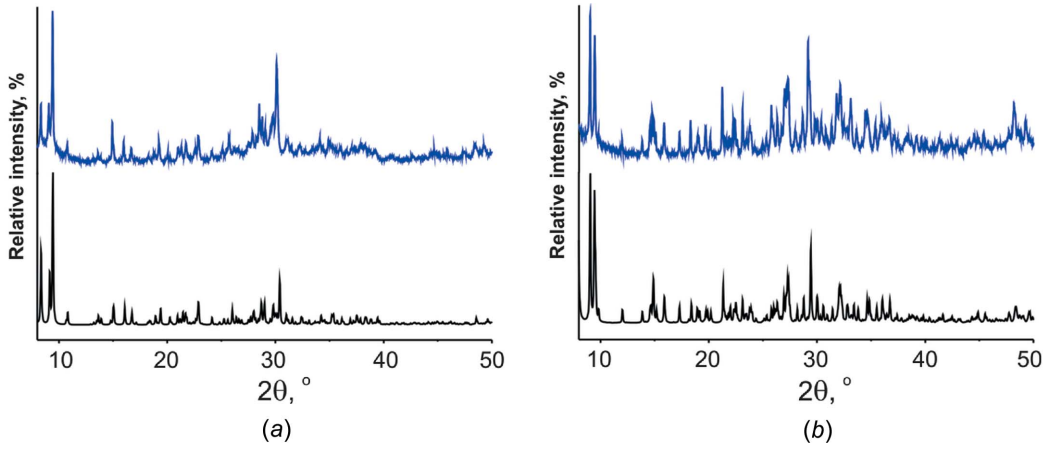

Figure 6
Experimental (blue) and simulated (black) X-ray diffraction patterns of (*a*) **Na_4Cu_3paraB** and (*b*) **$Na_5Fe_{2.5}$paraB**.

completed by three H_2O molecules. The octahedrally coordinated second Fe^{2+} atom (Fe1) is linked by two O_t from the $\{W_3O_{13}\}$ units of two neighbouring polyanions, two Na^+ bridging O atoms and two lattice H_2O molecules. The Fe1 octahedron and three $Na(H_2O)_6$ units from the infinite one-dimensional (1D) chain share a corner, thereby forming a two-dimensional sheet (2D) in the *ab* plane (Fig. 1*b*). Neighbouring sheets are connected to each other by Fe2 cations, giving rise to a complicated three-dimensional structure (Figs. 2 and 3). It should be noted that the double sodium–iron(II) paratungstate B $Na_5Fe_{2.5}[W_{12}O_{40}(OH)_2]\cdot 36H_2O$ reported in this work has the same cationic composition as reported in $Na_5[\{Fe(H_2O)_3\}_2\{Fe(H_2O)_4\}_{0.5}(H_2W_{12}O_{42})]\cdot 30H_2O$ (Yang *et al.*, 2003) (Table 1). However, the minor difference with respect to the water content in these two structures leads to a significant change in the unit-cell parameters (Tables 1 and 2) and the motif of crystal packing (Figs. 2 and 3).

In the crystal structure of **Na_4Cu_3paraB**, each paratungstate B anion is coordinated to six Cu^{2+} and six Na^+ *via* O_t and therefore acts as a dodecadentate ligand (Figs. 1*c* and 1*d*). There are three crystallographically unique copper centres with different coordination modes. Two (Cu1 and Cu2) out of three Cu^{2+} cations take part in the formation of infinite chains with alternating Na and Cu polyhedra connected by a common edge (Figs. 1*d* and 4) and have different coordination environments. The Cu2 atoms are linked by four O_t atoms of the belt-fragment $\{W_3O_{14}\}$ from two neighbouring $[W_{12}O_{40}(OH)_2]^{10-}$ anions and two Na^+ bridging H_2O molecules. The coordination sphere of Cu3 consists of two O_t of the capping $\{W_3O_{13}\}$ group of a neighbouring polyanion and is completed by four bridging H_2O molecules. The third Cu1 atom coordinates to four O_t atoms of the belt units $\{W_3O_{14}\}$ from two neighbouring $[W_{12}O_{40}(OH)_2]^{10-}$ anions and two H_2O molecules. The Cu^{2+} ions exhibit a distorted square–bipyramidal coordination geometry with elongated axial distances [2.365 (7)–2.520 (8) Å]. The three-dimensional (3D) structure of **Na_4Cu_3-paraB** consists of 2D sheets formed by two chains, namely $\{[(Na(H_2O)_2)_2W_{12}O_{40}(OH)_2]^{8-}\}_n$ and $\{[Na(H_2O)_2$–$Cu(H_2O)_2$–$Na(H_2O)_2$–$Cu(H_2O)_4]^{6+}\}_n$ parallel to the *ab* plane (Fig. 4). The 2D sheets are connected along the *c* axis by $[Cu(H_2O)_4]^{2+}$ cations (Fig. 5). The two $[Na(H_2O)_5]^+$ cations, which are connected to O_t of one polyanion and do not participate in the formation of sodium–copper chains, are located in 1D tunnels in the structure of **Na_4Cu_3-paraB**.

The results of the powder XRD patterns of **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB** have been investigated in the solid state at room temperature (Fig. 6). The simulated powder diffraction pattern was based on the single-crystal structural data. The simulated peak positions are in good agreement with those observed. A comparison of the experimental and simulated powder diffraction patterns confirms that the POTs structures had been solved accurately and that both products consist of a single phase.

In the IR spectra of **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3paraB**, the characteristic peaks at 975, 950, 932, 867, 676 and 488 cm^{-1}, and at 972, 937, 926, 872, 675 and 493 cm^{-1}, respectively, are attributed to the W═O_t and W—O—W vibrations in the

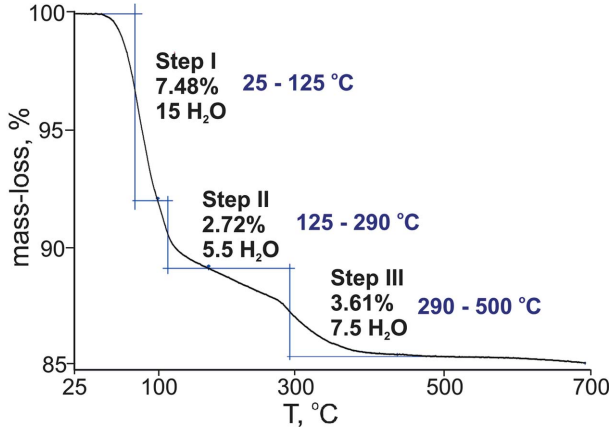

Figure 7
Thermogravimetric curve of **Na_4Cu_3paraB**.

paratungstate anion, which are in agreement with previously reported data (Table 1; Qu *et al.*, 2012). The slight peak displacements are due to the effects of different coordination modes of paratungstate B. The peaks at ~1600 and 3400 cm^{-1} are attributed to the vibration of water molecules.

The disordered water molecules in **Na_4Cu_3paraB** were treated with *SQUEEZE* (Spek, 2015) and the exact number of water molecules was determined by TGA. The TG curve shows a three-step weight-loss process (Fig. 7). The first weight loss of 7.48% in the temperature range 25–125 °C corresponds to all lattice H_2O and water molecules from coordinating Na^+ and Cu^{2+}. The second (2.72%) and third (3.61%) steps in the range 125–500 °C correspond to 13 H_2O molecules coordinating Na^+ and Cu^{2+}. The total weight loss is 13.83%, which results in the formula $Na_4Cu_3[W_{12}O_{40}(OH)_2]\cdot 28H_2O$.

The success in synthesizing **$Na_5Fe_{2.5}$paraB** and **Na_4Cu_3-paraB** shows that paratungstate B is a versatile building block, which can be modified by metal sites into high-dimensional architectures and the different connection principle of the transition metals has a big impact on the dimensionalities of the frameworks.

Acknowledgements

The authors are grateful to Assistant Professor Dr P. Unfried for support with the TGA and to Associate Professor K. Richter and M. Andraghetti for help with PXRD measurements at the Department of Inorganic Chemistry, University of Vienna. We thank RNDr Marek Bujdoš, PhD, for support with the ICP–MS and AAS analysis at the Institute of Laboratory Research on Geomaterials, Comenius University in Bratislava. We wish to thank E. Al-Sayed, MSc, and Dr J. Breibeck for valuable discussions regarding this work.

Funding information

Funding for this research was provided by: Austrian Science Fund (award No. M2203 to N. Gumerova; award No. P27534 to A. Rompel).

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Iron(II) and copper(II) paratungstates B: a single-crystal X-ray diffraction study

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Computing details

For both structures, data collection: *APEX3*; cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and shelXle (Hübschle *et al.*, 2011) for ando209_p-1; *SHELXS97* (Sheldrick, 2008) for mo_ando241_p-1. Program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) for ando209_p-1; *SHELXL2016* (Sheldrick, 2015) for mo_ando241_p-1. Molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) and *DIAMOND* (Brandenburg, 2006) for ando209_p-1; OLEX2 (Dolomanov *et al.*, 2009) for mo_ando241_p-1. For both structures, software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

(ando209_p-1)

Crystal data

$Na_4Cu_3[W_{12}O_{40}(OH)_2]\cdot 28H_2O$
M_r = 3621.13
Triclinic, $P\overline{1}$
a = 10.6516 (5) Å
b = 12.7532 (6) Å
c = 13.0730 (5) Å
α = 113.771 (1)°
β = 90.443 (1)°
γ = 112.502 (1)°
V = 1473.65 (11) Å^3
Z = 1
$F(000)$ = 1607
D_x = 4.080 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6027 reflections
θ = 3.0–30.0°
μ = 24.53 mm^{-1}
T = 100 K
Plate, blue
0.13 × 0.07 × 0.02 mm

Data collection

Bruker APEX-II CCD diffractometer
Radiation source: sealed xray tube, Incoatec IuS
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.004, T_{max} = 0.023
11292 measured reflections
5321 independent reflections
4720 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 25.4°, θ_{min} = 2.1°
h = −12→12
k = −15→14
l = −11→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.05
5321 reflections
463 parameters
100 restraints
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 6.2838P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 2.15 e Å^{-3}
$\Delta\rho_{min}$ = −1.63 e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00022 (6)

Special details

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

Refinement. _olex2_refinement_description
1. Fixed Uiso At 1.5 times of: All O(H,H) groups 2. Restrained distances Na2-H31A 2.8 with sigma of 0.05 H34B-H25A 2.2 with sigma of 0.02 H34A-H25A 2.2 with sigma of 0.03 H34B_$2-H31B 2.2 with sigma of 0.02 H34A_$4-H31B_$3 2.2 with sigma of 0.02 Cu3-H25A 2.7 with sigma of 0.05 Cu3-H25B 2.3 with sigma of 0.02 H35A-O24 1.8 with sigma of 0.06 H35B-O19 2 with sigma of 0.06 Na1-H27B 2.8 with sigma of 0.05 Na1-H27C = Na1-H27A = Na1-H27D 2.8 with sigma of 0.05 H33B-Na1 2.8 with sigma of 0.02 H33B-O27 2.4 with sigma of 0.05 Na1-H28A 2.7 with sigma of 0.04 H33B-H28A 2.4 with sigma of 0.04 H32A_$3-O26 1.8 with sigma of 0.04 Na2-H31B = Na2-H32B 2.8 with sigma of 0.075 O32-H27B_$5 2.3 with sigma of 0.04 H29A_$1-H22A 2.2 with sigma of 0.02 O31-H31A = O31-H31B = O26-H26B = O26-H26A = O29-H29B = O29-H29A = O30-H30A = O30-H30B = O32-H32A = O32-H32B = O27-H27A = O27-H27B = O22-H22A = O22-H22B = O25-H25A = O25-H25B = O28-H28A = O28-H28B = O33-H33A = O33-H33B 0.87 with sigma of 0.015 Na1_$5-H29A_$5 2.7 with sigma of 0.04 H31A-H31B ~ H32B-H32A ~ H29A-H29B ~ H30A-H30B ~ H26B-H26A ~ H27A-H27B ~ H22A- H22B ~ H25A-H25B ~ H28A-H28B ~ H33A-H33B with sigma of 0.01 3. Uiso/Uaniso restraints and constraints Uanis(O3) ~ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(O35) ~ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(O27) = Uanis(O27B) = Uanis(O33) 4. Others Fixed Sof: O27(0.5) H27A(0.5) H27B(0.5) O27B(0.5) H27C(0.5) H27D(0.5) O33(0.2) H33A(0.2) H33B(0.2) O34(0.8) H34A(0.8) H34B(0.8) 5.a Free rotating group: O27B(H27C,H27D), O35(H35A,H35B), O34(H34A,H34B) 5.b Rotating group: O26(H26A,H26B), O30(H30A,H30B)
_smtbx_masks_special_details ? loop_ _smtbx_masks_void_nr _smtbx_masks_void_average_x _smtbx_masks_void_average_y _smtbx_masks_void_average_z _smtbx_masks_void_volume _smtbx_masks_void_count_electrons _smtbx_masks_void_content 1 0.500 0.000 0.000 42.5 50.5 ?

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
W1	0.40078 (5)	0.59904 (4)	0.70077 (4)	0.02587 (13)	
W2	0.29232 (5)	0.29326 (4)	0.70980 (4)	0.02647 (13)	
W3	0.11342 (5)	0.30259 (4)	0.50852 (4)	0.02644 (13)	
W4	0.36784 (5)	0.55467 (4)	0.25109 (4)	0.02598 (13)	
W5	0.25460 (5)	0.24015 (4)	0.24532 (4)	0.02651 (13)	
W6	0.44888 (5)	0.25037 (4)	0.45361 (4)	0.02571 (13)	
Cu1	0.5000	0.5000	0.0000	0.0295 (4)	
Cu2	0.5000	0.0000	0.5000	0.0318 (4)	
Cu3	0.0000	0.0000	0.5000	0.0292 (4)	
Na1	0.1011 (5)	0.6455 (5)	0.8881 (4)	0.0388 (11)	
Na2	0.2217 (6)	−0.0459 (5)	0.6480 (4)	0.0453 (12)	
O1	0.4360 (8)	0.7354 (7)	0.6568 (6)	0.0307 (17)	
O2	0.2961 (8)	0.6304 (7)	0.7964 (6)	0.0321 (18)	
O3	0.2806 (8)	0.4797 (7)	0.5682 (6)	0.0274 (16)	
O4	0.4464 (8)	0.4809 (7)	0.7296 (6)	0.0287 (17)	
O5	0.2953 (7)	0.3510 (7)	0.8548 (6)	0.0278 (16)	
O6	0.1920 (8)	0.1290 (7)	0.6530 (7)	0.0311 (17)	
O7	0.4689 (7)	0.2862 (7)	0.7099 (6)	0.0265 (16)	

O8	0.1595 (8)	0.3407 (7)	0.6693 (6)	0.0280 (17)	
O9	0.3000 (7)	0.2617 (7)	0.5253 (6)	0.0256 (16)	
O10	0.0060 (8)	0.1394 (7)	0.4742 (6)	0.0283 (17)	
O11	0.1443 (7)	0.2788 (7)	0.3603 (6)	0.0273 (16)	
O12	−0.0075 (8)	0.3650 (7)	0.5232 (6)	0.0303 (17)	
O13	0.3723 (8)	0.5048 (7)	0.1034 (6)	0.0303 (17)	
O14	0.2479 (8)	0.6201 (7)	0.2670 (6)	0.0292 (17)	
O15	0.2601 (8)	0.3979 (7)	0.2454 (6)	0.0285 (17)	
O16	0.4167 (8)	0.2715 (7)	0.1837 (6)	0.0277 (17)	
O17	0.1273 (8)	0.1263 (7)	0.1285 (6)	0.0321 (18)	
O18	0.4261 (8)	0.3860 (7)	0.3991 (6)	0.0270 (16)	
O19	0.2939 (8)	0.1433 (7)	0.3058 (6)	0.0278 (16)	
O20	0.4522 (8)	0.1175 (7)	0.4616 (6)	0.0308 (17)	
O21	0.5820 (8)	0.3799 (7)	0.5722 (6)	0.0278 (17)	
O22	0.5004 (8)	0.6562 (7)	−0.0030 (7)	0.0322 (18)	
H22A	0.484 (6)	0.641 (10)	−0.074 (3)	0.048*	
H22B	0.572 (9)	0.722 (8)	0.045 (6)	0.048*	
O23	0.2659 (9)	−0.1426 (8)	0.4500 (7)	0.039 (2)	
O24	0.5333 (8)	−0.0689 (7)	0.3444 (7)	0.0329 (18)	
O25	0.1090 (9)	−0.0398 (7)	0.3744 (7)	0.039 (2)	
H25A	0.110 (4)	−0.105 (2)	0.3192 (19)	0.059*	
H25B	0.166 (10)	0.037 (2)	0.392 (8)	0.059*	
O26	0.0069 (9)	0.5944 (8)	0.7000 (7)	0.0376 (19)	
H26A	−0.0758	0.6059	0.6943	0.056*	
H26B	−0.0175	0.5090	0.6477	0.056*	
O28	−0.0711 (10)	0.6370 (10)	1.0034 (8)	0.053 (3)	
H28A	−0.148 (3)	0.585 (9)	0.954 (3)	0.080*	
H28B	−0.056 (11)	0.635 (12)	1.068 (7)	0.080*	
O29	0.2535 (9)	0.6809 (10)	1.0510 (8)	0.047 (2)	
H29A	0.310 (7)	0.654 (10)	1.013 (4)	0.070*	
H29B	0.282 (10)	0.757 (6)	1.107 (9)	0.070*	
O30	0.0122 (9)	0.4225 (8)	0.8273 (7)	0.039 (2)	
H30A	0.0498	0.3733	0.7612	0.058*	
H30B	−0.0916	0.3696	0.7900	0.058*	
O31	0.2749 (14)	0.1008 (11)	0.8572 (10)	0.072 (3)	
H31A	0.306 (13)	0.060 (8)	0.883 (4)	0.107*	
H31B	0.196 (6)	0.105 (11)	0.867 (7)	0.107*	
O32	0.2210 (10)	−0.1857 (9)	0.7127 (9)	0.051 (2)	
H32A	0.150 (6)	−0.252 (9)	0.712 (13)	0.077*	
H32B	0.305 (4)	−0.174 (11)	0.736 (14)	0.077*	
O27	0.158 (3)	0.860 (3)	0.922 (2)	0.057 (5)	0.5
H27A	0.246 (5)	0.904 (6)	0.946 (10)	0.086*	0.5
H27B	0.113 (6)	0.858 (6)	0.865 (4)	0.086*	0.5
O27B	0.119 (3)	0.853 (3)	0.960 (2)	0.057 (5)	0.5
H27C	0.0694	0.8626	0.9158	0.086*	0.5
H27D	0.2008	0.9067	0.9675	0.086*	0.5
O35	0.3779 (17)	−0.0594 (14)	0.1911 (10)	0.097 (5)	
H35A	0.4125	−0.0615	0.2488	0.145*	

H35B	0.3375	−0.0105	0.2126	0.145*	
O33	0.004 (6)	0.884 (4)	1.035 (4)	0.057 (5)	0.2
H33A	0.07 (5)	0.951 (12)	1.09 (4)	0.086*	0.2
H33B	−0.012 (17)	0.808 (8)	1.027 (16)	0.086*	0.2
O34	−0.0162 (12)	−0.1184 (11)	0.1541 (9)	0.050 (3)	0.8
H34A	0.0167	−0.0472	0.2126	0.075*	0.8
H34B	−0.0554	−0.1769	0.1746	0.075*	0.8

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.0266 (2)	0.0247 (2)	0.0263 (2)	0.01145 (19)	0.00481 (18)	0.01057 (19)
W2	0.0264 (2)	0.0259 (2)	0.0273 (2)	0.01121 (19)	0.00467 (18)	0.01163 (19)
W3	0.0264 (2)	0.0253 (2)	0.0273 (2)	0.01089 (19)	0.00448 (18)	0.01138 (19)
W4	0.0262 (2)	0.0257 (2)	0.0260 (2)	0.01136 (19)	0.00429 (18)	0.01098 (19)
W5	0.0270 (2)	0.0250 (2)	0.0265 (2)	0.01085 (19)	0.00361 (18)	0.01049 (19)
W6	0.0266 (2)	0.0245 (2)	0.0259 (2)	0.01144 (19)	0.00433 (18)	0.01039 (19)
Cu1	0.0326 (10)	0.0310 (10)	0.0286 (10)	0.0162 (9)	0.0076 (8)	0.0138 (8)
Cu2	0.0351 (11)	0.0298 (10)	0.0326 (10)	0.0152 (9)	0.0068 (8)	0.0142 (9)
Cu3	0.0302 (10)	0.0274 (10)	0.0319 (10)	0.0130 (8)	0.0059 (8)	0.0140 (8)
Na1	0.037 (3)	0.042 (3)	0.039 (3)	0.019 (2)	0.008 (2)	0.017 (2)
Na2	0.045 (3)	0.037 (3)	0.052 (3)	0.015 (2)	0.004 (2)	0.021 (2)
O1	0.027 (4)	0.029 (4)	0.031 (4)	0.009 (3)	0.002 (3)	0.011 (3)
O2	0.032 (4)	0.038 (4)	0.032 (4)	0.017 (4)	0.004 (3)	0.019 (4)
O3	0.028 (4)	0.028 (4)	0.028 (4)	0.009 (3)	0.009 (3)	0.016 (3)
O4	0.031 (4)	0.025 (4)	0.035 (4)	0.015 (3)	0.009 (3)	0.014 (3)
O5	0.023 (4)	0.030 (4)	0.030 (4)	0.010 (3)	0.004 (3)	0.014 (3)
O6	0.031 (4)	0.029 (4)	0.036 (4)	0.015 (3)	0.005 (3)	0.015 (4)
O7	0.024 (4)	0.028 (4)	0.029 (4)	0.012 (3)	0.002 (3)	0.012 (3)
O8	0.026 (4)	0.033 (4)	0.026 (4)	0.011 (3)	0.005 (3)	0.015 (3)
O9	0.026 (4)	0.028 (4)	0.021 (4)	0.009 (3)	0.004 (3)	0.012 (3)
O10	0.028 (4)	0.023 (4)	0.030 (4)	0.007 (3)	0.002 (3)	0.011 (3)
O11	0.023 (4)	0.031 (4)	0.031 (4)	0.013 (3)	0.004 (3)	0.016 (3)
O12	0.032 (4)	0.037 (4)	0.029 (4)	0.017 (4)	0.011 (3)	0.018 (4)
O13	0.028 (4)	0.035 (4)	0.029 (4)	0.013 (3)	0.007 (3)	0.014 (3)
O14	0.031 (4)	0.026 (4)	0.030 (4)	0.011 (3)	0.007 (3)	0.013 (3)
O15	0.029 (4)	0.025 (4)	0.030 (4)	0.009 (3)	0.006 (3)	0.013 (3)
O16	0.034 (4)	0.030 (4)	0.020 (4)	0.015 (3)	0.006 (3)	0.010 (3)
O17	0.039 (5)	0.032 (4)	0.028 (4)	0.017 (4)	0.006 (3)	0.014 (3)
O18	0.028 (4)	0.021 (4)	0.029 (4)	0.008 (3)	0.002 (3)	0.010 (3)
O19	0.025 (4)	0.028 (4)	0.032 (4)	0.012 (3)	0.007 (3)	0.013 (3)
O20	0.033 (4)	0.033 (4)	0.030 (4)	0.016 (4)	0.010 (3)	0.015 (4)
O21	0.024 (4)	0.030 (4)	0.025 (4)	0.008 (3)	0.006 (3)	0.011 (3)
O22	0.033 (5)	0.032 (4)	0.029 (4)	0.017 (4)	0.002 (3)	0.008 (4)
O23	0.037 (5)	0.034 (4)	0.040 (5)	0.016 (4)	0.002 (4)	0.009 (4)
O24	0.032 (4)	0.029 (4)	0.034 (4)	0.013 (4)	0.003 (3)	0.010 (3)
O25	0.043 (5)	0.024 (4)	0.042 (5)	0.010 (4)	0.012 (4)	0.011 (4)
O26	0.036 (5)	0.042 (5)	0.038 (5)	0.020 (4)	0.007 (4)	0.017 (4)

O28	0.043 (6)	0.082 (7)	0.036 (5)	0.032 (5)	0.011 (4)	0.023 (5)
O29	0.044 (5)	0.062 (6)	0.045 (5)	0.031 (5)	0.016 (4)	0.026 (5)
O30	0.036 (5)	0.051 (5)	0.029 (4)	0.021 (4)	0.009 (4)	0.014 (4)
O31	0.102 (10)	0.065 (7)	0.054 (6)	0.043 (7)	0.005 (6)	0.025 (6)
O32	0.039 (5)	0.052 (6)	0.070 (7)	0.021 (5)	0.012 (5)	0.033 (5)
O27	0.070 (15)	0.047 (7)	0.062 (16)	0.028 (10)	0.021 (9)	0.027 (10)
O27B	0.070 (15)	0.047 (7)	0.062 (16)	0.028 (10)	0.021 (9)	0.027 (10)
O35	0.126 (11)	0.088 (9)	0.065 (7)	0.078 (8)	−0.027 (7)	−0.007 (6)
O33	0.070 (15)	0.047 (7)	0.062 (16)	0.028 (10)	0.021 (9)	0.027 (10)
O34	0.047 (7)	0.041 (6)	0.030 (6)	−0.005 (5)	0.010 (5)	0.008 (5)

Geometric parameters (Å, º)

W1—O1	1.951 (7)	Cu1—O22	2.007 (8)
W1—O2	1.710 (8)	Cu1—O22^{iv}	2.007 (8)
W1—O3	1.818 (7)	Cu2—Na2	3.542 (6)
W1—O4	1.914 (7)	Cu2—Na2^{v}	3.542 (6)
W1—O16^{i}	2.067 (8)	Cu2—O20	1.985 (8)
W1—O18^{i}	2.260 (8)	Cu2—O20^{v}	1.985 (8)
W2—O4	2.230 (7)	Cu2—O23	2.345 (8)
W2—O5	1.730 (7)	Cu2—O23^{v}	2.345 (8)
W2—O6	1.762 (8)	Cu2—O24	1.961 (8)
W2—O7	1.917 (7)	Cu2—O24^{v}	1.961 (8)
W2—O8	1.884 (8)	Cu3—Na2	3.400 (5)
W2—O9	2.287 (7)	Cu3—Na2^{ii}	3.400 (5)
W3—Na2^{ii}	3.632 (5)	Cu3—O6	2.366 (8)
W3—O3	2.088 (7)	Cu3—O6^{ii}	2.366 (8)
W3—O8	1.968 (7)	Cu3—O10	1.918 (7)
W3—O9	2.268 (8)	Cu3—O10^{ii}	1.918 (7)
W3—O10	1.805 (7)	Cu3—O25^{ii}	2.027 (8)
W3—O11	1.888 (7)	Cu3—O25	2.027 (8)
W3—O12	1.730 (8)	Na1—O2	2.439 (9)
W4—O4^{i}	2.226 (8)	Na1—O26	2.376 (9)
W4—O7^{i}	1.963 (7)	Na1—O28	2.380 (10)
W4—O13	1.780 (7)	Na1—O29	2.446 (11)
W4—O14	1.747 (8)	Na1—O30	2.392 (10)
W4—O15	1.855 (7)	Na1—O27	2.41 (3)
W4—O21^{i}	2.098 (7)	Na1—O27B	2.35 (3)
W5—O11	1.938 (7)	Na2—W3^{ii}	3.632 (5)
W5—O15	1.990 (7)	Na2—O6	2.345 (9)
W5—O16	1.882 (8)	Na2—O10^{ii}	2.459 (9)
W5—O17	1.718 (8)	Na2—O23	2.516 (10)
W5—O18	2.273 (7)	Na2—O24^{v}	2.432 (10)
W5—O19	1.872 (7)	Na2—O31	2.519 (13)
W6—O1^{i}	1.920 (8)	Na2—O32	2.260 (10)
W6—O9	1.872 (7)	O1—W6^{i}	1.920 (8)
W6—O18	2.207 (7)	O4—W4^{i}	2.226 (8)
W6—O19	2.103 (7)	O5—Cu1^{vi}	2.413 (7)

W6—O20	1.753 (8)	O7—W4^{i}	1.963 (7)
W6—O21	1.803 (7)	O10—Na2^{ii}	2.459 (9)
Cu1—O5^{iii}	2.413 (7)	O16—W1^{i}	2.067 (7)
Cu1—O5^{i}	2.413 (7)	O18—W1^{i}	2.260 (8)
Cu1—O13	1.926 (8)	O21—W4^{i}	2.098 (7)
Cu1—O13^{iv}	1.926 (8)	O24—Na2^{v}	2.432 (10)

O1—W1—O16^{i}	82.4 (3)	O24—Cu2—Na2^{v}	41.1 (2)
O1—W1—O18^{i}	70.2 (3)	O24^{v}—Cu2—Na2^{v}	138.9 (2)
O2—W1—O1	99.5 (3)	O24^{v}—Cu2—Na2	41.1 (2)
O2—W1—O3	104.1 (4)	O24—Cu2—O20	87.1 (3)
O2—W1—O4	102.2 (3)	O24—Cu2—O20^{v}	92.9 (3)
O2—W1—O16^{i}	94.8 (3)	O24^{v}—Cu2—O20^{v}	87.1 (3)
O2—W1—O18^{i}	164.6 (3)	O24^{v}—Cu2—O20	92.9 (3)
O3—W1—O1	93.2 (3)	O24—Cu2—O23	93.9 (3)
O3—W1—O4	94.1 (3)	O24^{v}—Cu2—O23^{v}	93.9 (3)
O3—W1—O16^{i}	161.1 (3)	O24—Cu2—O23^{v}	86.1 (3)
O3—W1—O18^{i}	88.3 (3)	O24^{v}—Cu2—O23	86.1 (3)
O4—W1—O1	154.6 (3)	O24^{v}—Cu2—O24	180.0
O4—W1—O16^{i}	82.8 (3)	Na2—Cu3—Na2^{ii}	180.0
O4—W1—O18^{i}	85.7 (3)	O6^{ii}—Cu3—Na2^{ii}	43.6 (2)
O16^{i}—W1—O18^{i}	72.9 (3)	O6—Cu3—Na2	43.6 (2)
O4—W2—O9	77.3 (3)	O6—Cu3—Na2^{ii}	136.4 (2)
O5—W2—O4	91.7 (3)	O6^{ii}—Cu3—Na2	136.4 (2)
O5—W2—O6	105.6 (3)	O6—Cu3—O6^{ii}	180.0 (3)
O5—W2—O7	98.5 (3)	O10—Cu3—Na2	134.8 (2)
O5—W2—O8	98.8 (3)	O10—Cu3—Na2^{ii}	45.2 (2)
O5—W2—O9	167.4 (3)	O10^{ii}—Cu3—Na2^{ii}	134.8 (2)
O6—W2—O4	161.2 (3)	O10^{ii}—Cu3—Na2	45.2 (2)
O6—W2—O7	96.2 (3)	O10^{ii}—Cu3—O6	86.7 (3)
O6—W2—O8	99.2 (3)	O10^{ii}—Cu3—O6^{ii}	93.3 (3)
O6—W2—O9	86.2 (3)	O10—Cu3—O6	93.3 (3)
O7—W2—O4	73.6 (3)	O10—Cu3—O6^{ii}	86.7 (3)
O7—W2—O9	84.4 (3)	O10—Cu3—O10^{ii}	180.0
O8—W2—O4	85.1 (3)	O10—Cu3—O25	89.1 (3)
O8—W2—O7	152.8 (3)	O10—Cu3—O25^{ii}	90.9 (3)
O8—W2—O9	74.4 (3)	O10^{ii}—Cu3—O25	90.9 (3)
O3—W3—Na2^{ii}	159.2 (2)	O10^{ii}—Cu3—O25^{ii}	89.1 (3)
O3—W3—O9	76.3 (3)	O25—Cu3—Na2	85.0 (3)
O8—W3—Na2^{ii}	115.9 (2)	O25^{ii}—Cu3—Na2^{ii}	85.0 (3)
O8—W3—O3	79.4 (3)	O25—Cu3—Na2^{ii}	95.0 (3)
O8—W3—O9	73.4 (3)	O25^{ii}—Cu3—Na2	95.0 (3)
O9—W3—Na2^{ii}	120.3 (2)	O25^{ii}—Cu3—O6^{ii}	96.9 (3)
O10—W3—Na2^{ii}	37.5 (3)	O25^{ii}—Cu3—O6	83.1 (3)
O10—W3—O3	163.0 (3)	O25—Cu3—O6	96.9 (3)
O10—W3—O8	90.7 (3)	O25—Cu3—O6^{ii}	83.1 (3)
O10—W3—O9	87.7 (3)	O25—Cu3—O25^{ii}	180.0 (4)
O10—W3—O11	97.4 (3)	O2—Na1—O29	81.7 (3)

O11—W3—Na2^{ii}	82.2 (2)	O26—Na1—O2	80.5 (3)
O11—W3—O3	87.2 (3)	O26—Na1—O28	111.0 (4)
O11—W3—O8	157.1 (3)	O26—Na1—O29	161.9 (4)
O11—W3—O9	85.5 (3)	O26—Na1—O30	86.2 (3)
O12—W3—Na2^{ii}	71.8 (3)	O26—Na1—O27	84.4 (8)
O12—W3—O3	93.1 (3)	O28—Na1—O2	165.5 (4)
O12—W3—O8	97.5 (3)	O28—Na1—O29	86.1 (3)
O12—W3—O9	167.0 (3)	O28—Na1—O30	84.9 (4)
O12—W3—O10	101.9 (4)	O28—Na1—O27	94.3 (6)
O12—W3—O11	101.7 (3)	O30—Na1—O2	87.1 (3)
O7^{i}—W4—O4^{i}	72.8 (3)	O30—Na1—O29	89.7 (4)
O7^{i}—W4—O21^{i}	79.7 (3)	O30—Na1—O27	169.6 (9)
O13—W4—O4^{i}	88.2 (3)	O27—Na1—O2	95.8 (7)
O13—W4—O7^{i}	91.2 (3)	O27—Na1—O29	100.6 (9)
O13—W4—O15	98.3 (3)	O27B—Na1—O2	110.2 (7)
O13—W4—O21^{i}	164.6 (3)	O27B—Na1—O26	92.8 (8)
O14—W4—O4^{i}	164.9 (3)	O27B—Na1—O28	78.9 (6)
O14—W4—O7^{i}	95.4 (3)	O27B—Na1—O29	96.3 (9)
O14—W4—O13	101.8 (3)	O27B—Na1—O30	162.2 (8)
O14—W4—O15	101.3 (3)	Cu2—Na2—W3^{ii}	118.32 (15)
O14—W4—O21^{i}	91.5 (3)	Cu3—Na2—W3^{ii}	60.12 (9)
O15—W4—O4^{i}	88.2 (3)	Cu3—Na2—Cu2	100.18 (13)
O15—W4—O7^{i}	158.6 (3)	O6—Na2—W3^{ii}	101.7 (3)
O15—W4—O21^{i}	86.6 (3)	O6—Na2—Cu2	93.5 (2)
O21^{i}—W4—O4^{i}	77.3 (3)	O6—Na2—Cu3	44.0 (2)
O11—W5—O15	81.1 (3)	O6—Na2—O10^{ii}	76.0 (3)
O11—W5—O18	80.1 (3)	O6—Na2—O23	102.4 (3)
O15—W5—O18	80.2 (3)	O6—Na2—O24^{v}	87.4 (3)
O16—W5—O11	154.7 (3)	O6—Na2—O31	76.2 (4)
O16—W5—O15	86.7 (3)	O10^{ii}—Na2—W3^{ii}	26.54 (17)
O16—W5—O18	76.0 (3)	O10^{ii}—Na2—Cu2	113.4 (2)
O17—W5—O11	100.9 (3)	O10^{ii}—Na2—Cu3	33.59 (18)
O17—W5—O15	101.6 (3)	O10^{ii}—Na2—O23	76.4 (3)
O17—W5—O16	103.2 (3)	O10^{ii}—Na2—O31	123.3 (4)
O17—W5—O18	178.1 (3)	O23—Na2—W3^{ii}	77.0 (2)
O17—W5—O19	102.1 (3)	O23—Na2—Cu2	41.4 (2)
O19—W5—O11	89.2 (3)	O23—Na2—Cu3	79.5 (2)
O19—W5—O15	155.7 (3)	O23—Na2—O31	158.1 (4)
O19—W5—O16	93.1 (3)	O24^{v}—Na2—W3^{ii}	150.1 (3)
O19—W5—O18	76.2 (3)	O24^{v}—Na2—Cu2	32.0 (2)
O1^{i}—W6—O18	72.0 (3)	O24^{v}—Na2—Cu3	115.8 (2)
O1^{i}—W6—O19	81.2 (3)	O24^{v}—Na2—O10^{ii}	141.2 (3)
O9—W6—O1^{i}	154.3 (3)	O24^{v}—Na2—O23	73.3 (3)
O9—W6—O18	84.3 (3)	O24^{v}—Na2—O31	84.8 (4)
O9—W6—O19	82.9 (3)	O31—Na2—W3^{ii}	125.0 (4)
O19—W6—O18	73.4 (3)	O31—Na2—Cu2	116.7 (4)
O20—W6—O1^{i}	100.5 (3)	O31—Na2—Cu3	111.2 (3)
O20—W6—O9	100.5 (3)	O32—Na2—W3^{ii}	80.5 (3)

O20—W6—O18	166.0 (3)	O32—Na2—Cu2	106.6 (3)
O20—W6—O19	94.0 (3)	O32—Na2—Cu3	139.6 (3)
O20—W6—O21	102.8 (4)	O32—Na2—O6	156.0 (4)
O21—W6—O1^{i}	93.7 (3)	O32—Na2—O10^{ii}	106.6 (4)
O21—W6—O9	95.7 (3)	O32—Na2—O23	101.3 (4)
O21—W6—O18	89.6 (3)	O32—Na2—O24^{v}	102.6 (4)
O21—W6—O19	163.0 (3)	O32—Na2—O31	83.0 (4)
O5^{i}—Cu1—O5^{iii}	180.0 (4)	W6^{i}—O1—W1	119.2 (4)
O13^{iv}—Cu1—O5^{iii}	95.3 (3)	W1—O2—Na1	165.1 (4)
O13—Cu1—O5^{iii}	84.7 (3)	W1—O3—W3	138.3 (4)
O13—Cu1—O5^{i}	95.3 (3)	W1—O4—W2	124.5 (4)
O13^{iv}—Cu1—O5^{i}	84.7 (3)	W1—O4—W4^{i}	138.3 (4)
O13—Cu1—O13^{iv}	180.0	W4^{i}—O4—W2	95.7 (3)
O13^{iv}—Cu1—O22^{iv}	89.8 (3)	W2—O5—Cu1^{vi}	124.8 (4)
O13—Cu1—O22^{iv}	90.2 (3)	W2—O6—Cu3	128.5 (4)
O13^{iv}—Cu1—O22	90.2 (3)	W2—O6—Na2	136.6 (4)
O13—Cu1—O22	89.8 (3)	Na2—O6—Cu3	92.4 (3)
O22—Cu1—O5^{iii}	96.7 (3)	W2—O7—W4^{i}	116.8 (4)
O22^{iv}—Cu1—O5^{i}	96.7 (3)	W2—O8—W3	118.1 (4)
O22—Cu1—O5^{i}	83.3 (3)	W3—O9—W2	93.0 (3)
O22^{iv}—Cu1—O5^{iii}	83.3 (3)	W6—O9—W2	124.6 (4)
O22—Cu1—O22^{iv}	180.0	W6—O9—W3	140.5 (4)
Na2^{v}—Cu2—Na2	180.0	W3—O10—Cu3	142.8 (4)
O20—Cu2—Na2^{v}	89.6 (2)	W3—O10—Na2^{ii}	116.0 (4)
O20—Cu2—Na2	90.4 (2)	Cu3—O10—Na2^{ii}	101.2 (3)
O20^{v}—Cu2—Na2^{v}	90.4 (2)	W3—O11—W5	147.9 (4)
O20^{v}—Cu2—Na2	89.6 (2)	W4—O13—Cu1	141.2 (5)
O20—Cu2—O20^{v}	180.00 (15)	W4—O15—W5	147.1 (4)
O20—Cu2—O23	90.5 (3)	W5—O16—W1^{i}	115.9 (3)
O20—Cu2—O23^{v}	89.5 (3)	W1^{i}—O18—W5	95.2 (3)
O20^{v}—Cu2—O23	89.5 (3)	W6—O18—W1^{i}	96.7 (3)
O20^{v}—Cu2—O23^{v}	90.5 (3)	W6—O18—W5	96.3 (3)
O23^{v}—Cu2—Na2^{v}	45.2 (2)	W5—O19—W6	114.1 (4)
O23^{v}—Cu2—Na2	134.8 (2)	W6—O20—Cu2	165.2 (5)
O23—Cu2—Na2	45.2 (2)	W6—O21—W4^{i}	138.5 (4)
O23—Cu2—Na2^{v}	134.8 (2)	Cu2—O23—Na2	93.5 (3)
O23^{v}—Cu2—O23	180.0	Cu2—O24—Na2^{v}	107.0 (4)
O24—Cu2—Na2	138.9 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*+1; (iii) *x*, *y*, *z*−1; (iv) −*x*+1, −*y*+1, −*z*; (v) −*x*+1, −*y*, −*z*+1; (vi) *x*, *y*, *z*+1.

(mo_ando241_p-1)

Crystal data

$Na_5Fe_{2.5}[W_{12}O_{40}(OH)_2]\cdot 36H_2O$	α = 92.9341 (14)°
M_r = 3771.27	β = 100.6938 (14)°
Triclinic, $P\overline{1}$	γ = 94.1698 (15)°
a = 12.3758 (6) Å	V = 3378.1 (3) Å^3
b = 14.7752 (7) Å	Z = 2
c = 18.8919 (8) Å	$F(000)$ = 3388

D_x = 3.708 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9822 reflections
θ = 2.2–25.5°

μ = 21.02 mm^{-1}
T = 100 K
Needle, clear light orange
0.37 × 0.07 × 0.04 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: sealed xray tube, Incoatec IuS
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.012, T_{max} = 0.044
38068 measured reflections

12318 independent reflections
10876 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.4°, θ_{min} = 2.3°
h = −14→14
k = −17→17
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.058
S = 1.09
12318 reflections
980 parameters
405 restraints
Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 7.2977P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 1.57 e Å^{-3}
$\Delta\rho_{min}$ = −1.25 e Å^{-3}
Extinction correction: SHELXL2016 (Sheldrick, 2016), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000312 (12)

Special details

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

Refinement. _olex2_refinement_description
1. Fixed Uiso At 1.5 times of: All O(H,H) groups 2. Restrained distances H64A-H61B_$1 2.2 with sigma of 0.02 H59B-H63B 2.2 with sigma of 0.02 H63B_$2-H71A 2.2 with sigma of 0.02 H71A-H63B_$2 2.2 with sigma of 0.05 H49B-Na1 2.7 with sigma of 0.01 H51B-O35_$4 2.3 with sigma of 0.04 H51A-H51B 1.41 with sigma of 0.01 O51-H51A = O51-H51B 0.87 with sigma of 0.01 H52A-Na3 2.7 with sigma of 0.01 O52-H52B = O52-H52A 0.87 with sigma of 0.01 H52A-H52B 1.41 with sigma of 0.01 H53A-O36 2 with sigma of 0.04 H53A-H53B 1.41 with sigma of 0.01 O53-H53A = O53-H53B 0.87 with sigma of 0.01 H77B-H28A 2.2 with sigma of 0.02 H77A-H28A 2.2 with sigma of 0.02 O77-H77A = O77-H77B = O28-H28B = O28-H28A 0.87 with sigma of 0.01 H77A-H77B = H28B-H28A 1.41 with sigma of 0.01 H49B-Na2 2.7 with sigma of 0.01 Na2-H49A 2.7 with sigma of 0.02 O50-H50A ~ O50-H50B ~ O51-H51A ~ O51-H51B ~ O48-H48A ~ O48-H48B ~ O47-H47B O47-H47A ~ O65-H65B ~ O65-H65A ~ O64-H64A ~ O64-H64B ~ O74-H74A ~ O74-H74B O63-H63A ~ O63-H63B ~ O60-H60B ~ O60-H60A ~ O167-H16B ~ O167-H16A ~ O67-H67B O67-H67A ~ O27-H27B ~ O27-H27A ~ O28-H28A ~ O28-H28B ~ O77-H77A ~ O77-H77B with sigma of 0.02 3. Others Fixed Sof: O66(0.5) O67(0.5) H67A(0.5) H67B(0.5) O166(0.5) O167(0.5) H16A(0.5) H16B(0.5) 4.a Free rotating group: O49(H49A,H49B), O62(H62A,H62B), O57(H57A,H57B), O68(H68A,H68B), O69(H69A, H69B), O70(H70A,H70B), O71(H71A,H71B), O72(H72A,H72B), O73(H73A,H73B) 4.b Rotating group: O22(H22A,H22B), O23(H23A,H23B), O24(H24A,H24B), O27(H27A,H27B), O29(H29A, H29B), O47(H47A,H47B), O48(H48A,H48B), O50(H50A,H50B), O54(H54A,H54B), O55(H55A,H55B), O56(H56A,H56B), O58(H58A,H58B), O59(H59A,H59B), O60(H60A,H60B), O61(H61A,H61B), O63(H63A,H63B), O64(H64A,H64B), O65(H65A,H65B), O74(H74A, H74B), O67(H67A,H67B), O167(H16A,H16B)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
W1	0.43982 (2)	0.96245 (2)	1.17681 (2)	0.01193 (6)	
W2	0.25947 (2)	0.81700 (2)	1.03223 (2)	0.01230 (6)	
W3	0.39839 (2)	0.69804 (2)	0.93379 (2)	0.01231 (6)	
W4	0.61176 (2)	0.80885 (2)	0.88516 (2)	0.01207 (6)	
W5	0.34632 (2)	0.93167 (2)	0.87838 (2)	0.01145 (5)	
W6	0.41877 (2)	1.15417 (2)	0.92471 (2)	0.01161 (6)	
W7	0.09965 (2)	0.79501 (2)	0.57766 (2)	0.01183 (6)	
W8	0.24036 (2)	0.68517 (2)	0.47575 (2)	0.01201 (6)	
W9	0.15423 (2)	0.56265 (2)	0.62612 (2)	0.01127 (5)	
W10	0.08150 (2)	0.34469 (2)	0.56793 (2)	0.01140 (6)	
W11	−0.06153 (2)	0.45282 (2)	0.67587 (2)	0.01177 (6)	
W12	−0.11444 (2)	0.68342 (2)	0.62245 (2)	0.01181 (6)	
Fe1	0.000000	1.000000	0.500000	0.0146 (2)	
Fe2	0.07450 (6)	0.82233 (5)	0.76386 (4)	0.01358 (16)	
Fe3	0.42245 (6)	0.66855 (5)	0.74623 (4)	0.01375 (16)	
Na1	0.500000	0.000000	0.500000	0.0205 (7)	
Na2	0.28394 (19)	0.13921 (14)	0.60840 (11)	0.0213 (5)	
Na3	0.50905 (19)	0.63218 (14)	0.41748 (11)	0.0193 (5)	
Na4	−0.00109 (19)	1.11946 (14)	0.90833 (12)	0.0205 (5)	
Na5	0.19312 (19)	1.34276 (14)	0.89244 (12)	0.0216 (5)	
Na6	0.000000	1.500000	1.000000	0.0270 (7)	
O75	0.1001 (3)	0.8950 (2)	0.53226 (19)	0.0156 (8)	
O77	0.0108 (3)	1.0403 (3)	0.6088 (2)	0.0216 (9)	
H77A	−0.022 (3)	1.079 (2)	0.634 (2)	0.032*	
H77B	0.0826 (10)	1.056 (3)	0.6221 (19)	0.032*	
O1	0.3979 (3)	0.9495 (2)	1.25833 (19)	0.0168 (8)	
O78	−0.2529 (3)	0.7055 (2)	0.60234 (19)	0.0157 (8)	
O2	0.5723 (3)	1.0360 (2)	1.20459 (19)	0.0141 (8)	
O76	0.1546 (3)	1.0778 (2)	0.49860 (19)	0.0167 (8)	
O3	0.5139 (3)	0.8592 (2)	1.16577 (18)	0.0141 (8)	
O4	0.3706 (3)	1.0748 (2)	1.14768 (19)	0.0149 (8)	
O5	0.5025 (3)	0.9800 (2)	1.07220 (18)	0.0127 (7)	
O6	0.3153 (3)	0.9044 (2)	1.10875 (19)	0.0137 (8)	
O7	0.2386 (3)	0.7250 (2)	1.08414 (19)	0.0177 (8)	
O8	0.4370 (3)	0.7922 (2)	1.03049 (18)	0.0138 (8)	
O9	0.3135 (3)	0.9243 (2)	0.96673 (19)	0.0144 (8)	
O10	0.1258 (3)	0.8510 (2)	1.00611 (19)	0.0162 (8)	
O11	0.2618 (3)	0.7439 (2)	0.94416 (18)	0.0140 (8)	
O12	0.3941 (3)	0.6005 (2)	0.98167 (19)	0.0165 (8)	
O13	0.5521 (3)	0.7084 (2)	0.93601 (19)	0.0145 (8)	
O14	0.3535 (3)	0.6564 (2)	0.84180 (18)	0.0142 (8)	
O15	0.7498 (3)	0.7843 (2)	0.90512 (19)	0.0163 (8)	
O16	0.5632 (3)	0.7473 (2)	0.80024 (19)	0.0154 (8)	
O17	0.4373 (3)	0.8345 (2)	0.88711 (19)	0.0148 (8)	
O18	0.3123 (3)	1.0590 (2)	0.87348 (18)	0.0135 (7)	

O19	0.2265 (3)	0.8848 (2)	0.82087 (19)	0.0157 (8)
O20	0.3779 (3)	1.1284 (2)	1.00996 (18)	0.0135 (8)
O21	0.3490 (3)	1.2486 (2)	0.90007 (19)	0.0162 (8)
O22	0.4906 (3)	0.5437 (2)	0.7766 (2)	0.0176 (8)
H22A	0.471921	0.525896	0.818159	0.026*
H22B	0.565119	0.549590	0.783409	0.026*
O23	0.4817 (3)	0.6504 (2)	0.6488 (2)	0.0189 (8)
H23A	0.534097	0.610923	0.653309	0.028*
H23B	0.511449	0.703254	0.636478	0.028*
O24	0.3712 (3)	0.7970 (2)	0.71232 (19)	0.0170 (8)
H24A	0.400970	0.812752	0.674860	0.026*
H24B	0.392232	0.840087	0.747703	0.026*
O25	0.2710 (3)	0.6072 (2)	0.68784 (19)	0.0145 (8)
O26	0.1417 (3)	0.8342 (2)	0.67012 (19)	0.0163 (8)
O27	0.0118 (3)	0.8350 (2)	0.85913 (19)	0.0175 (8)
H27A	−0.019350	0.780861	0.870617	0.026*
H27B	−0.041858	0.874914	0.855558	0.026*
O28	0.0044 (3)	0.9491 (2)	0.73617 (19)	0.0171 (8)
H28A	0.025 (4)	0.961 (3)	0.6950 (14)	0.026*
H28B	0.025 (5)	0.999 (2)	0.7650 (19)	0.026*
O29	0.1294 (3)	0.6937 (2)	0.7944 (2)	0.0171 (8)
H29A	0.120845	0.654521	0.755798	0.026*
H29B	0.090838	0.670087	0.825449	0.026*
O30	−0.0686 (3)	0.7429 (2)	0.70806 (19)	0.0173 (8)
O31	−0.0565 (3)	0.7844 (2)	0.57317 (19)	0.0130 (7)
O32	0.0612 (3)	0.6594 (2)	0.62006 (19)	0.0152 (8)
O33	0.0626 (3)	0.7070 (2)	0.47893 (19)	0.0138 (8)
O34	0.1905 (3)	0.5774 (2)	0.53939 (19)	0.0158 (8)
O35	0.2371 (3)	0.7542 (2)	0.56669 (18)	0.0149 (8)
O36	0.2569 (3)	0.7839 (2)	0.42933 (19)	0.0150 (8)
O37	0.3757 (3)	0.6545 (2)	0.49892 (19)	0.0163 (8)
O38	−0.1295 (3)	0.5646 (2)	0.65250 (19)	0.0146 (8)
O39	−0.1851 (3)	0.3951 (2)	0.60394 (19)	0.0137 (7)
O40	−0.1030 (3)	0.4288 (2)	0.7553 (2)	0.0177 (8)
O41	0.0140 (3)	0.3492 (2)	0.65924 (18)	0.0134 (7)
O42	0.0032 (3)	0.4785 (2)	0.57249 (18)	0.0134 (8)
O43	0.0721 (3)	0.5233 (2)	0.70755 (19)	0.0143 (8)
O44	−0.1231 (3)	0.6218 (2)	0.51595 (18)	0.0128 (7)
O45	0.1879 (3)	0.4362 (2)	0.62501 (18)	0.0134 (7)
O46	0.1513 (3)	0.2498 (2)	0.58872 (19)	0.0157 (8)
O47	0.3478 (3)	0.2254 (2)	0.7211 (2)	0.0203 (9)
H47A	0.376148	0.281108	0.714149	0.030*
H47B	0.400373	0.197678	0.748989	0.030*
O48	0.2635 (4)	0.0174 (3)	0.6787 (2)	0.0340 (11)
H48A	0.329102	0.003969	0.702825	0.051*
H48B	0.232193	−0.032050	0.651118	0.051*
O49	0.4680 (4)	0.0895 (3)	0.6048 (2)	0.0229 (9)
H49A	0.505130	0.135577	0.631042	0.034*

H49B	0.466632	0.046477	0.634452	0.034*
O50	0.7003 (3)	0.0214 (2)	0.5578 (2)	0.0216 (9)
H50A	0.709887	0.009412	0.604986	0.032*
H50B	0.727030	0.080448	0.559699	0.032*
O51	0.5203 (4)	0.1320 (3)	0.4330 (2)	0.0265 (9)
H51A	0.478 (4)	0.139 (4)	0.3902 (16)	0.040*
H51B	0.5888 (17)	0.150 (4)	0.427 (3)	0.040*
O52	0.6197 (4)	0.7649 (2)	0.4778 (2)	0.0215 (9)
H52A	0.663 (3)	0.7394 (10)	0.5110 (18)	0.032*
H52B	0.577 (4)	0.797 (4)	0.499 (2)	0.032*
O53	0.4156 (3)	0.7413 (3)	0.3450 (2)	0.0232 (9)
H53A	0.355 (2)	0.745 (4)	0.362 (2)	0.035*
H53B	0.397 (4)	0.728 (4)	0.2988 (8)	0.035*
O54	0.6019 (3)	0.6050 (2)	0.32011 (19)	0.0185 (8)
H54A	0.569316	0.556728	0.292040	0.028*
H54B	0.671969	0.594865	0.336455	0.028*
O55	0.6443 (3)	0.5476 (2)	0.4892 (2)	0.0193 (8)
H55A	0.713115	0.572858	0.490711	0.029*
H55B	0.640827	0.489651	0.470739	0.029*
O56	0.4026 (3)	0.4899 (2)	0.3769 (2)	0.0205 (8)
H56A	0.351594	0.497092	0.338263	0.031*
H56B	0.369101	0.469394	0.411358	0.031*
O58	0.1426 (3)	1.0451 (2)	0.9812 (2)	0.0220 (9)
H58A	0.208095	1.069437	0.976634	0.033*
H58B	0.137172	0.986597	0.967312	0.033*
O59	0.1030 (3)	1.0982 (2)	0.8154 (2)	0.0196 (8)
H59A	0.172924	1.082290	0.833307	0.029*
H59B	0.111317	1.150360	0.791637	0.029*
O60	−0.1092 (3)	0.9738 (2)	0.8820 (2)	0.0231 (9)
H60A	−0.166090	0.977993	0.846658	0.035*
H60B	−0.134022	0.956833	0.920654	0.035*
O61	0.3140 (3)	1.4191 (2)	0.9940 (2)	0.0229 (9)
H61A	0.369086	1.458527	0.980717	0.034*
H61B	0.352070	1.378925	1.025227	0.034*
O62	0.1017 (4)	1.2528 (3)	0.9709 (2)	0.0218 (9)
H62A	0.145760	1.229523	1.005333	0.033*
H62B	0.060640	1.285112	0.993112	0.033*
O63	0.1595 (3)	1.2692 (2)	0.7723 (2)	0.0204 (8)
H63A	0.214911	1.286341	0.744070	0.031*
H63B	0.090044	1.282058	0.742511	0.031*
O64	−0.1812 (4)	1.4738 (3)	0.9349 (2)	0.0286 (10)
H64A	−0.234836	1.515714	0.949155	0.043*
H64B	−0.218263	1.412264	0.938246	0.043*
O65	−0.0222 (4)	1.3617 (3)	1.0594 (2)	0.0269 (9)
H65A	−0.092383	1.350512	1.064955	0.040*
H65B	0.021278	1.365054	1.103450	0.040*
O74	0.2373 (4)	1.4742 (3)	0.8282 (2)	0.0339 (11)
H74A	0.277054	1.459042	0.795994	0.051*

H74B	0.275256	1.516954	0.859008	0.051*	
O66	0.0455 (9)	1.4372 (6)	0.8932 (6)	0.025 (2)	0.5
O67	−0.0980 (10)	1.2057 (8)	0.8245 (6)	0.040 (3)	0.5
H67A	−0.172297	1.223060	0.834440	0.061*	0.5
H67B	−0.118922	1.176966	0.772875	0.061*	0.5
O166	0.0109 (11)	1.3927 (8)	0.8881 (6)	0.036 (3)	0.5
O167	−0.1337 (10)	1.1537 (9)	0.8069 (7)	0.047 (3)	0.5
H16A	−0.120091	1.218036	0.783218	0.070*	0.5
H16B	−0.219353	1.157915	0.813213	0.070*	0.5
O57	0.3650 (4)	0.6621 (3)	0.2063 (2)	0.0269 (9)	
H57A	0.426675	0.650088	0.193605	0.040*	
H57B	0.322656	0.684798	0.170648	0.040*	
O68	0.8504 (4)	0.6607 (2)	0.8242 (2)	0.0222 (9)	
H68A	0.874753	0.686576	0.789231	0.033*	
H68B	0.811052	0.697443	0.843819	0.033*	
O69	0.6958 (3)	0.5233 (3)	0.7662 (2)	0.0230 (9)	
H69A	0.706601	0.467755	0.777240	0.034*	
H69B	0.749060	0.560225	0.790897	0.034*	
O70	0.4874 (4)	0.4128 (3)	0.8762 (2)	0.0258 (9)	
H70A	0.526630	0.411288	0.919288	0.039*	
H70B	0.422232	0.385367	0.874613	0.039*	
O71	0.9183 (3)	0.1787 (2)	0.6740 (2)	0.0227 (9)	
H71A	0.945097	0.231566	0.664001	0.034*	
H71B	0.851249	0.167453	0.649725	0.034*	
O72	0.7852 (4)	0.9728 (3)	0.7021 (2)	0.0282 (10)	
H72A	0.741468	0.923175	0.697101	0.042*	
H72B	0.751210	1.018193	0.715589	0.042*	
O73	0.6434 (4)	0.8229 (2)	0.6820 (2)	0.0211 (9)	
H73A	0.614540	0.802804	0.717447	0.032*	
H73B	0.681198	0.781510	0.666241	0.032*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01172 (12)	0.01254 (10)	0.01175 (11)	0.00075 (8)	0.00268 (8)	0.00154 (8)
W2	0.01205 (12)	0.01225 (10)	0.01259 (11)	0.00030 (8)	0.00248 (8)	0.00132 (8)
W3	0.01267 (12)	0.01148 (10)	0.01268 (11)	0.00047 (8)	0.00234 (8)	0.00094 (8)
W4	0.01198 (12)	0.01195 (10)	0.01232 (11)	0.00099 (8)	0.00236 (8)	0.00104 (8)
W5	0.01123 (12)	0.01134 (10)	0.01177 (10)	0.00078 (8)	0.00211 (8)	0.00128 (8)
W6	0.01164 (12)	0.01129 (10)	0.01178 (10)	0.00095 (8)	0.00183 (8)	0.00125 (8)
W7	0.01197 (12)	0.01111 (10)	0.01233 (10)	0.00082 (8)	0.00213 (8)	0.00099 (8)
W8	0.01164 (12)	0.01182 (10)	0.01258 (11)	0.00048 (8)	0.00245 (8)	0.00124 (8)
W9	0.01105 (12)	0.01091 (10)	0.01184 (10)	0.00080 (8)	0.00205 (8)	0.00127 (8)
W10	0.01133 (12)	0.01107 (10)	0.01177 (10)	0.00089 (8)	0.00202 (8)	0.00114 (8)
W11	0.01170 (12)	0.01198 (10)	0.01187 (11)	0.00078 (8)	0.00277 (8)	0.00146 (8)
W12	0.01179 (12)	0.01161 (10)	0.01209 (11)	0.00098 (8)	0.00230 (8)	0.00121 (8)
Fe1	0.0158 (6)	0.0140 (5)	0.0141 (5)	0.0019 (4)	0.0030 (4)	0.0021 (4)
Fe2	0.0130 (4)	0.0142 (3)	0.0132 (4)	0.0001 (3)	0.0022 (3)	0.0005 (3)

Fe3	0.0133 (4)	0.0137 (3)	0.0140 (4)	−0.0001 (3)	0.0023 (3)	0.0005 (3)
Na1	0.0215 (18)	0.0183 (15)	0.0213 (16)	0.0016 (13)	0.0035 (13)	0.0010 (12)
Na2	0.0235 (13)	0.0208 (10)	0.0191 (11)	0.0053 (10)	0.0010 (9)	0.0018 (9)
Na3	0.0198 (13)	0.0191 (10)	0.0198 (11)	0.0021 (9)	0.0057 (9)	0.0023 (9)
Na4	0.0204 (13)	0.0220 (11)	0.0208 (11)	0.0027 (9)	0.0074 (9)	0.0044 (9)
Na5	0.0222 (13)	0.0223 (11)	0.0206 (11)	0.0046 (10)	0.0032 (9)	0.0024 (9)
Na6	0.0214 (19)	0.0287 (17)	0.0322 (19)	0.0043 (15)	0.0050 (15)	0.0118 (14)
O75	0.014 (2)	0.0130 (17)	0.0200 (19)	0.0037 (15)	0.0038 (15)	0.0025 (14)
O77	0.019 (2)	0.025 (2)	0.020 (2)	0.0053 (17)	0.0017 (17)	−0.0017 (16)
O1	0.017 (2)	0.0177 (18)	0.0156 (19)	−0.0001 (16)	0.0028 (15)	−0.0009 (15)
O78	0.014 (2)	0.0158 (17)	0.0178 (19)	0.0008 (15)	0.0033 (15)	0.0003 (14)
O2	0.013 (2)	0.0142 (17)	0.0142 (18)	−0.0001 (15)	0.0011 (15)	0.0016 (14)
O76	0.017 (2)	0.0150 (17)	0.0184 (19)	0.0002 (15)	0.0045 (16)	0.0013 (15)
O3	0.016 (2)	0.0140 (17)	0.0128 (18)	0.0000 (15)	0.0045 (15)	0.0042 (14)
O4	0.015 (2)	0.0136 (17)	0.0171 (19)	0.0022 (15)	0.0052 (15)	0.0009 (14)
O5	0.013 (2)	0.0111 (16)	0.0135 (18)	−0.0014 (15)	0.0024 (15)	−0.0003 (14)
O6	0.012 (2)	0.0143 (17)	0.0159 (18)	0.0033 (15)	0.0039 (15)	0.0011 (14)
O7	0.021 (2)	0.0144 (17)	0.0174 (19)	−0.0015 (16)	0.0046 (16)	0.0022 (15)
O8	0.014 (2)	0.0127 (17)	0.0147 (18)	0.0021 (15)	0.0019 (15)	0.0028 (14)
O9	0.016 (2)	0.0135 (17)	0.0138 (18)	0.0016 (15)	0.0025 (15)	0.0016 (14)
O10	0.015 (2)	0.0137 (17)	0.0184 (19)	−0.0022 (15)	0.0012 (15)	−0.0007 (14)
O11	0.011 (2)	0.0149 (17)	0.0148 (18)	−0.0024 (15)	0.0003 (15)	−0.0010 (14)
O12	0.018 (2)	0.0147 (17)	0.0169 (19)	0.0038 (16)	0.0033 (16)	0.0023 (14)
O13	0.012 (2)	0.0163 (17)	0.0146 (18)	0.0023 (15)	0.0002 (15)	0.0003 (14)
O14	0.015 (2)	0.0183 (18)	0.0095 (17)	0.0022 (15)	0.0027 (14)	0.0003 (14)
O15	0.014 (2)	0.0161 (18)	0.0182 (19)	0.0009 (15)	0.0013 (15)	0.0007 (15)
O16	0.016 (2)	0.0160 (17)	0.0133 (18)	−0.0009 (15)	0.0020 (15)	−0.0003 (14)
O17	0.014 (2)	0.0129 (17)	0.0180 (19)	0.0029 (15)	0.0039 (15)	0.0044 (14)
O18	0.013 (2)	0.0138 (17)	0.0147 (18)	0.0038 (15)	0.0028 (15)	0.0027 (14)
O19	0.018 (2)	0.0138 (17)	0.0160 (19)	0.0027 (15)	0.0029 (15)	0.0021 (14)
O20	0.014 (2)	0.0128 (17)	0.0136 (18)	−0.0009 (15)	0.0037 (15)	−0.0009 (14)
O21	0.016 (2)	0.0149 (17)	0.0171 (19)	0.0007 (15)	0.0018 (15)	0.0016 (15)
O22	0.013 (2)	0.0175 (18)	0.021 (2)	0.0005 (16)	0.0000 (16)	0.0004 (15)
O23	0.017 (2)	0.0179 (18)	0.023 (2)	0.0025 (16)	0.0065 (16)	0.0014 (15)
O24	0.022 (2)	0.0154 (18)	0.0125 (18)	0.0026 (16)	0.0007 (16)	0.0007 (14)
O25	0.016 (2)	0.0141 (17)	0.0139 (18)	0.0022 (15)	0.0029 (15)	0.0005 (14)
O26	0.014 (2)	0.0159 (17)	0.0192 (19)	0.0007 (15)	0.0035 (15)	0.0003 (15)
O27	0.017 (2)	0.0180 (18)	0.0181 (19)	0.0028 (16)	0.0035 (16)	0.0023 (15)
O28	0.020 (2)	0.0147 (17)	0.0152 (19)	−0.0001 (16)	0.0015 (16)	−0.0009 (15)
O29	0.020 (2)	0.0152 (18)	0.0157 (19)	0.0030 (16)	0.0017 (16)	−0.0011 (14)
O30	0.018 (2)	0.0194 (18)	0.0145 (19)	0.0013 (16)	0.0019 (15)	0.0023 (15)
O31	0.0106 (19)	0.0127 (16)	0.0159 (18)	0.0025 (15)	0.0019 (14)	0.0028 (14)
O32	0.017 (2)	0.0133 (17)	0.0163 (19)	0.0012 (15)	0.0047 (15)	0.0034 (14)
O33	0.014 (2)	0.0131 (17)	0.0152 (18)	0.0025 (15)	0.0036 (15)	0.0031 (14)
O34	0.018 (2)	0.0128 (17)	0.0180 (19)	0.0031 (15)	0.0075 (16)	0.0005 (14)
O35	0.012 (2)	0.0174 (18)	0.0143 (18)	−0.0024 (15)	0.0029 (15)	−0.0012 (14)
O36	0.018 (2)	0.0109 (17)	0.0161 (18)	−0.0002 (15)	0.0039 (15)	0.0011 (14)
O37	0.014 (2)	0.0140 (17)	0.0188 (19)	−0.0014 (15)	−0.0003 (15)	−0.0019 (14)

O38	0.011 (2)	0.0153 (17)	0.0182 (19)	0.0011 (15)	0.0034 (15)	0.0029 (14)
O39	0.013 (2)	0.0149 (17)	0.0137 (18)	0.0044 (15)	0.0017 (15)	0.0020 (14)
O40	0.016 (2)	0.0197 (18)	0.0183 (19)	0.0029 (16)	0.0049 (16)	0.0037 (15)
O41	0.014 (2)	0.0143 (17)	0.0115 (17)	0.0004 (15)	0.0025 (15)	0.0025 (14)
O42	0.016 (2)	0.0116 (16)	0.0119 (17)	−0.0014 (15)	0.0004 (15)	0.0010 (14)
O43	0.013 (2)	0.0158 (17)	0.0140 (18)	0.0013 (15)	0.0023 (15)	−0.0011 (14)
O44	0.0098 (19)	0.0121 (16)	0.0155 (18)	−0.0009 (14)	0.0016 (14)	−0.0020 (14)
O45	0.012 (2)	0.0141 (17)	0.0145 (18)	0.0036 (15)	0.0038 (15)	0.0017 (14)
O46	0.015 (2)	0.0143 (17)	0.0172 (19)	0.0001 (15)	0.0023 (15)	0.0014 (14)
O47	0.023 (2)	0.0176 (18)	0.020 (2)	0.0025 (17)	0.0021 (17)	0.0033 (15)
O48	0.032 (3)	0.027 (2)	0.035 (3)	−0.010 (2)	−0.013 (2)	0.0112 (19)
O49	0.029 (3)	0.0205 (19)	0.019 (2)	0.0028 (18)	0.0034 (17)	0.0034 (16)
O50	0.023 (2)	0.0148 (18)	0.026 (2)	0.0003 (17)	0.0049 (18)	−0.0003 (16)
O51	0.026 (2)	0.027 (2)	0.027 (2)	−0.0014 (19)	0.0041 (18)	0.0060 (18)
O52	0.023 (2)	0.0185 (19)	0.021 (2)	0.0062 (17)	−0.0009 (17)	0.0043 (16)
O53	0.021 (2)	0.030 (2)	0.021 (2)	0.0054 (18)	0.0070 (17)	0.0020 (18)
O54	0.019 (2)	0.0185 (18)	0.0167 (19)	0.0018 (16)	0.0011 (16)	0.0002 (15)
O55	0.019 (2)	0.0170 (18)	0.022 (2)	0.0009 (16)	0.0042 (17)	0.0041 (16)
O56	0.020 (2)	0.0204 (19)	0.021 (2)	−0.0001 (17)	0.0053 (17)	0.0002 (16)
O58	0.022 (2)	0.0171 (19)	0.030 (2)	0.0059 (17)	0.0077 (18)	0.0077 (16)
O59	0.020 (2)	0.0163 (18)	0.022 (2)	0.0026 (16)	0.0018 (17)	0.0020 (15)
O60	0.021 (2)	0.023 (2)	0.024 (2)	0.0038 (17)	0.0026 (17)	0.0005 (17)
O61	0.027 (2)	0.0155 (18)	0.026 (2)	0.0017 (17)	0.0041 (18)	0.0049 (16)
O62	0.021 (2)	0.021 (2)	0.023 (2)	0.0034 (17)	0.0019 (17)	0.0039 (16)
O63	0.019 (2)	0.0216 (19)	0.020 (2)	0.0010 (17)	0.0016 (16)	0.0040 (16)
O64	0.027 (3)	0.018 (2)	0.042 (3)	0.0026 (18)	0.009 (2)	0.0024 (18)
O65	0.026 (2)	0.030 (2)	0.025 (2)	0.0000 (19)	0.0054 (18)	0.0091 (18)
O74	0.044 (3)	0.026 (2)	0.026 (2)	−0.008 (2)	−0.003 (2)	0.0047 (18)
O66	0.024 (6)	0.024 (5)	0.025 (5)	0.003 (4)	0.001 (4)	0.002 (5)
O67	0.030 (7)	0.075 (9)	0.028 (6)	0.033 (6)	0.017 (5)	0.027 (6)
O166	0.050 (8)	0.043 (7)	0.021 (5)	0.025 (6)	0.011 (5)	0.011 (5)
O167	0.029 (7)	0.079 (9)	0.042 (7)	0.013 (6)	0.021 (6)	0.033 (7)
O57	0.034 (3)	0.027 (2)	0.019 (2)	0.008 (2)	0.0013 (18)	0.0053 (17)
O68	0.025 (2)	0.0220 (19)	0.022 (2)	−0.0006 (18)	0.0110 (17)	0.0005 (16)
O69	0.017 (2)	0.0207 (19)	0.029 (2)	−0.0010 (17)	0.0008 (17)	0.0005 (17)
O70	0.025 (3)	0.031 (2)	0.020 (2)	−0.0015 (19)	−0.0007 (17)	0.0079 (18)
O71	0.023 (2)	0.0154 (18)	0.028 (2)	−0.0029 (17)	0.0007 (18)	0.0046 (16)
O72	0.024 (3)	0.021 (2)	0.041 (3)	0.0019 (18)	0.011 (2)	−0.0005 (19)
O73	0.026 (2)	0.0209 (19)	0.019 (2)	0.0026 (18)	0.0106 (17)	0.0032 (16)

Geometric parameters (Å, º)

W1—O1	1.729 (4)	Fe1—O77^{iii}	2.087 (4)
W1—O2	1.873 (4)	Fe1—O77	2.087 (4)
W1—O3	1.859 (3)	Fe1—O76^{iii}	2.165 (4)
W1—O4	1.979 (3)	Fe1—O76	2.165 (4)
W1—O5	2.273 (3)	Fe2—O19	2.108 (4)
W1—O6	1.930 (4)	Fe2—O26	2.101 (4)

W2—O6	1.882 (3)	Fe2—O27	2.093 (4)
W2—O7	1.748 (3)	Fe2—O28	2.169 (4)
W2—O8	2.259 (4)	Fe2—O29	2.136 (4)
W2—O9	2.201 (3)	Fe2—O30	2.122 (4)
W2—O10	1.754 (4)	Fe3—O14	2.145 (3)
W2—O11	1.943 (3)	Fe3—O16	2.087 (4)
W3—O8	2.195 (3)	Fe3—O22	2.145 (4)
W3—O11	1.905 (4)	Fe3—O23	2.116 (4)
W3—O12	1.743 (3)	Fe3—O24	2.136 (3)
W3—O13	1.890 (4)	Fe3—O25	2.106 (4)
W3—O14	1.786 (3)	Na1—O49	2.434 (4)
W3—O17	2.297 (3)	Na1—O49^{iv}	2.434 (4)
W4—O4^{i}	1.869 (3)	Na1—O50	2.507 (4)
W4—O13	1.980 (3)	Na1—O50^{iv}	2.507 (4)
W4—O15	1.748 (4)	Na1—O51^{iv}	2.402 (4)
W4—O16	1.782 (3)	Na1—O51	2.402 (4)
W4—O17	2.226 (4)	Na2—Na3^{v}	4.194 (3)
W4—O20^{i}	2.122 (3)	Na2—O76^{vi}	2.460 (4)
W5—O2^{i}	2.071 (4)	Na2—O46	2.394 (4)
W5—O5^{i}	2.224 (4)	Na2—O47	2.395 (4)
W5—O9	1.796 (3)	Na2—O48	2.317 (4)
W5—O17	1.883 (3)	Na2—O49	2.456 (5)
W5—O18	1.960 (3)	Na2—O52^{v}	2.606 (4)
W5—O19	1.743 (4)	Na3—Na2^{v}	4.194 (3)
W6—O3^{i}	2.043 (3)	Na3—O37	2.484 (4)
W6—O5^{i}	2.271 (3)	Na3—O52	2.412 (4)
W6—O8^{i}	1.923 (4)	Na3—O53	2.392 (5)
W6—O18	1.942 (4)	Na3—O54	2.375 (4)
W6—O20	1.826 (3)	Na3—O55	2.416 (4)
W6—O21	1.732 (4)	Na3—O56	2.408 (4)
W7—O75	1.746 (3)	Na4—Na5	3.996 (3)
W7—O26	1.781 (4)	Na4—O10^{vii}	2.477 (4)
W7—O31	1.913 (4)	Na4—O58	2.407 (5)
W7—O32	2.247 (3)	Na4—O59	2.383 (4)
W7—O33	2.174 (3)	Na4—O60	2.427 (4)
W7—O35	1.888 (4)	Na4—O62	2.395 (4)
W8—O33	2.258 (4)	Na4—O67	2.302 (11)
W8—O34	2.166 (3)	Na4—O167	2.382 (13)
W8—O35	1.961 (3)	Na5—Na6	4.167 (2)
W8—O36	1.759 (3)	Na5—O21	2.447 (4)
W8—O37	1.750 (4)	Na5—O61	2.380 (4)
W8—O39^{ii}	1.860 (3)	Na5—O62	2.418 (4)
W9—O25	1.743 (4)	Na5—O63	2.416 (4)
W9—O32	1.895 (4)	Na5—O74	2.424 (4)
W9—O34	1.797 (4)	Na5—O66	2.379 (11)
W9—O42	2.213 (4)	Na5—O166	2.412 (12)
W9—O43	2.079 (4)	Na6—Na5^{viii}	4.167 (2)
W9—O45	1.943 (3)	Na6—O64^{viii}	2.344 (4)

W10—O33^{ii}	1.922 (4)	Na6—O64	2.344 (4)
W10—O41	2.052 (3)	Na6—O65	2.404 (4)
W10—O42	2.268 (3)	Na6—O65^{viii}	2.404 (4)
W10—O44^{ii}	1.835 (3)	Na6—O66	2.358 (11)
W10—O45	1.947 (4)	Na6—O66^{viii}	2.358 (11)
W10—O46	1.724 (4)	Na6—O166^{viii}	2.606 (11)
W11—O38	1.942 (3)	Na6—O166	2.606 (11)
W11—O39	1.958 (4)	O2—W5^{i}	2.071 (3)
W11—O40	1.719 (4)	O76—Na2^{ix}	2.460 (4)
W11—O41	1.892 (3)	O3—W6^{i}	2.043 (3)
W11—O42	2.283 (3)	O4—W4^{i}	1.869 (3)
W11—O43	1.870 (4)	O5—W5^{i}	2.224 (3)
W12—O78	1.743 (4)	O5—W6^{i}	2.271 (3)
W12—O30	1.775 (4)	O8—W6^{i}	1.923 (4)
W12—O31	1.960 (3)	O10—Na4^{vii}	2.477 (4)
W12—O32	2.237 (4)	O20—W4^{i}	2.122 (3)
W12—O38	1.879 (3)	O33—W10^{ii}	1.922 (4)
W12—O44	2.146 (3)	O39—W8^{ii}	1.860 (3)
Fe1—O75^{iii}	2.100 (3)	O44—W10^{ii}	1.835 (3)
Fe1—O75	2.100 (3)	O52—Na2^{v}	2.606 (4)

O67a—Na4—Na5	72.3 (3)	O38—W12—O44	86.63 (14)
O167b—Na4—Na5	91.8 (3)	O44—W12—O32	76.83 (13)
O67a—Na4—O10^{vii}	91.4 (3)	O75^{iii}—Fe1—O75	180.00 (17)
O1—W1—O2	102.23 (16)	O75—Fe1—O76	84.52 (14)
O1—W1—O3	102.82 (16)	O75^{iii}—Fe1—O76^{iii}	84.51 (14)
O1—W1—O4	100.36 (16)	O75—Fe1—O76^{iii}	95.48 (14)
O1—W1—O5	177.56 (16)	O75^{iii}—Fe1—O76	95.49 (14)
O1—W1—O6	102.08 (16)	O77—Fe1—O75	88.54 (15)
O167b—Na4—O10^{vii}	92.8 (3)	O77^{iii}—Fe1—O75^{iii}	88.54 (15)
O167b—Na4—O58	160.3 (3)	O77^{iii}—Fe1—O75	91.46 (15)
O67a—Na4—O58	164.0 (3)	O77—Fe1—O75^{iii}	91.46 (15)
O167b—Na4—O59	80.4 (3)	O77^{iii}—Fe1—O77	180.0 (2)
O67a—Na4—O59	82.0 (3)	O77—Fe1—O76^{iii}	89.27 (15)
O67a—Na4—O60	100.9 (3)	O77^{iii}—Fe1—O76^{iii}	90.73 (15)
O167b—Na4—O60	79.8 (3)	O77^{iii}—Fe1—O76	89.27 (15)
O67a—Na4—O62	91.2 (3)	O77—Fe1—O76	90.73 (15)
O167b—Na4—O62	112.6 (3)	O76^{iii}—Fe1—O76	180.0
O66a—Na5—Na4	91.9 (2)	O19—Fe2—O28	94.86 (14)
O2—W1—O4	86.64 (15)	O19—Fe2—O29	88.73 (14)
O2—W1—O5	75.66 (14)	O19—Fe2—O30	172.37 (14)
O2—W1—O6	154.94 (15)	O26—Fe2—O19	86.58 (14)
O166b—Na5—Na4	74.3 (3)	O26—Fe2—O28	84.95 (14)
O66a—Na5—Na6	28.3 (3)	O26—Fe2—O29	99.31 (14)
O166b—Na5—Na6	35.4 (3)	O26—Fe2—O30	93.00 (14)
O166b—Na5—O21	163.0 (3)	O27—Fe2—O19	88.57 (15)
O3—W1—O2	92.10 (16)	O27—Fe2—O26	170.10 (14)
O3—W1—O4	156.51 (14)	O27—Fe2—O28	86.87 (14)

O3—W1—O5	76.16 (13)	O27—Fe2—O29	89.20 (14)
O3—W1—O6	88.40 (15)	O27—Fe2—O30	92.94 (15)
O4—W1—O5	80.82 (13)	O29—Fe2—O28	174.61 (15)
O6—W1—O4	83.09 (15)	O30—Fe2—O28	92.69 (14)
O6—W1—O5	80.15 (14)	O30—Fe2—O29	83.82 (14)
O6—W2—O8	86.58 (14)	O16—Fe3—O14	93.57 (14)
O6—W2—O9	82.77 (14)	O16—Fe3—O22	92.74 (14)
O6—W2—O11	155.70 (15)	O16—Fe3—O23	94.67 (15)
O7—W2—O6	97.75 (16)	O16—Fe3—O24	83.16 (14)
O7—W2—O8	93.99 (16)	O16—Fe3—O25	171.65 (14)
O7—W2—O9	170.19 (16)	O22—Fe3—O14	83.38 (14)
O7—W2—O10	102.74 (17)	O23—Fe3—O14	167.85 (14)
O7—W2—O11	95.65 (15)	O23—Fe3—O22	87.31 (14)
O66a—Na5—O21	176.3 (3)	O23—Fe3—O24	88.30 (14)
O66a—Na5—O61	96.4 (3)	O24—Fe3—O14	101.55 (14)
O166b—Na5—O62	71.7 (3)	O24—Fe3—O22	173.74 (15)
O66a—Na5—O62	84.3 (3)	O25—Fe3—O14	87.26 (14)
O66a—Na5—O63	105.1 (3)	O25—Fe3—O22	95.61 (14)
O166b—Na5—O63	97.0 (3)	O25—Fe3—O23	85.89 (14)
O166b—Na5—O74	88.6 (3)	O25—Fe3—O24	88.53 (14)
O66a—Na5—O74	74.2 (3)	O49—Na1—O49^{iv}	180.0
O66a^{viii}—Na6—Na5^{viii}	28.5 (3)	O49—Na1—O50^{iv}	94.06 (13)
O166b—Na6—Na5^{viii}	147.6 (3)	O49^{iv}—Na1—O50^{iv}	85.94 (13)
O66a—Na6—Na5^{viii}	151.5 (3)	O49^{iv}—Na1—O50	94.06 (13)
O166b^{viii}—Na6—Na5	147.6 (3)	O49—Na1—O50	85.94 (13)
O66a^{viii}—Na6—Na5	151.5 (3)	O50^{iv}—Na1—O50	180.0
O166b^{viii}—Na6—Na5^{viii}	32.4 (3)	O51—Na1—O49^{iv}	87.15 (13)
O166b—Na6—Na5	32.4 (3)	O51—Na1—O49	92.85 (13)
O9—W2—O8	76.25 (13)	O51^{iv}—Na1—O49	87.15 (13)
O10—W2—O6	100.05 (16)	O51^{iv}—Na1—O49^{iv}	92.85 (13)
O10—W2—O8	160.90 (15)	O51^{iv}—Na1—O50^{iv}	90.54 (14)
O10—W2—O9	86.76 (15)	O51—Na1—O50^{iv}	89.46 (14)
O10—W2—O11	96.62 (16)	O51^{iv}—Na1—O50	89.46 (14)
O11—W2—O8	72.31 (14)	O51—Na1—O50	90.54 (14)
O11—W2—O9	80.65 (13)	O51—Na1—O51^{iv}	180.0
O8—W3—O17	77.47 (13)	O76^{vi}—Na2—Na3^{v}	115.31 (11)
O11—W3—O8	74.48 (14)	O76^{vi}—Na2—O52^{v}	85.72 (14)
O11—W3—O17	85.82 (14)	O46—Na2—Na3^{v}	80.08 (10)
O12—W3—O8	94.71 (15)	O46—Na2—O76^{vi}	76.13 (14)
O12—W3—O11	100.68 (16)	O46—Na2—O47	83.98 (14)
O12—W3—O13	97.09 (16)	O46—Na2—O49	151.08 (16)
O12—W3—O14	103.75 (16)	O46—Na2—O52^{v}	83.19 (14)
O12—W3—O17	168.24 (16)	O47—Na2—Na3^{v}	69.12 (11)
O13—W3—O8	85.38 (14)	O47—Na2—O76^{vi}	158.13 (17)
O13—W3—O11	154.04 (14)	O47—Na2—O49	92.49 (15)
O13—W3—O17	73.75 (14)	O47—Na2—O52^{v}	101.02 (15)
O14—W3—O8	160.44 (14)	O48—Na2—Na3^{v}	144.46 (14)
O14—W3—O11	95.49 (16)	O48—Na2—O76^{vi}	97.84 (16)

O14—W3—O13	98.50 (16)	O48—Na2—O46	122.29 (18)
O14—W3—O17	85.19 (14)	O48—Na2—O47	85.06 (16)
O4^{i}—W4—O13	158.70 (15)	O48—Na2—O49	85.78 (16)
O4^{i}—W4—O17	87.50 (14)	O48—Na2—O52^{v}	154.45 (18)
O4^{i}—W4—O20^{i}	87.80 (14)	O49—Na2—Na3^{v}	71.91 (11)
O13—W4—O17	73.81 (14)	O49—Na2—O76^{vi}	109.31 (15)
O13—W4—O20^{i}	78.33 (13)	O49—Na2—O52^{v}	69.29 (14)
O15—W4—O4^{i}	99.78 (16)	O52^{v}—Na2—Na3^{v}	31.89 (9)
O15—W4—O13	96.69 (16)	O37—Na3—Na2^{v}	116.60 (11)
O15—W4—O16	102.35 (17)	O52—Na3—Na2^{v}	34.80 (10)
O15—W4—O17	166.45 (15)	O52—Na3—O37	88.80 (14)
O15—W4—O20^{i}	91.54 (16)	O52—Na3—O55	85.00 (15)
O16—W4—O4^{i}	98.64 (16)	O53—Na3—Na2^{v}	66.75 (11)
O16—W4—O13	90.86 (15)	O53—Na3—O37	86.52 (14)
O16—W4—O17	87.68 (16)	O53—Na3—O52	83.44 (15)
O16—W4—O20^{i}	163.37 (16)	O53—Na3—O55	165.38 (17)
O20^{i}—W4—O17	77.24 (14)	O53—Na3—O56	104.30 (16)
O2^{i}—W5—O5^{i}	73.17 (13)	O54—Na3—Na2^{v}	69.01 (10)
O9—W5—O2^{i}	161.79 (16)	O54—Na3—O37	167.68 (17)
O9—W5—O5^{i}	88.63 (15)	O54—Na3—O52	100.05 (16)
O9—W5—O17	94.60 (16)	O54—Na3—O53	86.01 (15)
O9—W5—O18	92.85 (15)	O54—Na3—O55	87.22 (15)
O17—W5—O2^{i}	83.63 (14)	O54—Na3—O56	86.22 (14)
O17—W5—O5^{i}	86.14 (15)	O55—Na3—Na2^{v}	98.71 (11)
O66a—Na6—Na5	28.5 (3)	O55—Na3—O37	102.18 (14)
O66a—Na6—O65^{viii}	81.5 (3)	O56—Na3—Na2^{v}	153.79 (12)
O66a^{viii}—Na6—O65^{viii}	98.5 (3)	O56—Na3—O37	86.15 (14)
O66a^{viii}—Na6—O65	81.5 (3)	O56—Na3—O52	170.45 (16)
O66a—Na6—O65	98.5 (3)	O56—Na3—O55	88.15 (15)
O66a—Na6—O66^{viii}	180.0	O10^{vii}—Na4—Na5	110.91 (11)
O166b—Na6—O166^{viii}	180.0	O58—Na4—Na5	94.56 (12)
Na5—O166b—Na6	112.2 (5)	O58—Na4—O10^{vii}	102.18 (15)
Na6—O66a—Na5	123.2 (5)	O58—Na4—O60	89.00 (15)
O17—W5—O18	156.21 (16)	O59—Na4—Na5	68.57 (10)
O18—W5—O2^{i}	82.29 (14)	O59—Na4—O10^{vii}	173.18 (17)
O18—W5—O5^{i}	71.47 (14)	O59—Na4—O58	84.62 (15)
O19—W5—O2^{i}	94.39 (15)	O59—Na4—O60	95.17 (15)
O19—W5—O5^{i}	163.66 (14)	O59—Na4—O62	98.88 (15)
O19—W5—O9	103.63 (17)	O60—Na4—Na5	162.87 (13)
O19—W5—O17	103.30 (16)	O60—Na4—O10^{vii}	84.57 (14)
O19—W5—O18	96.82 (16)	O62—Na4—Na5	34.07 (10)
O3^{i}—W6—O5^{i}	72.91 (13)	O62—Na4—O10^{vii}	82.69 (14)
O8^{i}—W6—O3^{i}	84.52 (15)	O62—Na4—O58	82.18 (15)
O8^{i}—W6—O5^{i}	85.68 (14)	O62—Na4—O60	162.60 (16)
O8^{i}—W6—O18	155.62 (15)	Na4—Na5—Na6	90.45 (5)
O18—W6—O3^{i}	82.76 (14)	O21—Na5—Na4	88.71 (11)
O18—W6—O5^{i}	70.73 (14)	O21—Na5—Na6	148.08 (11)
O20—W6—O3^{i}	160.28 (14)	O61—Na5—Na4	122.47 (12)

O20—W6—O5^{i}	87.38 (14)	O61—Na5—Na6	73.42 (11)
O20—W6—O8^{i}	94.35 (16)	O61—Na5—O21	80.23 (14)
O20—W6—O18	90.72 (15)	O61—Na5—O62	90.73 (15)
O21—W6—O3^{i}	96.16 (15)	O61—Na5—O63	151.18 (18)
O21—W6—O5^{i}	165.95 (15)	O61—Na5—O74	85.58 (15)
O21—W6—O8^{i}	102.36 (16)	O61—Na5—O166	108.6 (3)
O21—W6—O18	99.63 (16)	O62—Na5—Na4	33.69 (10)
O21—W6—O20	103.29 (16)	O62—Na5—Na6	68.87 (11)
O75—W7—O26	103.42 (16)	O62—Na5—O21	94.18 (15)
O75—W7—O31	94.64 (16)	O62—Na5—O74	157.62 (18)
O75—W7—O32	167.01 (16)	O63—Na5—Na4	76.45 (11)
O75—W7—O33	93.94 (15)	O63—Na5—Na6	131.93 (13)
O75—W7—O35	100.95 (16)	O63—Na5—O21	78.65 (14)
O26—W7—O31	98.53 (16)	O63—Na5—O62	110.12 (15)
O26—W7—O32	85.41 (14)	O63—Na5—O74	82.05 (15)
O26—W7—O33	161.89 (14)	O74—Na5—Na4	150.39 (14)
O26—W7—O35	95.91 (16)	O74—Na5—Na6	88.95 (13)
O31—W7—O32	74.41 (14)	O74—Na5—O21	106.88 (17)
O31—W7—O33	84.98 (14)	Na5^{viii}—Na6—Na5	180.0
O33—W7—O32	78.40 (13)	O64—Na6—Na5	106.43 (10)
O35—W7—O31	155.66 (14)	O64^{viii}—Na6—Na5^{viii}	106.43 (11)
O35—W7—O32	87.39 (14)	O64—Na6—Na5^{viii}	73.57 (10)
O35—W7—O33	75.47 (14)	O64^{viii}—Na6—Na5	73.57 (11)
O34—W8—O33	76.31 (13)	O64—Na6—O64^{viii}	180.0
O35—W8—O33	72.16 (14)	O64—Na6—O65^{viii}	89.83 (14)
O35—W8—O34	79.27 (14)	O64—Na6—O65	90.17 (15)
O36—W8—O33	92.20 (15)	O64^{viii}—Na6—O65	89.83 (14)
O36—W8—O34	167.70 (15)	O64^{viii}—Na6—O65^{viii}	90.17 (15)
O36—W8—O35	93.19 (15)	O64^{viii}—Na6—O66	96.6 (3)
O36—W8—O39^{ii}	97.99 (15)	O64—Na6—O66	83.4 (3)
O37—W8—O33	162.25 (15)	O64—Na6—O66^{viii}	96.6 (3)
O37—W8—O34	88.05 (15)	O64^{viii}—Na6—O66^{viii}	83.4 (3)
O37—W8—O35	97.00 (16)	O64—Na6—O166^{viii}	105.8 (3)
O37—W8—O36	102.61 (17)	O64—Na6—O166	74.2 (3)
O37—W8—O39^{ii}	101.14 (16)	O64^{viii}—Na6—O166^{viii}	74.2 (3)
O39^{ii}—W8—O33	86.20 (15)	O64^{viii}—Na6—O166	105.8 (3)
O39^{ii}—W8—O34	85.75 (14)	O65—Na6—Na5	81.74 (11)
O39^{ii}—W8—O35	156.00 (15)	O65^{viii}—Na6—Na5^{viii}	81.74 (11)
O25—W9—O32	103.17 (16)	O65—Na6—Na5^{viii}	98.26 (11)
O25—W9—O34	104.38 (17)	O65^{viii}—Na6—Na5	98.26 (11)
O25—W9—O42	163.37 (14)	O65—Na6—O65^{viii}	180.0
O25—W9—O43	92.49 (15)	O65—Na6—O166^{viii}	95.1 (3)
O25—W9—O45	97.59 (16)	O65^{viii}—Na6—O166^{viii}	84.9 (3)
O32—W9—O42	84.68 (14)	O65^{viii}—Na6—O166	95.1 (3)
O32—W9—O43	84.03 (14)	O65—Na6—O166	84.9 (3)
O32—W9—O45	155.61 (16)	W7—O75—Fe1	141.2 (2)
O34—W9—O32	94.46 (15)	W1—O2—W5^{i}	115.40 (17)
O34—W9—O42	89.37 (15)	Fe1—O76—Na2^{ix}	123.52 (16)

O34—W9—O43	162.93 (16)	W1—O3—W6^{i}	116.84 (17)
O34—W9—O45	92.62 (15)	W4^{i}—O4—W1	147.3 (2)
O43—W9—O42	73.56 (13)	W5^{i}—O5—W1	95.76 (13)
O45—W9—O42	72.07 (14)	W5^{i}—O5—W6^{i}	97.18 (14)
O45—W9—O43	82.42 (14)	W6^{i}—O5—W1	94.06 (12)
O33^{ii}—W10—O41	84.49 (14)	W2—O6—W1	149.1 (2)
O33^{ii}—W10—O42	85.99 (14)	W3—O8—W2	95.05 (14)
O33^{ii}—W10—O45	155.71 (15)	W6^{i}—O8—W2	137.59 (17)
O41—W10—O42	72.95 (13)	W6^{i}—O8—W3	125.95 (18)
O44^{ii}—W10—O33^{ii}	94.56 (15)	W5—O9—W2	137.20 (18)
O44^{ii}—W10—O41	160.62 (14)	W2—O10—Na4^{vii}	123.67 (18)
O44^{ii}—W10—O42	87.67 (14)	W3—O11—W2	117.26 (18)
O44^{ii}—W10—O45	91.49 (15)	W3—O13—W4	117.31 (18)
O45—W10—O41	82.10 (14)	W3—O14—Fe3	133.7 (2)
O45—W10—O42	70.76 (13)	W4—O16—Fe3	138.8 (2)
O46—W10—O33^{ii}	102.68 (16)	W4—O17—W3	93.90 (13)
O46—W10—O41	95.21 (15)	W5—O17—W3	125.71 (18)
O46—W10—O42	164.79 (15)	W5—O17—W4	139.11 (18)
O46—W10—O44^{ii}	103.85 (16)	W6—O18—W5	119.54 (18)
O46—W10—O45	98.64 (16)	W5—O19—Fe2	172.3 (2)
O38—W11—O39	84.45 (15)	W6—O20—W4^{i}	138.94 (18)
O38—W11—O42	81.24 (14)	W6—O21—Na5	154.0 (2)
O39—W11—O42	79.88 (14)	W9—O25—Fe3	169.9 (2)
O40—W11—O38	102.46 (16)	W7—O26—Fe2	135.4 (2)
O40—W11—O39	101.77 (16)	W12—O30—Fe2	137.9 (2)
O40—W11—O41	100.97 (16)	W7—O31—W12	116.06 (17)
O40—W11—O42	176.04 (16)	W9—O32—W7	124.93 (18)
O40—W11—O43	102.78 (17)	W9—O32—W12	139.49 (18)
O41—W11—O38	156.18 (15)	W12—O32—W7	94.25 (13)
O41—W11—O39	86.64 (15)	W7—O33—W8	95.16 (14)
O41—W11—O42	75.46 (13)	W10^{ii}—O33—W7	125.80 (18)
O43—W11—O38	87.92 (15)	W10^{ii}—O33—W8	137.86 (18)
O43—W11—O39	155.33 (15)	W9—O34—W8	139.68 (18)
O43—W11—O41	91.09 (15)	W7—O35—W8	116.42 (18)
O43—W11—O42	75.78 (14)	W8—O37—Na3	127.58 (19)
O78—W12—O30	102.32 (17)	W12—O38—W11	147.9 (2)
O78—W12—O31	97.07 (15)	W8^{ii}—O39—W11	150.9 (2)
O78—W12—O32	166.24 (15)	W11—O41—W10	116.54 (16)
O78—W12—O38	99.83 (16)	W9—O42—W10	96.86 (14)
O78—W12—O44	91.39 (15)	W9—O42—W11	95.65 (13)
O30—W12—O31	91.54 (15)	W10—O42—W11	95.01 (12)
O30—W12—O32	88.42 (16)	W11—O43—W9	114.98 (17)
O30—W12—O38	99.13 (16)	W10^{ii}—O44—W12	136.52 (18)
O30—W12—O44	163.89 (16)	W9—O45—W10	119.05 (18)
O31—W12—O32	73.79 (13)	W10—O46—Na2	166.1 (2)
O31—W12—O44	78.25 (13)	Na1—O49—Na2	120.25 (17)

O38—W12—O31	157.54 (15)	Na3—O52—Na2^{v}	113.31 (16)
O38—W12—O32	86.74 (14)	Na4—O62—Na5	112.24 (17)

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