



Structural characterization of quaternary selenites of tungsten(VI), $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb, K$ or Tl)

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Received 22 February 2021

Accepted 13 March 2021

Edited by P. Roussel, ENSCL, France

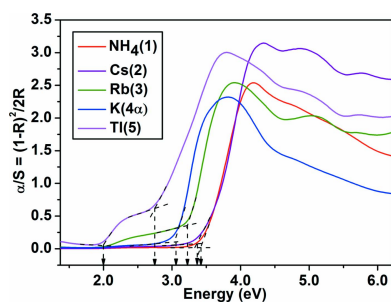
Keywords: single-crystal X-ray structure; quaternary selenite; tungsten.**CCDC references:** 2000910; 2000899; 2000898; 2000897**Supporting information:** this article has supporting information at journals.iucr.org/e

The quaternary $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb, K$ or Tl) selenites have been prepared in the form of single crystals by hydrothermal and novel solid-state reactions. They were characterized by X-ray diffraction, thermal and spectroscopic studies. All of them have a hexagonal tungsten oxide (HTO) related $[W_3SeO_{12}]^{2-}$ anionic framework with pyramidally coordinated Se^{4+} ions. The known $A_2W_3SeO_{12}$ ($A = NH_4, Cs$ or Rb) compounds are isostructural with the $Cs_2W_3TeO_{12}$ compound and have a non-centrosymmetric layered structure containing intra-layer $Se-O$ bonds. The new compound $K_2W_3SeO_{12}(\alpha)$ is isostructural with the $K_2W_3TeO_{12}$ compound and has a centrosymmetric three-dimensional structure containing interlayer $Se-O$ bonds. It is inferred that the new $Tl_2W_3SeO_{12}$ compound has the same three-dimensional structure as $K_2W_3SeO_{12}(\alpha)$.

1. Chemical context

Non-centrosymmetric (NCS) compounds are widely studied as they have potentially useful symmetry-dependent properties such as piezoelectricity, ferroelectricity and second-order non-linear optical (NLO) behaviour (Halasyamani & Poeppelmeier 1998). Many crystalline selenites and tellurites containing d^0 transition-metal ions such as V^{5+} , Mo^{6+} , W^{6+} are non-centrosymmetric compounds. The solid-state chemistry of these oxides is interesting from the point of view of both structural diversity and second harmonic generation (SHG) activity. They have two types of second-order Jahn–Teller (SOJT) distortion. One is the distorted octahedral coordination of the d^0 transition-metal ion and the other is pyramidal, disphenoidal and square-pyramidal coordinations of Se^{4+} and Te^{4+} , which have stereoactive lone pairs. Both SOJT distortions lead to acentric coordination environments that are conducive for NCS structures (Halasyamani 2004). For example, $Cs_2Mo_3TeO_{12}$ (Vidyavathy Balraj & Vidyasagar, 1998) and $YVSe_2O_8$ (Kim *et al.*, 2014) have non-centrosymmetric layered structures with these SOJT distortions and exhibit SHG activity. It needs to be mentioned that quaternary selenites and tellurites containing d^0 transition-metal ions, such as $YVTe_2O_8$ (Kim *et al.*, 2014), are also known to have centrosymmetric structures and exhibit no SHG activity.

$A_2Mo_3SeO_{12}$ ($A = NH_4, Cs, Rb, Tl$) (Harrison *et al.*, 1994; Dussack *et al.*, 1996; Chang *et al.*, 2010), $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb, K$) (Harrison *et al.*, 1995; Huang *et al.*, 2014*a,b*) and $Na_2W_3SeO_{12} \cdot 2H_2O$ (Nguyen & Halasyamani 2013), $A_2Mo_3TeO_{12}$ ($A = Cs, NH_4$) (Vidyavathy Balraj & Vidyasagar 1998), $A_2W_3TeO_{12}$ ($A = K, Rb$ and Cs) (Goodey *et al.*, 2003; Zhao *et al.*, 2015) are the 14 quaternary selenites and tellurites



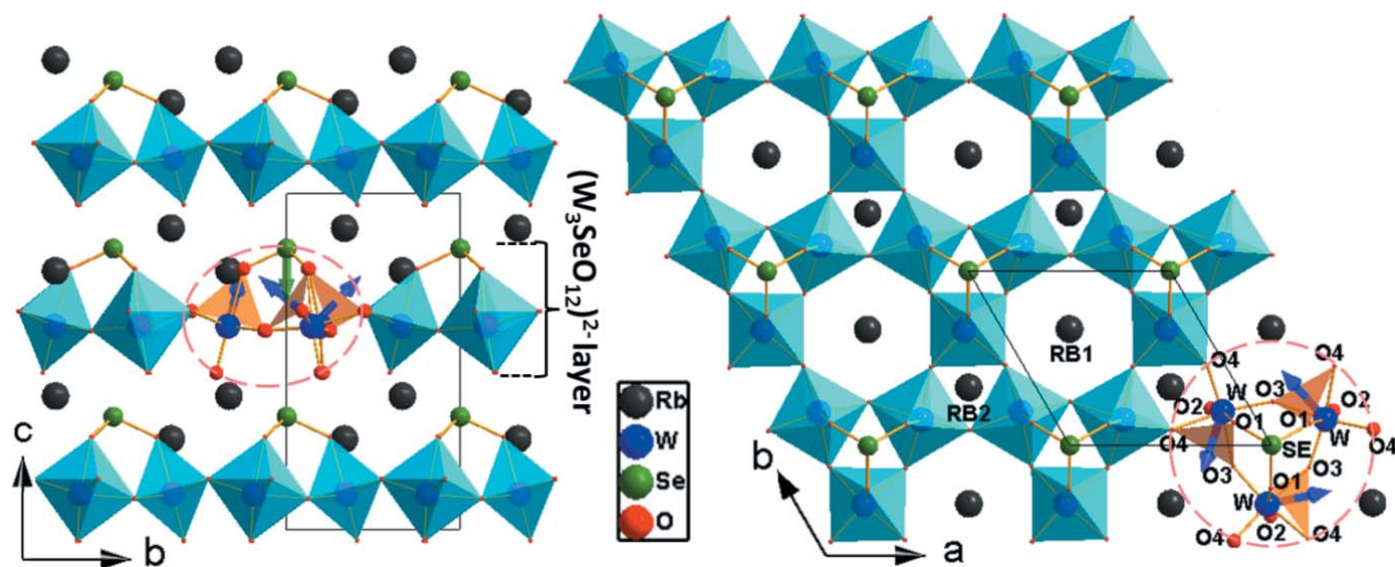


Figure 1

Polyhedral representation of (left) the unit-cell structure viewed along the *a* axis and (right) a $(W_3SeO_{12})^{2-}$ layer along with the Rb^+ counter-cations, viewed along the *c* axis, of $Rb_2W_3SeO_{12}$ (**3**). A W_3O_{15} moiety with a pyramidal selenium atom is indicated by a dashed red line and the net dipole directions of the WO_6 octahedra and pyramidal SeO_3 are shown.

of hexavalent molybdenum and tungsten that have hexagonal tungsten oxide (HTO) related $[M_3XO_{12}]^{2-}$ ($M = Mo, W; X = Se, Te$) anionic frameworks with pyramidally coordinated Se^{4+} and Te^{4+} ions. The single-crystal X-ray structures were determined for all except for the $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb$) compounds, which were synthesized in polycrystalline form by the hydrothermal method; the structures of the $(NH_4)_2W_3SeO_{12}$ and $Cs_2W_3SeO_{12}$ compounds were determined by powder neutron diffraction (Harrison *et al.*, 1995). $K_2W_3TeO_{12}$ has a centrosymmetric three-dimensional structure (Goodey *et al.*, 2003), whereas all of the others exhibit a non-centrosymmetric two-dimensional structure and show SHG response. It is noteworthy that the tellurites were synthesized by both hydrothermal and solid-state reactions, whereas the selenites were synthesized only by the hydrothermal method.

$Ag_2Mo_3SeO_{12}$ (Ling & Albrecht-Schmitt 2007), $Li_2Mo_3TeO_{12}$ (Oh *et al.*, 2018) and $A_4Mo_6Te_2O_{24} \cdot 6H_2O$ ($A = Rb, K$) (Vidyavathy Balraj & Vidyasagar 1998) compounds are quaternary selenite and tellurites of molybdenum, whose $[Mo_3XO_{12}]^{2-}$ ($X = Se, Te$) anionic framework structures are not related to HTO. They have centrosymmetric layered and zero-dimensional structures and contain pyramidally coordinated Se^{4+} and pyramidally and disphenoidally coordinated Te^{4+} ions.

In this context, the structural characterization of new and known quaternary $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb, K, Tl$) selenites of tungsten(VI) by single-crystal X-ray diffraction was considered necessary for their complete structural study and, therefore, was undertaken. This report is concerned with crystal growth by solid-state reactions and structural characterization of the known compounds $A_2W_3SeO_{12}$ [$A = NH_4$ (**1**), Cs (**2**) and Rb (**3**)] and new compounds $K_2W_3SeO_{12}$ (**4a**) and $Tl_2W_3SeO_{12}$ (**5**).

2. Structural commentary

The structures of compounds **1–5** are of two types, which contain a hexagonal tungsten oxide (HTO) related $[W_3SeO_{12}]^{2-}$ anionic framework. $(NH_4)_2W_3SeO_{12}$ (**1**), $Cs_2W_3SeO_{12}$ (**2**) and $Rb_2W_3SeO_{12}$ (**3**) crystallize in the $P6_3$ space group and have the structure of $Cs_2W_3TeO_{12}$ (Zhao *et al.*, 2015). They contain ammonium/caesium/rubidium ions between non-centrosymmetric HTO-related $[W_3SeO_{12}]^{2-}$ layers, which have only intra-layer type $Se-O$ bonds. The absolute structure configuration of the rubidium compound (**3**) is the inverse of that of the ammonium (**1**) and caesium (**2**) compounds.

As an illustrative example, the structure of $Rb_2W_3SeO_{12}$ (**3**) is discussed. Its asymmetric unit content of $Rb_{2/3}WTe_{1/3}O_4$ has two, one, one and four crystallographically distinct rubidium, tungsten, selenium and oxygen atoms, respectively. The tungsten atom is octahedrally coordinated to the apical O1 and O2 atoms and two each of equatorial O3 and O4 atoms (Fig. 1). The WO_6 octahedron resides near the threefold rotation axis located at the Wyckoff site $2a$ and shares its two *cis* O3 equatorial oxygen atoms with two such octahedra to form a W_3O_{15} moiety. Such trinuclear moieties are connected to one another through sharing of equatorial O4 atoms, forming a hexagonal-tungsten-oxide (HTO) layer of composition WO_4 or W_3O_{12} . In other words, the HTO layer of WO_4 is formed from the sharing of four equatorial O3 and O4 atoms of every WO_6 octahedron with four such octahedra. The HTO layer of WO_4 has three-ring holes made of either O3 or O4 atoms and six-ring holes made of alternating O3 and O4 atoms. The selenium atom resides on a threefold rotation axis located at the $2a$ site and has a pyramidal coordination of C_{3v} symmetry, with three equivalent $Se-O$ bonds. Thus, only three-ring holes of O3 are capped on one side of the layer, by

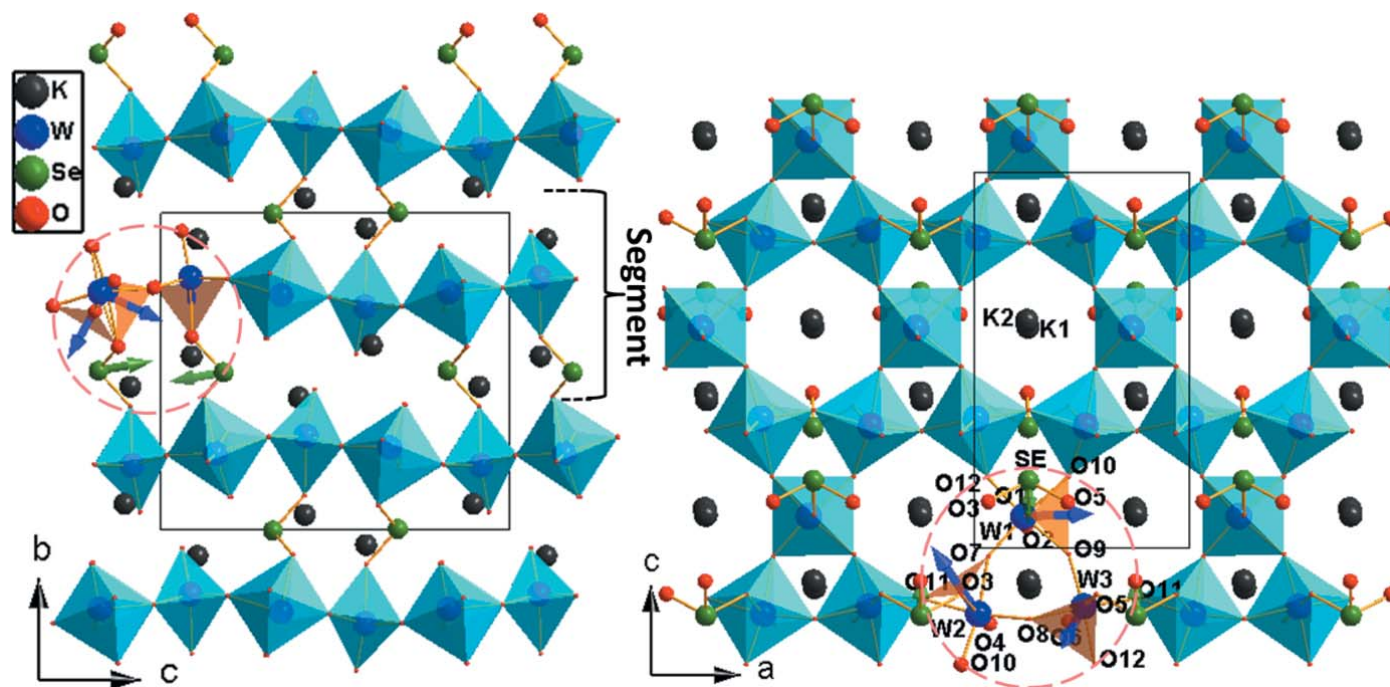


Figure 2

Polyhedral representation of (left) the unit-cell structure viewed along the $-a$ axis and (right) a segment of the $(W_3SeO_{12})^{2-}$ structure along with the K^+ counter-cations, viewed along the $-b$ axis, of $K_2W_3SeO_{12}$ (**4a**). A $W_1W_2W_3O_{15}$ moiety with pyramidal selenium is indicated by a dashed red line and the net dipole directions of octahedral WO_6 and pyramidal SeO_3 are shown.

bonding of the selenium atom to apical O1 oxygen atoms, to give rise to an asymmetric $(W_3SeO_{12})^{2-}$ layer. These layers are stacked, as shown in Fig. 1, along the crystallographic c -axis direction in the $ABAB\dots$ fashion because adjacent layers are rotated with respect to each other such that the six-ring hole of one layer is above the uncapped three-ring hole of the next layer. As the other apical oxygen O2 atoms are not bonded to selenium, the Se–O bonding is described as intra-layer bonding and, therefore, the structure is two-dimensional. The pyramidal SeO_3 moieties and the lone-pair of electrons of Se^{4+} are respectively parallel and perpendicular to the HTO layers of WO_4 . The selenites **1–5** of the present study are found to contain the same staggered stacking of the HTO-related WO_4 layers.

$K_2W_3SeO_{12}$ (**β**) was reported (Huang *et al.*, 2014*a,b*) to be obtained under hydrothermal conditions and found to contain similar non-centrosymmetric HTO-related $[W_3SeO_{12}]^{2-}$ layers with intra-layer Se–O bonds. On the other hand, $K_2W_3SeO_{12}$ (**4a**) of the present study was prepared by solid-state reaction and is isostructural with the reported $K_2W_3TeO_{12}$ (Goodey *et al.*, 2003). Its centrosymmetric, three-dimensional HTO-related $[W_3SeO_{12}]^{2-}$ framework contains inter-layer Se–O bonds (Fig. 2) and its asymmetric unit has one formula unit. The three W1–W3 atoms are octahedrally coordinated to six apical O1–O6 and six equatorial O7–O12 oxygen atoms. The three WO_6 octahedra in the trinuclear $W_1W_2W_3O_{15}$ moieties share equatorial O7–O9 oxygen atoms and these moieties are connected to one another through the other equatorial O10–O12 oxygen atoms to form the WO_4 layer. The Se atom forms interlayer Se–O bonds, by bonding

to the apical O7, O10 and O12 oxygen atoms of $W_1W_2W_3O_{15}$ moieties of adjacent HTO layers (Fig. 2) and thus the $[W_3SeO_{12}]^{2-}$ framework is three-dimensional in nature.

$Tl_2W_3SeO_{12}$ (**5**) has an orthorhombic unit cell with $a_o = 11.5962$ (10) Å, $b_o = 12.7206$ (5) Å and $c_o = 7.2362$ (9) Å. The structure refinements in the non-centrosymmetric $Pna2_1$ and centrosymmetric $Pnam$ space groups led to the respective structure agreement factor values of 6.37% and 15.98%; the structure refinements were unsatisfactory, mostly due to X-ray absorption. Its single crystal X-ray structure solution model is found to be same as the three-dimensional structure of $K_2W_3SeO_{12}$ (**4a**) and its observed powder XRD pattern (Figure S1b in the supporting information) agrees reasonably with the one simulated on the basis of this model structure. Moreover, the powder XRD patterns and unit-cell parameters of these two compounds are similar. The orthorhombic unit-cell parameters of the thallium (**5**) compound are related to the monoclinic unit-cell parameters of the potassium (**4a**) compound as follows: $a_o \simeq b_m$, $b_o \simeq c_m$, $c_o \simeq a_m$ and $\alpha_o = 90^\circ \simeq \beta_m$. The single-crystal X-ray data for the thallium compound (**5**) in the centrosymmetric $P2_1/n$ space group, corresponding to the potassium compound (**4a**), led to the same structure model and a high value of 19.18% for the structure-agreement factor. It is inferred from these observations that the $Tl_2W_3SeO_{12}$ compound (**5**) has the same three-dimensional structure as $K_2W_3SeO_{12}$ (**4a**).

In the structurally characterized compounds **1–4a** of the present study, the WO_6 octahedra have C_3 distortion as three W–O bonds are <1.9 Å long and their three *trans* W–O bonds are >1.9 Å long; the values of WO_6 intraoctahedral

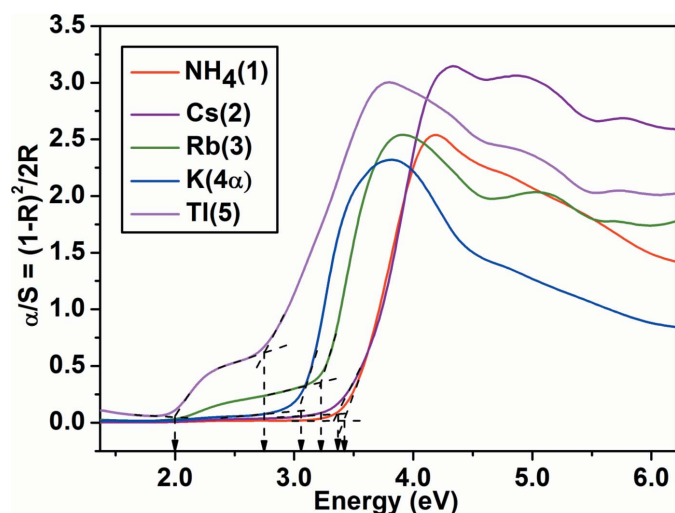


Figure 3
Solid state UV-visible absorption spectra for the $A_2W_3SeO_{12}$ [$A = NH_4$ (1), Cs (2), Rb (3), K (4a) and Tl (5)] compounds.

distortions (Halasyamani 2004), Δ_d , are calculated to be in the 0.73–0.86 range (Table S1). The Se^{4+} ions have pyramidal coordination. The W–O and Se–O bond-length values are in the 1.703 (17)–2.184 (9) Å and 1.695 (10)–1.739 (10) Å ranges, respectively. The ammonium and alkali metal ions are found to be six- to nine-coordinated (Figure S2), when the cut-off value of 3.6 Å is considered for N···O non-bonding distances and A–O bond lengths. The calculated values (Brese & O’Keeffe 1991) of bond-valence sums for W^{6+} , Se^{4+} and monovalent alkali metal ions are in the 6.079–6.283, 3.807–3.975 and 0.060–1.275 ranges, respectively. The respective values of 3.210, 3.322 and 3.207 Å for the shortest interlayer O···O non-bonding distances of compounds 1–3 with intra-layer Se–O bonds are significantly higher than the corresponding value of 2.563 Å for compound 4a with interlayer Se–O bonds.

The net dipole moment values for the WO_6 and SeO_3 polyhedra were calculated by vector summation of the dipole moments (Maggard *et al.*, 2003; Ok & Halasyamani 2005; Galy *et al.*, 1975) of six W–O bonds and three Se–O bonds and found to be in the 0.79–1.85 D and 5.73–9.13 D ranges, respectively (Tables S1–S3). The net dipole for the WO_6 octahedron points towards the triangular face of three oxygen atoms with W–O bonds >1.9 Å long, whereas the net dipoles for the SeO_3 polyhedra point opposite to the lone pair of electrons of selenium. In compounds 1–3, as shown for $Rb_2W_3SeO_{12}$ (3) in Fig. 1, the intra-layer SeO_3 dipole is oriented along the *c*-axis direction and perpendicular to the HTO layer. For the WO_6 octahedra, the net dipole moment components along the *a* and *b* axes cancel one another, whereas the *c*-axis component is antiparallel and additive to the net dipole moment of pyramidal SeO_3 . In the case of centrosymmetric three-dimensional $K_2W_3SeO_{12}$ (4a), as shown in Fig. 2, the net dipole moments of the WO_6 and SeO_3 polyhedra macroscopically cancel one another and result in a zero net dipole moment.

The solid state UV–Visible absorption spectra (Fig. 3) of compounds 1–5 reveal that their band gap values are in the range 2.7–3.5 eV (Kubelka & Munk, 1931). The additional absorption edge observed for the $Tl_2W_3SeO_{12}$ compound (5) corresponds to band gap value of 2.0 eV. When compared to $Cs_2W_3SeO_{12}$ (2), the corresponding $Cs_2W_3TeO_{12}$ tellurite (Zhao *et al.*, 2015) has a lower band gap of 2.89 eV.

$Rb_2W_3SeO_{12}$ (3), $K_2W_3SeO_{12}$ (4a) and $Tl_2W_3SeO_{12}$ (5) undergo thermal decompositions and give rise to endothermic peaks at ~600, ~575 and ~575°C and their respective observed weight losses of 10.0%, 12.3% and 9.0% compare well with those calculated for the loss of SeO_2 (Figure S3). The other endothermic peaks at ~850 and 750°C could not be assigned. It was reported (Harrison *et al.*, 1995) that a similar thermal loss of SeO_2 occurs in a single step between 500 and 600°C for $Cs_2W_3SeO_{12}$ (2) and in two steps at 350 and 450°C for $(NH_4)_2W_3SeO_{12}$ (1). When compared to the tungsten selenites 1–5, analogous $A_2W_3TeO_{12}$ ($A = K, Rb, Cs$) tellurites of tungsten (Goodey *et al.*, 2003; Zhao *et al.*, 2015) and $A_2Mo_3SeO_{12}$ ($A = Rb, Tl$) selenites of molybdenum (Chang *et al.*, 2010) undergo single-step thermal decomposition at higher and lower temperatures of >700 and 300°C, respectively.

3. Syntheses and crystallization

Cs_2CO_3 (Alfa Aesar), Rb_2CO_3 (Alfa Aesar), $TiNO_3$ (Sigma Aldrich), H_2WO_4 (Sigma Aldrich), SeO_2 (Sigma Aldrich), NH_4Cl (Sarabhai M Chemicals) of >99% purity, NH_4OH (Fischer Scientific) of 25% dilution, WO_3 and Tl_2WO_4 were used for the synthesis and crystal growth of compounds 1–5. WO_3 was obtained by heating H_2WO_4 in the open air. Tl_2WO_4 was prepared by heating a stoichiometric mixture of $TiNO_3$ and H_2WO_4 . Teflon-lined stainless steel acid digestion vessels of 23 mL capacity were employed for the hydrothermal reactions.

The reactants and their quantities, the temperature and duration of heating and the yields of products for the synthesis and crystal growth of compounds 1–5 are presented in Table S4. The ammonium compound (1) was synthesized by the hydrothermal method, with or without NH_4Cl as mineralizer. The other four compounds (2–5) were obtained by solid-state reactions. The reactant mixtures were heated first in the open air and later in evacuated sealed silica ampoules. After the reaction, the solid product contents were washed with water to dissolve away the excess SeO_2 .

The hydrothermal and solid-state synthetic methods enabled the growth and isolation of single crystals of compounds 1–5. The utilization of excess SeO_2 as flux in the novel solid-state synthetic procedure facilitated the growth of single crystals of compounds 2–5. The powder XRD patterns of compounds 1–5 are presented in Figures S1a and S1b. $(NH_4)_2W_3SeO_{12}$ (1), $Rb_2W_3SeO_{12}$ (3) and $Tl_2W_3SeO_{12}$ (5) were obtained as homogeneous phases, as their observed powder XRD patterns compare reasonably well with the simulated ones. The powder XRD patterns of $Cs_2W_3SeO_{12}$ (2), $Rb_2W_3SeO_{12}$ (3) and $K_2W_3SeO_{12}$ (4a) contained two or three additional reflections of <10% intensity due to WO_3 or an

Table 1
Experimental details.

	1	2	3	4
Crystal data				
Chemical formula	(NH ₄) ₂ W ₃ SeO ₁₂	Cs ₂ W ₃ SeO ₁₂	Rb ₂ W ₃ SeO ₁₂	K ₂ W ₃ SeO ₁₂
<i>M_r</i>	858.59	1088.33	993.40	900.66
Crystal system, space group	Hexagonal, <i>P</i> 6 ₃	Hexagonal, <i>P</i> 6 ₃	Hexagonal, <i>P</i> 6 ₃	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	297	293	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2303 (3), 7.2303 (3), 12.1491 (5)	7.2580 (3), 7.2580 (3), 12.5291 (5)	7.2380 (1), 7.2380 (1), 12.1115 (3)	7.2310 (2), 11.4863 (4), 12.6486 (4)
α , β , γ (°)	90, 90, 120	90, 90, 120	90, 90, 120	90, 90.096 (2), 90
<i>V</i> (Å ³)	550.03 (5)	571.59 (5)	549.50 (2)	1050.56 (6)
<i>Z</i>	2	2	2	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	34.67	39.63	43.49	37.09
Crystal size (mm)	0.10 × 0.10 × 0.05	0.10 × 0.08 × 0.05	0.10 × 0.05 × 0.05	0.08 × 0.05 × 0.02
Data collection				
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.129, 0.276	0.110, 0.242	0.098, 0.220	0.155, 0.524
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	14419, 1079, 1069	2825, 831, 730	3497, 675, 654	26562, 4026, 3456
<i>R</i> _{int}	0.049	0.058	0.033	0.073
(sin θ/λ) _{max} (Å ⁻¹)	0.702	0.643	0.666	0.770
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.052, 1.27	0.029, 0.054, 1.02	0.018, 0.033, 1.06	0.032, 0.105, 1.15
No. of reflections	1079	831	675	4026
No. of parameters	57	56	57	165
No. of restraints	1	13	7	24
H-atom treatment	H-atom parameters not defined	–	–	–
Δρ _{max} , Δρ _{min} (e Å ⁻³)	2.63, -2.37	1.90, -1.65	0.90, -1.14	3.94, -3.11
Absolute structure	Flack <i>x</i> determined using 492 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 297 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 182 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	–
Absolute structure parameter	0.015 (13)	0.00 (3)	-0.08 (3)	–

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXT* (Sheldrick, 2015a), *SHELXL2013* (Sheldrick, 2015b), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Pennington, 1999) and *SHELXL97* (Sheldrick, 2008).

unidentified phase; however, the homogeneous polycrystalline sample of Rb₂W₃SeO₁₂ (**3**) could be obtained (Figure S1b), under a different set of solid-state synthetic conditions mentioned in Table S4. Cs₂W₃SeO₁₂ (**2**) was prepared in polycrystalline form by the reported hydrothermal method (Harrison *et al.*, 1995). It is evident from the scanning electron micrographs (Figure S4) that crystallites of compounds **1** and **2** have a hexagonal prism shape and compounds **3–5** have block-shaped morphologies. The EDXA analyses confirmed the expected ratios of metal contents for all compounds **1–5**.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The crystals of the ammonium (**1**) and rubidium (**3**) compounds are twinned by merohedry (Spek 2020) by the [−1 0 0 1 1 0 0 0 − 1] and [1 0 0 − 1 − 1 0 0 0 − 1] twin laws and their twinned lattices are generated through twofold rotation of the primary lattices about the [120] direction and the *b* axis, respectively. The crystal of the potassium (**4a**) compound is twinned by pseudo-merohedry

(Spek 2020) by the twin law [−1 0 0 0 − 1 0 0 0 1] and the twinned lattice is generated through twofold rotation of the primary lattice about the *c* axis, as the value of the β angle of its monoclinic system is very close to 90°. The respective values of refined batch scale factor for the ammonium (**1**), rubidium (**3**) and potassium (**4a**) compounds are 0.029, 0.192 and 0.385. The hydrogen atoms of the NH₄⁺ ions in the ammonium compound (**1**) were not located in the difference-Fourier maps but are included in the formula. The final difference-Fourier maps did not show any chemically significant features and the Fourier difference peaks with an electron density of >1 e Å⁻³ were found to be ghosts. No reasonable structure solutions and refinements in the centrosymmetric *P*6₃/*m* space group were found for compounds **1–3**.

The powder X-ray diffraction (XRD) patterns of compounds **1–5** were recorded on a Bruker D8 Advanced powder X-ray diffractometer using Cu *K*α (λ = 1.5418 Å) radiation. The monophasic nature of each of these compounds was verified by comparing their powder XRD patterns with those simulated, using *Mercury* (Macrae *et al.*, 2020), on the basis of their single crystal X-ray structures.

Acknowledgements

Miss Rintu Robert helped immensely by redoing the single-crystal X-ray structure determinations and some of the crystal growth experiments. We thank Mrs S. Srividya and Mr V. Ramkumar of the Department of Chemistry for the powder and single-crystal X-ray data collection, respectively. The X-ray powder diffractometer in the Department of Chemistry of the IIT Madras was purchased with financial assistance, received under the FIST scheme (SR/FST/CSI-158/2007), from the SERC Division of the Department of Science and Technology, Ministry of Science and Technology, Government of India. We thank the Departments of Chemistry, Physics and SAIF of the IIT Madras for the powder and single-crystal X-ray data, SEM, EDXA and thermal studies.

References

- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chang, H. Y., Kim, S. W. & Halasyamani, P. S. (2010). *Chem. Mater.* **22**, 3241–3250.
- Dussack, L. L., Harrison, W. T. A. & Jacobson, A. J. (1996). *Mater. Res. Bull.* **31**, 249–255.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Galy, J., Meunier, G., Andersson, S. & Åström, A. (1975). *J. Solid State Chem.* **13**, 142–159.
- Goodey, J., Min Ok, K., Broussard, J., Hofmann, C., Escobedo, F. V. & Halasyamani, P. S. (2003). *J. Solid State Chem.* **175**, 3–12.
- Halasyamani, P. S. (2004). *Chem. Mater.* **16**, 3586–3592.
- Halasyamani, P. S. & Poeppelmeier, K. R. (1998). *Chem. Mater.* **10**, 2753–2769.
- Harrison, W. T. A., Dussack, L. L. & Jacobson, A. J. (1994). *Inorg. Chem.* **33**, 6043–6049.
- Harrison, W. T. A., Dussack, L. L., Vogt, T. & Jacobson, A. J. (1995). *J. Solid State Chem.* **120**, 112–120.
- Huang, Y., Chen, X. & Qin, J. (2014a). *Faming Zhuanli Shenqing* 1–8.
- Huang, Y., Meng, X. & Qin, J. (2014b). *Chin. J. Inorg. Chem.* **30**, 179–184.
- Kim, Y. H., Lee, D. W. & Ok, K. M. (2014). *Inorg. Chem.* **53**, 1250–1256.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Kubelka, F. & Munk, P. (1931). *Z. Tech. Phys.* **12**, 593–601.
- Ling, J. & Albrecht-Schmitt, T. E. (2007). *J. Solid State Chem.* **180**, 1601–1607.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Maggard, P. A., Nault, T. S., Stern, C. L. & Poeppelmeier, K. R. (2003). *J. Solid State Chem.* **175**, 27–33.
- Nguyen, S. D. & Halasyamani, P. S. (2013). *Inorg. Chem.* **52**, 2637–2647.
- Oh, S. J., Lim, S. J., You, T. S. & Ok, K. M. (2018). *Chem. Eur. J.* **24**, 6712–6716.
- Ok, K. M. & Halasyamani, P. S. (2005). *Inorg. Chem.* **44**, 3919–3925.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Pennington, W. T. (1999). *J. Appl. Cryst.* **32**, 1028–1029.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Vidyavathy Balraj, V. & Vidyasagar, K. (1998). *Inorg. Chem.* **37**, 4764–4774.
- Zhao, P., Cong, H., Tian, X., Sun, Y., Zhang, C., Xia, S., Gao, Z. & Tao, X. (2015). *Cryst. Growth Des.* **15**, 4484–4489.

supporting information

Acta Cryst. (2021). E77, 406-411 [https://doi.org/10.1107/S2056989021002735]

Structural characterization of quaternary selenites of tungsten(VI), $A_2W_3SeO_{12}$ ($A = NH_4, Cs, Rb, K$ or Tl)

Vineela Balisetty and Kanamaluru Vidyasagar

Computing details

For all structures, data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE* (Bruker, 2004). Program(s) used to solve structure: *SHELXT2013* (Sheldrick, 2015a) for $NH_4W_3SeO_{12}$; *SHELXT2014/7* (Sheldrick, 2015a) for $Cs_2W_3SeO_{12}$, $Rb_2W_3SeO_{12}$, $K_2W_3SeO_{12}$. Program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015b) for $NH_4W_3SeO_{12}$; *SHELXL2014/7* (Sheldrick, 2015b) for $Cs_2W_3SeO_{12}$, $K_2W_3SeO_{12}$; *SHELXL2018/3* (Sheldrick, 2015b) for $Rb_2W_3SeO_{12}$. For all structures, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Pennington, 1999); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Diammonium tritungsten selenite ($NH_4W_3SeO_{12}$)

Crystal data

$(NH_4)_2W_3SeO_{12}$
 $M_r = 858.59$
 Hexagonal, $P6_3$
 $a = 7.2303$ (3) Å
 $c = 12.1491$ (5) Å
 $V = 550.03$ (5) Å³
 $Z = 2$
 $F(000) = 748$

$D_x = 5.184$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 7856 reflections
 $\theta = 3.3\text{--}30.4^\circ$
 $\mu = 34.67$ mm⁻¹
 $T = 297$ K
 Block, colourless
 0.10 × 0.10 × 0.05 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.129$, $T_{\max} = 0.276$
 14419 measured reflections

1079 independent reflections
 1069 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.4^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.052$
 $S = 1.27$
 1079 reflections
 57 parameters

1 restraint
 H-atom parameters not defined
 $w = 1/[\sigma^2(F_o^2) + (0.0097P)^2 + 8.3615P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.63$ e Å⁻³
 $\Delta\rho_{\min} = -2.37$ e Å⁻³

Extinction correction: SHELXL-2018/3
(Sheldrick 2015b),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0100 (5)

Absolute structure: Flack x determined using
492 quotients $[(F^+) - (F^-)] / [(F^+) + (F^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.015 (13)

Special details

Experimental. Single crystals of compounds **1–5** were obtained along with the polycrystalline sample and the crystals were hand-picked for XRD study and mounted on thin glass fibres with epoxy glue and optically aligned on a Bruker APEXII charge-coupled device X-ray diffractometer using a digital camera. Intensity data were measured at 25 °C using Mo $K\alpha$ ($\lambda = 0.7103 \text{ \AA}$) radiation. APEX II software (Bruker AXS) was used for preliminary determination of the cell constants and data collection control. The determination of integral intensities and global refinement were performed using SAINT-plus (Bruker AXS). A semi-empirical absorption correction was subsequently applied using SADABS. Space group determination, structure solution and least-squares refinement were carried out using SHELXTL (Sheldrick 2008) program. DIAMOND 3.0 (PENNINGTON 1999) and ORTEP-3 (Farrugia 1997) for windows were the graphic programs employed to draw the structures. The structures were solved by direct methods and refined by full matrix least squares on F^2 .

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. Refined as a two-component twin

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.333333	0.666667	0.115 (3)	0.042 (8)
N2	0.666667	0.333333	0.237 (2)	0.025 (5)
W	0.19142 (6)	0.33979 (5)	0.40000 (10)	0.00766 (15)
Se	0.000000	0.000000	0.16680 (15)	0.0102 (5)
O1	0.1264 (15)	0.2465 (16)	0.2271 (7)	0.0134 (17)
O2	0.4083 (16)	0.1964 (16)	0.0370 (8)	0.0137 (18)
O3	0.2494 (12)	0.1188 (12)	0.4103 (12)	0.0101 (19)
O4	0.0850 (15)	0.5365 (14)	0.3526 (8)	0.0111 (16)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.052 (13)	0.052 (13)	0.023 (14)	0.026 (7)	0.000	0.000
N2	0.025 (8)	0.025 (8)	0.024 (12)	0.012 (4)	0.000	0.000
W	0.0069 (2)	0.00476 (19)	0.0108 (2)	0.00250 (14)	-0.0007 (3)	-0.0006 (3)
Se	0.0091 (5)	0.0091 (5)	0.0124 (12)	0.0045 (2)	0.000	0.000
O1	0.013 (4)	0.010 (4)	0.015 (4)	0.005 (4)	-0.004 (3)	0.001 (3)
O2	0.010 (4)	0.013 (5)	0.016 (4)	0.004 (4)	-0.001 (3)	0.002 (3)
O3	0.006 (3)	0.006 (3)	0.019 (5)	0.003 (2)	-0.002 (5)	0.005 (5)
O4	0.011 (4)	0.004 (4)	0.018 (4)	0.004 (3)	-0.003 (3)	-0.002 (3)

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

W—O2 ⁱ	1.722 (10)	W—O1	2.184 (9)
W—O3	1.848 (8)	Se—O1 ⁱⁱⁱ	1.709 (10)
W—O4 ⁱⁱ	1.874 (9)	Se—O1	1.709 (10)

W—O3 ⁱⁱⁱ	1.985 (8)	Se—O1 ^{iv}	1.709 (10)
W—O4	2.010 (9)		
O2 ⁱ —W—O3	99.2 (6)	O3—W—O1	84.5 (5)
O2 ⁱ —W—O4 ⁱⁱ	99.3 (5)	O4 ⁱⁱ —W—O1	86.0 (4)
O3—W—O4 ⁱⁱ	96.7 (4)	O3 ⁱⁱⁱ —W—O1	80.7 (5)
O2 ⁱ —W—O3 ⁱⁱⁱ	93.4 (6)	O4—W—O1	81.0 (4)
O3—W—O3 ⁱⁱⁱ	89.7 (4)	O1 ⁱⁱⁱ —Se—O1	102.9 (4)
O4 ⁱⁱ —W—O3 ⁱⁱⁱ	164.6 (5)	O1 ⁱⁱⁱ —Se—O1 ^{iv}	102.9 (4)
O2 ⁱ —W—O4	94.7 (4)	O1—Se—O1 ^{iv}	102.9 (4)
O3—W—O4	164.5 (5)	Se—O1—W	130.9 (5)
O4 ⁱⁱ —W—O4	87.8 (6)	W—O3—W ^{iv}	149.1 (5)
O3 ⁱⁱⁱ —W—O4	82.6 (4)	W ^v —O4—W	132.5 (5)
O2 ⁱ —W—O1	173.1 (4)		

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

Dicaesium tritungsten selenite (Cs₂W₃SeO₁₂)

Crystal data

Cs₂W₃SeO₁₂
 $M_r = 1088.33$
 Hexagonal, $P6_3$
 $a = 7.2580$ (3) Å
 $c = 12.5291$ (5) Å
 $V = 571.59$ (5) Å³
 $Z = 2$
 $F(000) = 924$

$D_x = 6.323$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 706 reflections
 $\theta = 3.6$ – 26.3°
 $\mu = 39.63$ mm⁻¹
 $T = 293$ K
 Block, colourless
 $0.10 \times 0.08 \times 0.05$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 phi and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.110$, $T_{\max} = 0.242$
 2825 measured reflections

831 independent reflections
 730 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 27.2^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -6 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -16 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.054$
 $S = 1.02$
 831 reflections
 56 parameters
 13 restraints
 $w = 1/[\sigma^2(F_o^2)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.90$ e Å⁻³
 $\Delta\rho_{\min} = -1.65$ e Å⁻³
 Extinction correction: SHELXL2018/3
 (Sheldrick 2015b),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0081 (4)
 Absolute structure: Flack x determined using
 297 quotients $[(I^-) - (I^+)] / [(I^-) + (I^+)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.00 (3)

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.333333	0.666667	0.0902 (2)	0.0269 (9)
Cs2	0.666667	0.333333	0.22953 (19)	0.0143 (7)
W	0.14949 (10)	0.33884 (11)	0.39443 (8)	0.0056 (2)
Se	0.000000	0.000000	0.1700 (2)	0.0058 (7)
O1	0.125 (2)	0.250 (2)	0.2270 (11)	0.007 (3)
O2	0.401 (2)	0.207 (2)	0.0265 (14)	0.015 (3)
O3	0.2495 (18)	0.1279 (17)	0.4056 (14)	0.008 (3)
O4	0.088 (2)	0.549 (2)	0.3529 (11)	0.010 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0277 (13)	0.0277 (13)	0.0251 (16)	0.0139 (6)	0.000	0.000
Cs2	0.0160 (10)	0.0160 (10)	0.0110 (13)	0.0080 (5)	0.000	0.000
W	0.0048 (4)	0.0031 (4)	0.0083 (4)	0.0016 (3)	0.0004 (5)	-0.0001 (5)
Se	0.0066 (9)	0.0066 (9)	0.0042 (18)	0.0033 (5)	0.000	0.000
O1	0.013 (8)	0.004 (7)	0.002 (6)	0.004 (7)	0.000 (6)	-0.001 (6)
O2	0.015 (8)	0.011 (9)	0.020 (9)	0.007 (7)	-0.010 (7)	0.003 (7)
O3	0.008 (3)	0.008 (3)	0.009 (3)	0.0042 (18)	0.0001 (14)	-0.0003 (14)
O4	0.009 (3)	0.009 (3)	0.010 (3)	0.0050 (19)	0.0000 (14)	-0.0001 (14)

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

Cs1—O1 ⁱ	3.132 (15)	Cs2—O4 ⁱⁱ	3.066 (14)
Cs1—O1	3.132 (15)	Cs2—O3 ^{vi}	3.427 (13)
Cs1—O1 ⁱⁱ	3.132 (15)	Cs2—O3	3.427 (13)
Cs1—O3 ⁱⁱⁱ	3.497 (15)	Cs2—O3 ^{vii}	3.427 (13)
Cs1—O3 ^{iv}	3.497 (15)	Cs2—O1 ^{vii}	3.667 (13)
Cs1—O3 ^v	3.497 (15)	Cs2—O1	3.667 (13)
Cs1—O4 ⁱ	3.634 (14)	Cs2—O1 ^{vi}	3.667 (13)
Cs1—O4 ⁱⁱ	3.634 (14)	W—O2 ^x	1.703 (17)
Cs1—O4	3.634 (14)	W—O3 ^{xi}	1.840 (11)
Cs1—O2 ⁱ	3.695 (14)	W—O4	1.863 (13)
Cs1—O2 ⁱⁱ	3.695 (14)	W—O4 ⁱⁱ	2.000 (13)
Cs1—O2	3.695 (14)	W—O3	2.000 (10)
Cs2—O2	3.044 (16)	W—O1	2.176 (14)
Cs2—O2 ^{vi}	3.044 (16)	Se—O1 ^{xi}	1.723 (15)
Cs2—O2 ^{vii}	3.044 (16)	Se—O1	1.724 (15)
Cs2—O4 ^{viii}	3.066 (14)	Se—O1 ^{ix}	1.724 (15)

Cs2—O4 ^{ix}	3.066 (14)		
O1 ⁱ —Cs1—O1	92.9 (4)	O4 ⁱⁱ —Cs2—O1 ^{vi}	143.4 (3)
O1 ⁱ —Cs1—O1 ⁱⁱ	92.9 (4)	O3 ^{vi} —Cs2—O1 ^{vi}	45.0 (3)
O1—Cs1—O1 ⁱⁱ	92.9 (4)	O3—Cs2—O1 ^{vi}	97.0 (3)
O1 ⁱ —Cs1—O3 ⁱⁱⁱ	74.6 (3)	O3 ^{vii} —Cs2—O1 ^{vi}	127.0 (3)
O1—Cs1—O3 ⁱⁱⁱ	132.9 (3)	O1 ^{vii} —Cs2—O1 ^{vi}	119.992 (7)
O1 ⁱⁱ —Cs1—O3 ⁱⁱⁱ	132.1 (3)	O1—Cs2—O1 ^{vi}	119.993 (8)
O1 ⁱ —Cs1—O3 ^{iv}	132.1 (3)	O2 ^x —W—O3 ^{xi}	97.7 (8)
O1—Cs1—O3 ^{iv}	74.6 (3)	O2 ^x —W—O4	98.5 (7)
O1 ⁱⁱ —Cs1—O3 ^{iv}	132.9 (3)	O3 ^{xi} —W—O4	96.6 (5)
O3 ⁱⁱⁱ —Cs1—O3 ^{iv}	81.0 (4)	O2 ^x —W—O4 ⁱⁱ	93.8 (6)
O1 ⁱ —Cs1—O3 ^v	132.9 (3)	O3 ^{xi} —W—O4 ⁱⁱ	167.0 (7)
O1—Cs1—O3 ^v	132.1 (3)	O4—W—O4 ⁱⁱ	87.4 (8)
O1 ⁱⁱ —Cs1—O3 ^v	74.6 (3)	O2 ^x —W—O3	92.3 (7)
O3 ⁱⁱⁱ —Cs1—O3 ^v	81.0 (4)	O3 ^{xi} —W—O3	89.9 (7)
O3 ^{iv} —Cs1—O3 ^v	81.0 (4)	O4—W—O3	166.5 (7)
O1 ⁱ —Cs1—O4 ⁱ	48.2 (3)	O4 ⁱⁱ —W—O3	83.7 (5)
O1—Cs1—O4 ⁱ	81.9 (3)	O2 ^x —W—O1	172.7 (6)
O1 ⁱⁱ —Cs1—O4 ⁱ	47.2 (3)	O3 ^{xi} —W—O1	85.8 (7)
O3 ⁱⁱⁱ —Cs1—O4 ⁱ	116.3 (3)	O4—W—O1	87.5 (6)
O3 ^{iv} —Cs1—O4 ⁱ	156.5 (3)	O4 ⁱⁱ —W—O1	82.1 (5)
O3 ^v —Cs1—O4 ⁱ	115.9 (3)	O3—W—O1	81.2 (6)
O1 ⁱ —Cs1—O4 ⁱⁱ	81.9 (3)	O2 ^x —W—Cs2 ^{xii}	123.2 (5)
O1—Cs1—O4 ⁱⁱ	47.2 (3)	O3 ^{xi} —W—Cs2 ^{xii}	57.3 (4)
O1 ⁱⁱ —Cs1—O4 ⁱⁱ	48.2 (3)	O4—W—Cs2 ^{xii}	46.0 (4)
O3 ⁱⁱⁱ —Cs1—O4 ⁱⁱ	156.5 (3)	O4 ⁱⁱ —W—Cs2 ^{xii}	120.1 (4)
O3 ^{iv} —Cs1—O4 ⁱⁱ	115.9 (3)	O3—W—Cs2 ^{xii}	132.2 (4)
O3 ^v —Cs1—O4 ⁱⁱ	116.3 (3)	O1—W—Cs2 ^{xii}	64.1 (3)
O4 ⁱ —Cs1—O4 ⁱⁱ	43.1 (4)	O2 ^x —W—Cs1 ^{xiii}	59.3 (5)
O1 ⁱ —Cs1—O4	47.2 (3)	O3 ^{xi} —W—Cs1 ^{xiii}	53.6 (5)
O1—Cs1—O4	48.2 (3)	O4—W—Cs1 ^{xiii}	68.7 (4)
O1 ⁱⁱ —Cs1—O4	81.9 (3)	O4 ⁱⁱ —W—Cs1 ^{xiii}	138.9 (4)
O3 ⁱⁱⁱ —Cs1—O4	115.9 (3)	O3—W—Cs1 ^{xiii}	124.3 (4)
O3 ^{iv} —Cs1—O4	116.3 (3)	O1—W—Cs1 ^{xiii}	127.4 (3)
O3 ^v —Cs1—O4	156.5 (3)	Cs2 ^{xii} —W—Cs1 ^{xiii}	65.81 (5)
O4 ⁱ —Cs1—O4	43.1 (4)	O2 ^x —W—Cs2	114.7 (5)
O4 ⁱⁱ —Cs1—O4	43.1 (4)	O3 ^{xi} —W—Cs2	127.9 (4)
O1 ⁱ —Cs1—O2 ⁱ	57.5 (4)	O4—W—Cs2	116.1 (4)
O1—Cs1—O2 ⁱ	91.3 (3)	O4 ⁱⁱ —W—Cs2	40.4 (4)
O1 ⁱⁱ —Cs1—O2 ⁱ	150.4 (4)	O3—W—Cs2	51.3 (4)
O3 ⁱⁱⁱ —Cs1—O2 ⁱ	43.5 (3)	O1—W—Cs2	58.5 (3)
O3 ^{iv} —Cs1—O2 ⁱ	76.4 (3)	Cs2 ^{xii} —W—Cs2	120.63 (6)
O3 ^v —Cs1—O2 ⁱ	122.2 (4)	Cs1 ^{xiii} —W—Cs2	173.49 (5)
O4 ⁱ —Cs1—O2 ⁱ	104.7 (4)	O2 ^x —W—Cs1	138.0 (6)
O4 ⁱⁱ —Cs1—O2 ⁱ	121.5 (3)	O3 ^{xi} —W—Cs1	116.2 (5)
O4—Cs1—O2 ⁱ	79.1 (3)	O4—W—Cs1	55.9 (4)
O1 ⁱ —Cs1—O2 ⁱⁱ	91.3 (3)	O4 ⁱⁱ —W—Cs1	56.4 (4)

O1—Cs1—O2 ⁱⁱ	150.4 (4)	O3—W—Cs1	110.6 (5)
O1 ⁱⁱ —Cs1—O2 ⁱⁱ	57.5 (4)	O1—W—Cs1	43.4 (4)
O3 ⁱⁱⁱ —Cs1—O2 ⁱⁱ	76.4 (3)	Cs2 ^{xii} —W—Cs1	65.44 (3)
O3 ^{iv} —Cs1—O2 ⁱⁱ	122.2 (4)	Cs1 ^{xiii} —W—Cs1	122.50 (3)
O3 ^v —Cs1—O2 ⁱⁱ	43.5 (3)	Cs2—W—Cs1	63.41 (3)
O4 ⁱ —Cs1—O2 ⁱⁱ	79.1 (3)	O2 ^x —W—Cs1 ^{xiv}	54.8 (5)
O4 ⁱⁱ —Cs1—O2 ⁱⁱ	104.7 (4)	O3 ^{xi} —W—Cs1 ^{xiv}	120.7 (4)
O4—Cs1—O2 ⁱⁱ	121.5 (3)	O4—W—Cs1 ^{xiv}	134.5 (4)
O2 ⁱ —Cs1—O2 ⁱⁱ	115.47 (19)	O4 ⁱⁱ —W—Cs1 ^{xiv}	62.2 (4)
O1 ⁱ —Cs1—O2	150.4 (4)	O3—W—Cs1 ^{xiv}	48.1 (4)
O1—Cs1—O2	57.5 (4)	O1—W—Cs1 ^{xiv}	117.9 (3)
O1 ⁱⁱ —Cs1—O2	91.3 (3)	Cs2 ^{xii} —W—Cs1 ^{xiv}	177.46 (4)
O3 ⁱⁱⁱ —Cs1—O2	122.2 (4)	Cs1 ^{xiii} —W—Cs1 ^{xiv}	111.82 (6)
O3 ^{iv} —Cs1—O2	43.5 (3)	Cs2—W—Cs1 ^{xiv}	61.72 (4)
O3 ^v —Cs1—O2	76.4 (3)	Cs1—W—Cs1 ^{xiv}	117.06 (2)
O4 ⁱ —Cs1—O2	121.5 (3)	O1 ^{xi} —Se—O1	104.0 (5)
O4 ⁱⁱ —Cs1—O2	79.1 (3)	O1 ^{xi} —Se—O1 ^{ix}	104.0 (5)
O4—Cs1—O2	104.7 (4)	O1—Se—O1 ^{ix}	104.0 (5)
O2 ⁱ —Cs1—O2	115.47 (19)	O1 ^{xi} —Se—Cs2 ^{xv}	58.6 (4)
O2 ⁱⁱ —Cs1—O2	115.47 (19)	O1—Se—Cs2 ^{xv}	145.4 (5)
O2—Cs2—O2 ^{vi}	56.8 (5)	O1 ^{ix} —Se—Cs2 ^{xv}	58.6 (4)
O2—Cs2—O2 ^{vii}	56.8 (5)	O1 ^{xi} —Se—Cs2	145.4 (5)
O2 ^{vi} —Cs2—O2 ^{vii}	56.8 (5)	O1—Se—Cs2	58.6 (4)
O2—Cs2—O4 ^{viii}	153.5 (4)	O1 ^{ix} —Se—Cs2	58.6 (4)
O2 ^{vi} —Cs2—O4 ^{viii}	101.6 (4)	Cs2 ^{xv} —Se—Cs2	116.99 (3)
O2 ^{vii} —Cs2—O4 ^{viii}	99.6 (4)	O1 ^{xi} —Se—Cs2 ^{xii}	58.6 (4)
O2—Cs2—O4 ^{ix}	101.6 (4)	O1—Se—Cs2 ^{xii}	58.6 (4)
O2 ^{vi} —Cs2—O4 ^{ix}	99.6 (4)	O1 ^{ix} —Se—Cs2 ^{xii}	145.4 (5)
O2 ^{vii} —Cs2—O4 ^{ix}	153.5 (4)	Cs2 ^{xv} —Se—Cs2 ^{xii}	116.99 (3)
O4 ^{viii} —Cs2—O4 ^{ix}	96.8 (3)	Cs2—Se—Cs2 ^{xii}	116.99 (3)
O2—Cs2—O4 ⁱⁱ	99.6 (4)	O1 ^{xi} —Se—Cs1 ^{xv}	37.9 (5)
O2 ^{vi} —Cs2—O4 ⁱⁱ	153.5 (4)	O1—Se—Cs1 ^{xv}	122.6 (4)
O2 ^{vii} —Cs2—O4 ⁱⁱ	101.6 (4)	O1 ^{ix} —Se—Cs1 ^{xv}	122.6 (4)
O4 ^{viii} —Cs2—O4 ⁱⁱ	96.8 (3)	Cs2 ^{xv} —Se—Cs1 ^{xv}	64.012 (17)
O4 ^{ix} —Cs2—O4 ⁱⁱ	96.8 (3)	Cs2—Se—Cs1 ^{xv}	176.68 (9)
O2—Cs2—O3 ^{vi}	139.0 (3)	Cs2 ^{xii} —Se—Cs1 ^{xv}	64.014 (17)
O2 ^{vi} —Cs2—O3 ^{vi}	96.8 (4)	O1 ^{xi} —Se—Cs1	122.6 (4)
O2 ^{vii} —Cs2—O3 ^{vi}	137.8 (3)	O1—Se—Cs1	37.9 (5)
O4 ^{viii} —Cs2—O3 ^{vi}	50.0 (3)	O1 ^{ix} —Se—Cs1	122.6 (4)
O4 ^{ix} —Cs2—O3 ^{vi}	48.2 (3)	Cs2 ^{xv} —Se—Cs1	176.68 (9)
O4 ⁱⁱ —Cs2—O3 ^{vi}	109.7 (4)	Cs2—Se—Cs1	64.013 (17)
O2—Cs2—O3	96.8 (4)	Cs2 ^{xii} —Se—Cs1	64.013 (17)
O2 ^{vi} —Cs2—O3	137.8 (3)	Cs1 ^{xv} —Se—Cs1	114.79 (4)
O2 ^{vii} —Cs2—O3	139.0 (3)	O1 ^{xi} —Se—Cs1 ^{xvi}	122.6 (4)
O4 ^{viii} —Cs2—O3	109.7 (4)	O1—Se—Cs1 ^{xvi}	122.6 (4)
O4 ^{ix} —Cs2—O3	50.0 (3)	O1 ^{ix} —Se—Cs1 ^{xvi}	37.9 (5)
O4 ⁱⁱ —Cs2—O3	48.2 (3)	Cs2 ^{xv} —Se—Cs1 ^{xvi}	64.014 (17)
O3 ^{vi} —Cs2—O3	83.0 (4)	Cs2—Se—Cs1 ^{xvi}	64.013 (17)

O2—Cs2—O3 ^{vii}	137.8 (3)	Cs2 ^{xii} —Se—Cs1 ^{xvi}	176.68 (9)
O2 ^{vi} —Cs2—O3 ^{vii}	139.0 (3)	Cs1 ^{xv} —Se—Cs1 ^{xvi}	114.79 (4)
O2 ^{vii} —Cs2—O3 ^{vii}	96.8 (4)	Cs1—Se—Cs1 ^{xvi}	114.79 (4)
O4 ^{viii} —Cs2—O3 ^{vii}	48.2 (3)	Se—O1—W	129.4 (8)
O4 ^{ix} —Cs2—O3 ^{vii}	109.7 (4)	Se—O1—Cs1	122.3 (6)
O4 ⁱⁱ —Cs2—O3 ^{vii}	50.0 (3)	W—O1—Cs1	108.1 (5)
O3 ^{vi} —Cs2—O3 ^{vii}	83.0 (4)	Se—O1—Cs2	97.7 (5)
O3—Cs2—O3 ^{vii}	83.0 (4)	W—O1—Cs2	91.2 (4)
O2—Cs2—O1 ^{vii}	114.5 (4)	Cs1—O1—Cs2	83.4 (3)
O2 ^{vi} —Cs2—O1 ^{vii}	95.0 (4)	Se—O1—Cs2 ^{xii}	97.7 (5)
O2 ^{vii} —Cs2—O1 ^{vii}	58.5 (4)	W—O1—Cs2 ^{xii}	83.6 (4)
O4 ^{viii} —Cs2—O1 ^{vii}	47.1 (3)	Cs1—O1—Cs2 ^{xii}	83.4 (3)
O4 ^{ix} —Cs2—O1 ^{vii}	143.4 (3)	Cs2—O1—Cs2 ^{xii}	163.5 (5)
O4 ⁱⁱ —Cs2—O1 ^{vii}	83.8 (3)	W ^{xvii} —O2—Cs2	159.8 (9)
O3 ^{vi} —Cs2—O1 ^{vii}	97.0 (3)	W ^{xvii} —O2—Cs1	97.3 (5)
O3—Cs2—O1 ^{vii}	127.0 (3)	Cs2—O2—Cs1	84.1 (4)
O3 ^{vii} —Cs2—O1 ^{vii}	45.0 (3)	W ^{xvii} —O2—Cs1 ^{xvi}	103.6 (6)
O2—Cs2—O1	58.5 (4)	Cs2—O2—Cs1 ^{xvi}	82.6 (3)
O2 ^{vi} —Cs2—O1	114.5 (4)	Cs1—O2—Cs1 ^{xvi}	152.0 (6)
O2 ^{vii} —Cs2—O1	95.0 (4)	W ^{ix} —O3—W	148.6 (7)
O4 ^{viii} —Cs2—O1	143.4 (3)	W ^{ix} —O3—Cs2	95.8 (5)
O4 ^{ix} —Cs2—O1	83.8 (3)	W—O3—Cs2	101.6 (5)
O4 ⁱⁱ —Cs2—O1	47.1 (3)	W ^{ix} —O3—Cs1 ^{xiv}	101.4 (5)
O3 ^{vi} —Cs2—O1	127.0 (3)	W—O3—Cs1 ^{xiv}	106.7 (5)
O3—Cs2—O1	45.0 (3)	Cs2—O3—Cs1 ^{xiv}	81.5 (2)
O3 ^{vii} —Cs2—O1	97.0 (3)	W—O4—W ⁱ	135.7 (8)
O1 ^{vii} —Cs2—O1	119.993 (7)	W—O4—Cs2 ^{xii}	108.0 (5)
O2—Cs2—O1 ^{vi}	95.0 (4)	W ⁱ —O4—Cs2 ^{xii}	114.6 (5)
O2 ^{vi} —Cs2—O1 ^{vi}	58.5 (4)	W—O4—Cs1	99.0 (5)
O2 ^{vii} —Cs2—O1 ^{vi}	114.5 (4)	W ⁱ —O4—Cs1	96.3 (5)
O4 ^{viii} —Cs2—O1 ^{vi}	83.8 (3)	Cs2 ^{xii} —O4—Cs1	84.8 (3)
O4 ^{ix} —Cs2—O1 ^{vi}	47.1 (3)		

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

Dirubidium tritungsten selenite (Rb₂W₃SeO₁₂)

Crystal data

Rb₂W₃SeO₁₂

$M_r = 993.40$

Hexagonal, $P6_3$

$a = 7.2380$ (1) Å

$c = 12.1115$ (3) Å

$V = 549.50$ (2) Å³

$Z = 2$

$F(000) = 852$

$D_x = 6.004$ Mg m⁻³

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

Cell parameters from 19378 reflections

$\theta = 3.3$ – 28.2°

$\mu = 43.49$ mm⁻¹

$T = 293$ K

Block, colourless

$0.10 \times 0.05 \times 0.05$ mm

Data collection

Bruker APEXII CCD
diffractometer
Radiation source: fine-focus sealed tube
phi and ω scans
Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.098$, $T_{\max} = 0.220$
3497 measured reflections

675 independent reflections
654 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 1.7^\circ$
 $h = -9 \rightarrow 8$
 $k = -8 \rightarrow 9$
 $l = -11 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.033$
 $S = 1.06$
675 reflections
57 parameters
7 restraints
 $w = 1/[\sigma^2(F_o^2) + (0.0065P)^2 + 2.2061P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.90 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.14 \text{ e } \text{\AA}^{-3}$
Extinction correction: SHELXL2018/3
(Sheldrick 2015b),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0058 (2)
Absolute structure: Flack x determined using
182 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: -0.08 (3)

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. Refined as a two-component twin

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb1	0.666667	0.333333	0.8979 (2)	0.0389 (9)
Rb2	0.333333	0.666667	0.77053 (18)	0.0181 (6)
W	0.80778 (6)	0.66034 (6)	0.60562 (3)	0.00482 (12)
Se	1.000000	1.000000	0.83669 (14)	0.0057 (4)
O1	0.8727 (15)	0.7523 (15)	0.7767 (6)	0.0106 (18)
O2	0.5942 (14)	0.8028 (15)	0.9677 (7)	0.0106 (17)
O3	0.7494 (12)	0.8784 (12)	0.5928 (8)	0.0084 (16)
O4	0.9117 (13)	0.4617 (13)	0.6512 (6)	0.0069 (15)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0433 (13)	0.0433 (13)	0.0300 (16)	0.0216 (7)	0.000	0.000
Rb2	0.0202 (9)	0.0202 (9)	0.0139 (11)	0.0101 (4)	0.000	0.000
W	0.0036 (2)	0.0027 (2)	0.00779 (17)	0.00128 (19)	0.0005 (4)	-0.0003 (3)
Se	0.0062 (5)	0.0062 (5)	0.0047 (10)	0.0031 (3)	0.000	0.000
O1	0.016 (5)	0.008 (5)	0.010 (4)	0.008 (4)	0.003 (4)	0.003 (4)
O2	0.002 (4)	0.011 (5)	0.015 (4)	0.000 (4)	-0.003 (3)	-0.004 (4)

O3	0.007 (3)	0.006 (4)	0.012 (5)	0.004 (3)	0.000 (4)	0.001 (4)
O4	0.0065 (18)	0.0069 (19)	0.0077 (18)	0.0038 (12)	-0.0003 (12)	-0.0002 (12)

Geometric parameters (Å, °)

Rb1—O1 ⁱ	3.009 (9)	Rb2—O4 ⁱ	3.012 (8)
Rb1—O1	3.009 (9)	Rb2—O3	3.382 (8)
Rb1—O1 ⁱⁱ	3.009 (9)	Rb2—O3 ^{vi}	3.382 (8)
Rb1—O4 ⁱⁱ	3.360 (8)	Rb2—O3 ^{vii}	3.382 (8)
Rb1—O4 ⁱ	3.360 (8)	Rb2—W	3.9926 (11)
Rb1—O4	3.360 (8)	Rb2—W ^{vii}	3.9926 (11)
Rb1—O3 ⁱⁱⁱ	3.518 (9)	Rb2—W ^{vi}	3.9926 (11)
Rb1—O3 ^{iv}	3.518 (9)	W—O2 ^x	1.726 (8)
Rb1—O3 ^v	3.518 (9)	W—O3	1.833 (8)
Rb1—W	4.094 (2)	W—O4 ⁱ	1.860 (8)
Rb1—W ⁱ	4.094 (2)	W—O4	2.005 (8)
Rb1—W ⁱⁱ	4.094 (2)	W—O3 ^{xi}	2.011 (8)
Rb2—O2	2.894 (8)	W—O1	2.155 (8)
Rb2—O2 ^{vi}	2.894 (8)	Se—O1 ^{ix}	1.714 (9)
Rb2—O2 ^{vii}	2.894 (8)	Se—O1	1.714 (9)
Rb2—O4 ^{viii}	3.012 (8)	Se—O1 ^{xi}	1.714 (9)
Rb2—O4 ^{ix}	3.012 (8)		
O1 ⁱ —Rb1—O1	98.2 (2)	O4 ^{ix} —Rb2—O3 ^{vii}	111.8 (2)
O1 ⁱ —Rb1—O1 ⁱⁱ	98.2 (2)	O4 ⁱ —Rb2—O3 ^{vii}	48.78 (18)
O1—Rb1—O1 ⁱⁱ	98.2 (2)	O3—Rb2—O3 ^{vii}	83.8 (2)
O1 ⁱ —Rb1—O4 ⁱⁱ	51.2 (2)	O3 ^{vi} —Rb2—O3 ^{vii}	83.8 (2)
O1—Rb1—O4 ⁱⁱ	88.0 (2)	O2—Rb2—W	89.89 (19)
O1 ⁱⁱ —Rb1—O4 ⁱⁱ	50.2 (2)	O2 ^{vi} —Rb2—W	147.69 (19)
O1 ⁱ —Rb1—O4 ⁱ	50.2 (2)	O2 ^{vii} —Rb2—W	113.3 (2)
O1—Rb1—O4 ⁱ	51.2 (2)	O4 ^{viii} —Rb2—W	114.82 (16)
O1 ⁱⁱ —Rb1—O4 ⁱ	88.0 (2)	O4 ^{ix} —Rb2—W	75.92 (16)
O4 ⁱⁱ —Rb1—O4 ⁱ	46.7 (2)	O4 ⁱ —Rb2—W	26.34 (16)
O1 ⁱ —Rb1—O4	88.0 (2)	O3—Rb2—W	27.21 (13)
O1—Rb1—O4	50.2 (2)	O3 ^{vi} —Rb2—W	105.50 (16)
O1 ⁱⁱ —Rb1—O4	51.2 (2)	O3 ^{vii} —Rb2—W	70.55 (14)
O4 ⁱⁱ —Rb1—O4	46.7 (2)	O2—Rb2—W ^{vii}	147.69 (19)
O4 ⁱ —Rb1—O4	46.7 (2)	O2 ^{vi} —Rb2—W ^{vii}	113.3 (2)
O1 ⁱ —Rb1—O3 ⁱⁱⁱ	130.6 (2)	O2 ^{vii} —Rb2—W ^{vii}	89.89 (19)
O1—Rb1—O3 ⁱⁱⁱ	130.6 (2)	O4 ^{viii} —Rb2—W ^{vii}	26.34 (16)
O1 ⁱⁱ —Rb1—O3 ⁱⁱⁱ	71.3 (2)	O4 ^{ix} —Rb2—W ^{vii}	114.82 (16)
O4 ⁱⁱ —Rb1—O3 ⁱⁱⁱ	114.97 (19)	O4 ⁱ —Rb2—W ^{vii}	75.92 (16)
O4 ⁱ —Rb1—O3 ⁱⁱⁱ	159.4 (2)	O3—Rb2—W ^{vii}	105.50 (16)
O4—Rb1—O3 ⁱⁱⁱ	115.6 (2)	O3 ^{vi} —Rb2—W ^{vii}	70.55 (14)
O1 ⁱ —Rb1—O3 ^{iv}	130.6 (2)	O3 ^{vii} —Rb2—W ^{vii}	27.21 (13)
O1—Rb1—O3 ^{iv}	71.3 (2)	W—Rb2—W ^{vii}	97.16 (4)
O1 ⁱⁱ —Rb1—O3 ^{iv}	130.6 (2)	O2—Rb2—W ^{vi}	113.3 (2)
O4 ⁱⁱ —Rb1—O3 ^{iv}	159.4 (2)	O2 ^{vi} —Rb2—W ^{vi}	89.89 (19)

O4 ⁱ —Rb1—O3 ^{iv}	115.6 (2)	O2 ^{vii} —Rb2—W ^{vi}	147.69 (19)
O4—Rb1—O3 ^{iv}	115.0 (2)	O4 ^{viii} —Rb2—W ^{vi}	75.92 (16)
O3 ⁱⁱⁱ —Rb1—O3 ^{iv}	79.9 (2)	O4 ^{ix} —Rb2—W ^{vi}	26.34 (16)
O1 ⁱ —Rb1—O3 ^v	71.3 (2)	O4 ⁱ —Rb2—W ^{vi}	114.82 (16)
O1—Rb1—O3 ^v	130.6 (2)	O3—Rb2—W ^{vi}	70.55 (14)
O1 ⁱⁱ —Rb1—O3 ^v	130.6 (2)	O3 ^{vi} —Rb2—W ^{vi}	27.21 (13)
O4 ⁱⁱ —Rb1—O3 ^v	115.6 (2)	O3 ^{vii} —Rb2—W ^{vi}	105.50 (16)
O4 ⁱ —Rb1—O3 ^v	114.97 (19)	W—Rb2—W ^{vi}	97.16 (4)
O4—Rb1—O3 ^v	159.4 (2)	W ^{vii} —Rb2—W ^{vi}	97.16 (4)
O3 ⁱⁱⁱ —Rb1—O3 ^v	79.9 (2)	O2 ^x —W—O3	98.3 (4)
O3 ^{iv} —Rb1—O3 ^v	79.9 (2)	O2 ^x —W—O4 ⁱ	99.3 (4)
O1 ⁱ —Rb1—W	76.74 (18)	O3—W—O4 ⁱ	97.5 (3)
O1—Rb1—W	30.77 (17)	O2 ^x —W—O4	93.8 (4)
O1 ⁱⁱ —Rb1—W	79.82 (18)	O3—W—O4	166.2 (4)
O4 ⁱⁱ —Rb1—W	57.35 (14)	O4 ⁱ —W—O4	87.0 (5)
O4 ⁱ —Rb1—W	26.63 (15)	O2 ^x —W—O3 ^{xi}	91.7 (5)
O4—Rb1—W	29.14 (14)	O3—W—O3 ^{xi}	90.0 (4)
O3 ⁱⁱⁱ —Rb1—W	142.01 (14)	O4 ⁱ —W—O3 ^{xi}	165.5 (4)
O3 ^{iv} —Rb1—W	102.05 (14)	O4—W—O3 ^{xi}	83.0 (3)
O3 ^v —Rb1—W	138.07 (13)	O2 ^x —W—O1	172.2 (4)
O1 ⁱ —Rb1—W ⁱ	30.77 (17)	O3—W—O1	85.6 (4)
O1—Rb1—W ⁱ	79.82 (18)	O4 ⁱ —W—O1	86.8 (3)
O1 ⁱⁱ —Rb1—W ⁱ	76.74 (17)	O4—W—O1	81.6 (3)
O4 ⁱⁱ —Rb1—W ⁱ	26.63 (14)	O3 ^{xi} —W—O1	81.4 (4)
O4 ⁱ —Rb1—W ⁱ	29.14 (15)	O2 ^x —W—Rb2	123.2 (3)
O4—Rb1—W ⁱ	57.35 (14)	O3—W—Rb2	57.5 (3)
O3 ⁱⁱⁱ —Rb1—W ⁱ	138.07 (13)	O4 ⁱ —W—Rb2	45.9 (2)
O3 ^{iv} —Rb1—W ⁱ	142.01 (14)	O4—W—Rb2	120.2 (2)
O3 ^v —Rb1—W ⁱ	102.05 (14)	O3 ^{xi} —W—Rb2	133.0 (3)
W—Rb1—W ⁱ	51.57 (3)	O1—W—Rb2	64.6 (2)
O1 ⁱ —Rb1—W ⁱⁱ	79.82 (18)	O2 ^x —W—Rb1	135.6 (3)
O1—Rb1—W ⁱⁱ	76.73 (17)	O3—W—Rb1	118.2 (3)
O1 ⁱⁱ —Rb1—W ⁱⁱ	30.77 (17)	O4 ⁱ —W—Rb1	54.1 (2)
O4 ⁱⁱ —Rb1—W ⁱⁱ	29.14 (15)	O4—W—Rb1	54.7 (2)
O4 ⁱ —Rb1—W ⁱⁱ	57.35 (14)	O3 ^{xi} —W—Rb1	111.4 (3)
O4—Rb1—W ⁱⁱ	26.63 (14)	O1—W—Rb1	45.6 (3)
O3 ⁱⁱⁱ —Rb1—W ⁱⁱ	102.05 (14)	Rb2—W—Rb1	66.84 (2)
O3 ^{iv} —Rb1—W ⁱⁱ	138.07 (13)	O2 ^x —W—Rb1 ^{xii}	59.3 (3)
O3 ^v —Rb1—W ⁱⁱ	142.01 (14)	O3—W—Rb1 ^{xii}	53.8 (3)
W—Rb1—W ⁱⁱ	51.57 (3)	O4 ⁱ —W—Rb1 ^{xii}	70.4 (2)
W ⁱ —Rb1—W ⁱⁱ	51.57 (3)	O4—W—Rb1 ^{xii}	139.6 (2)
O2—Rb2—O2 ^{vi}	58.6 (3)	O3 ^{xi} —W—Rb1 ^{xii}	123.7 (2)
O2—Rb2—O2 ^{vii}	58.6 (3)	O1—W—Rb1 ^{xii}	127.9 (3)
O2 ^{vi} —Rb2—O2 ^{vii}	58.6 (3)	Rb2—W—Rb1 ^{xii}	66.06 (5)
O2—Rb2—O4 ^{viii}	153.0 (2)	Rb1—W—Rb1 ^{xii}	123.06 (2)
O2 ^{vi} —Rb2—O4 ^{viii}	97.5 (2)	O2 ^x —W—Rb2 ^{xiii}	113.1 (3)
O2 ^{vii} —Rb2—O4 ^{viii}	99.5 (3)	O3—W—Rb2 ^{xiii}	128.1 (3)
O2—Rb2—O4 ^{ix}	97.5 (2)	O4 ⁱ —W—Rb2 ^{xiii}	115.7 (2)

O2 ^{vi} —Rb2—O4 ^{ix}	99.5 (2)	O4—W—Rb2 ^{xiii}	39.5 (2)
O2 ^{vii} —Rb2—O4 ^{ix}	153.0 (2)	O3 ^{xi} —W—Rb2 ^{xiii}	50.7 (2)
O4 ^{viii} —Rb2—O4 ^{ix}	98.91 (18)	O1—W—Rb2 ^{xiii}	59.5 (2)
O2—Rb2—O4 ⁱ	99.5 (2)	Rb2—W—Rb2 ^{xiii}	122.13 (5)
O2 ^{vi} —Rb2—O4 ⁱ	153.0 (2)	Rb1—W—Rb2 ^{xiii}	64.26 (2)
O2 ^{vii} —Rb2—O4 ⁱ	97.5 (2)	Rb1 ^{xii} —W—Rb2 ^{xiii}	171.73 (3)
O4 ^{viii} —Rb2—O4 ⁱ	98.91 (18)	O1 ^{ix} —Se—O1	103.3 (3)
O4 ^{ix} —Rb2—O4 ⁱ	98.91 (18)	O1 ^{ix} —Se—O1 ^{xi}	103.3 (3)
O2—Rb2—O3	95.1 (2)	O1—Se—O1 ^{xi}	103.3 (3)
O2 ^{vi} —Rb2—O3	138.5 (3)	Se—O1—W	130.6 (5)
O2 ^{vii} —Rb2—O3	137.5 (3)	Se—O1—Rb1	125.7 (4)
O4 ^{viii} —Rb2—O3	111.8 (2)	W—O1—Rb1	103.7 (3)
O4 ^{ix} —Rb2—O3	48.78 (18)	W ^{xiv} —O2—Rb2	159.3 (5)
O4 ⁱ —Rb2—O3	51.09 (19)	W—O3—W ^{ix}	148.3 (5)
O2—Rb2—O3 ^{vi}	137.5 (3)	W—O3—Rb2	95.3 (3)
O2 ^{vi} —Rb2—O3 ^{vi}	95.1 (2)	W ^{ix} —O3—Rb2	101.9 (3)
O2 ^{vii} —Rb2—O3 ^{vi}	138.5 (2)	W—O3—Rb1 ^{xii}	101.4 (3)
O4 ^{viii} —Rb2—O3 ^{vi}	48.78 (18)	W ^{ix} —O3—Rb1 ^{xii}	107.3 (3)
O4 ^{ix} —Rb2—O3 ^{vi}	51.09 (19)	Rb2—O3—Rb1 ^{xii}	81.68 (17)
O4 ⁱ —Rb2—O3 ^{vi}	111.8 (2)	W ⁱⁱ —O4—W	134.3 (4)
O3—Rb2—O3 ^{vi}	83.8 (2)	W ⁱⁱ —O4—Rb2 ^{xiii}	107.7 (3)
O2—Rb2—O3 ^{vii}	138.5 (2)	W—O4—Rb2 ^{xiii}	115.5 (3)
O2 ^{vi} —Rb2—O3 ^{vii}	137.5 (3)	W ⁱⁱ —O4—Rb1	99.3 (3)
O2 ^{vii} —Rb2—O3 ^{vii}	95.1 (2)	W—O4—Rb1	96.2 (3)
O4 ^{viii} —Rb2—O3 ^{vii}	51.09 (19)	Rb2 ^{xiii} —O4—Rb1	88.54 (18)

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

Dipotassium tritungsten selenite (K₂W₃SeO₁₂)

Crystal data

K₂W₃SeO₁₂

$M_r = 900.66$

Monoclinic, $P2_1/n$

$a = 7.2310$ (2) Å

$b = 11.4863$ (4) Å

$c = 12.6486$ (4) Å

$\beta = 90.096$ (2)°

$V = 1050.56$ (6) Å³

$Z = 4$

$F(000) = 1559$

$D_x = 5.694$ Mg m⁻³

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

Cell parameters from 9566 reflections

$\theta = 3.2\text{--}33.2^\circ$

$\mu = 37.09$ mm⁻¹

$T = 293$ K

Block, colourless

$0.08 \times 0.05 \times 0.02$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

phi and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.155$, $T_{\max} = 0.524$

26562 measured reflections

4026 independent reflections

3456 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$

$\theta_{\max} = 33.2^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -11 \rightarrow 11$

$k = -17 \rightarrow 17$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.105$
 $S = 1.15$
 4026 reflections
 165 parameters
 24 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 3.94 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -3.11 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2018/3
 (Sheldrick 2015b),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00176 (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. Refined as a two-component twin

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.2501 (5)	0.4522 (3)	0.9115 (3)	0.0223 (6)
K2	0.2548 (5)	0.0822 (3)	0.8952 (3)	0.0234 (7)
W1	0.22893 (7)	0.79646 (4)	0.08433 (4)	0.00612 (10)
W2	0.01720 (7)	0.75074 (4)	0.82437 (4)	0.00629 (11)
W3	0.50663 (8)	0.75947 (4)	0.84420 (4)	0.00583 (11)
Se	0.25041 (19)	0.49742 (10)	0.17926 (9)	0.0078 (2)
O1	0.2536 (13)	0.6087 (8)	0.0913 (8)	0.0164 (19)
O2	0.2387 (16)	0.9444 (8)	0.0619 (7)	0.016 (2)
O3	0.0634 (14)	0.4225 (9)	0.1258 (9)	0.013 (2)
O4	0.0680 (14)	0.8954 (9)	0.7993 (9)	0.014 (2)
O5	0.4324 (14)	0.4206 (9)	0.1236 (8)	0.012 (2)
O6	0.4376 (14)	0.8956 (9)	0.8021 (9)	0.015 (2)
O7	0.0615 (15)	0.7625 (9)	0.9781 (9)	0.012 (2)
O8	0.2548 (14)	0.6902 (7)	0.8102 (7)	0.0093 (16)
O9	0.4378 (15)	0.7668 (9)	0.9828 (8)	0.0100 (19)
O10	0.9354 (14)	0.7050 (10)	0.6903 (8)	0.014 (2)
O11	0.7529 (15)	0.7855 (8)	0.8637 (7)	0.0096 (16)
O12	0.0599 (14)	0.7924 (9)	0.1938 (8)	0.0110 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0208 (14)	0.0264 (14)	0.0197 (14)	0.0030 (13)	-0.0020 (17)	0.0005 (13)
K2	0.0269 (17)	0.0211 (14)	0.0223 (16)	0.0007 (14)	-0.0005 (14)	0.0060 (12)
W1	0.00737 (19)	0.00678 (18)	0.00421 (17)	0.00057 (16)	-0.00022 (19)	0.00021 (17)
W2	0.0049 (2)	0.0084 (2)	0.0056 (2)	-0.0003 (2)	-0.00087 (18)	0.00082 (15)
W3	0.0047 (2)	0.0074 (2)	0.0054 (2)	0.00025 (19)	0.00025 (19)	-0.00006 (16)
Se	0.0090 (5)	0.0065 (4)	0.0078 (5)	0.0005 (4)	-0.0003 (5)	0.0003 (4)
O1	0.017 (2)	0.016 (2)	0.016 (2)	0.0001 (10)	0.0001 (10)	0.0005 (10)

O2	0.030 (6)	0.006 (4)	0.012 (4)	0.001 (4)	-0.005 (4)	0.002 (3)
O3	0.008 (4)	0.010 (4)	0.021 (5)	0.002 (4)	-0.009 (4)	-0.002 (4)
O4	0.013 (2)	0.014 (2)	0.014 (2)	0.0003 (10)	0.0000 (10)	0.0001 (10)
O5	0.011 (4)	0.010 (4)	0.016 (5)	0.003 (4)	0.003 (4)	0.003 (4)
O6	0.013 (5)	0.005 (4)	0.025 (6)	0.000 (4)	-0.002 (4)	0.008 (4)
O7	0.012 (2)	0.012 (2)	0.011 (2)	0.0002 (10)	-0.0004 (10)	0.0002 (10)
O8	0.003 (4)	0.010 (4)	0.015 (4)	0.003 (4)	-0.003 (4)	-0.001 (3)
O9	0.010 (2)	0.010 (2)	0.010 (2)	-0.0002 (10)	0.0005 (10)	-0.0004 (10)
O10	0.006 (4)	0.026 (6)	0.008 (5)	0.005 (4)	-0.004 (3)	0.000 (4)
O11	0.008 (4)	0.011 (4)	0.009 (4)	-0.002 (4)	-0.003 (4)	-0.004 (3)
O12	0.007 (4)	0.019 (5)	0.007 (4)	0.006 (4)	0.000 (3)	0.001 (4)

Geometric parameters (Å, °)

K1—O3 ⁱ	2.726 (10)	K2—W1 ⁱⁱ	3.993 (4)
K1—O5 ⁱⁱ	2.757 (11)	W1—O2	1.724 (9)
K1—O1 ⁱⁱⁱ	2.899 (10)	W1—O7 ^x	1.849 (11)
K1—O5 ⁱⁱⁱ	3.009 (11)	W1—O12	1.849 (10)
K1—O8	3.019 (9)	W1—O10 ^{xi}	2.005 (10)
K1—O4 ^{iv}	3.046 (11)	W1—O9 ^x	2.013 (11)
K1—O3 ⁱⁱⁱ	3.050 (12)	W1—O1	2.166 (9)
K1—O6 ^{iv}	3.091 (12)	W2—O4	1.731 (11)
K1—Se ⁱⁱⁱ	3.427 (4)	W2—O8	1.863 (10)
K1—Se ⁱⁱ	3.835 (4)	W2—O10 ^{xii}	1.870 (10)
K1—Se ⁱ	3.839 (3)	W2—O7	1.975 (11)
K1—W2	3.975 (3)	W2—O11 ^{xii}	2.016 (11)
K2—O2 ^v	2.639 (9)	W2—O3 ⁱ	2.167 (10)
K2—O6 ^{vi}	2.780 (11)	W3—O6	1.726 (10)
K2—O4 ^{vi}	2.809 (11)	W3—O11	1.822 (11)
K2—O10 ^{vii}	2.861 (11)	W3—O9	1.825 (11)
K2—O8 ^{iv}	2.879 (9)	W3—O12 ^{xiii}	2.031 (10)
K2—O12 ⁱ	2.918 (10)	W3—O8	2.032 (10)
K2—O9 ^{viii}	3.213 (11)	W3—O5 ⁱⁱ	2.153 (10)
K2—O7 ^{ix}	3.316 (12)	Se—O1	1.695 (10)
K2—O11 ^{viii}	3.408 (9)	Se—O5	1.735 (10)
K2—W2 ^{iv}	3.767 (3)	Se—O3	1.739 (10)
K2—W1 ⁱ	3.775 (4)		
O3 ⁱ —K1—O5 ⁱⁱ	112.6 (3)	O12—W1—K2 ⁱ	49.0 (3)
O3 ⁱ —K1—O1 ⁱⁱⁱ	79.3 (3)	O10 ^{xi} —W1—K2 ⁱ	130.3 (3)
O5 ⁱⁱ —K1—O1 ⁱⁱⁱ	78.0 (3)	O9 ^x —W1—K2 ⁱ	143.4 (3)
O3 ⁱ —K1—O5 ⁱⁱⁱ	125.5 (3)	O1—W1—K2 ⁱ	116.2 (3)
O5 ⁱⁱ —K1—O5 ⁱⁱⁱ	81.0 (3)	O2—W1—K2 ⁱⁱ	68.2 (4)
O1 ⁱⁱⁱ —K1—O5 ⁱⁱⁱ	51.1 (3)	O7 ^x —W1—K2 ⁱⁱ	137.1 (4)
O3 ⁱ —K1—O8	57.2 (3)	O12—W1—K2 ⁱⁱ	125.4 (3)
O5 ⁱⁱ —K1—O8	56.1 (3)	O10 ^{xi} —W1—K2 ⁱⁱ	42.7 (3)
O1 ⁱⁱⁱ —K1—O8	76.8 (3)	O9 ^x —W1—K2 ⁱⁱ	53.0 (3)
O5 ⁱⁱⁱ —K1—O8	118.8 (3)	O1—W1—K2 ⁱⁱ	105.6 (3)

O3 ⁱ —K1—O4 ^{iv}	108.8 (3)	K2 ⁱ —W1—K2 ⁱⁱ	137.13 (9)
O5 ⁱⁱ —K1—O4 ^{iv}	67.2 (3)	O2—W1—K2 ^{xiv}	26.6 (3)
O1 ⁱⁱⁱ —K1—O4 ^{iv}	144.7 (3)	O7 ^x —W1—K2 ^{xiv}	76.9 (3)
O5 ⁱⁱⁱ —K1—O4 ^{iv}	124.4 (3)	O12—W1—K2 ^{xiv}	119.5 (3)
O8—K1—O4 ^{iv}	79.5 (3)	O10 ^{xi} —W1—K2 ^{xiv}	111.4 (3)
O3 ⁱ —K1—O3 ⁱⁱⁱ	81.0 (3)	O9 ^x —W1—K2 ^{xiv}	74.1 (3)
O5 ⁱⁱ —K1—O3 ⁱⁱⁱ	124.9 (3)	O1—W1—K2 ^{xiv}	145.5 (3)
O1 ⁱⁱⁱ —K1—O3 ⁱⁱⁱ	51.3 (3)	K2 ⁱ —W1—K2 ^{xiv}	77.64 (8)
O5 ⁱⁱⁱ —K1—O3 ⁱⁱⁱ	52.3 (2)	K2 ⁱⁱ —W1—K2 ^{xiv}	73.29 (8)
O8—K1—O3 ⁱⁱⁱ	118.9 (3)	O4—W2—O8	98.3 (4)
O4 ^{iv} —K1—O3 ⁱⁱⁱ	161.2 (3)	O4—W2—O10 ^{xii}	99.8 (5)
O3 ⁱ —K1—O6 ^{iv}	66.2 (3)	O8—W2—O10 ^{xii}	95.6 (4)
O5 ⁱⁱ —K1—O6 ^{iv}	109.6 (3)	O4—W2—O7	94.6 (5)
O1 ⁱⁱⁱ —K1—O6 ^{iv}	145.0 (3)	O8—W2—O7	88.4 (4)
O5 ⁱⁱⁱ —K1—O6 ^{iv}	160.9 (3)	O10 ^{xii} —W2—O7	164.3 (5)
O8—K1—O6 ^{iv}	79.9 (3)	O4—W2—O11 ^{xii}	93.2 (4)
O4 ^{iv} —K1—O6 ^{iv}	51.6 (3)	O8—W2—O11 ^{xii}	166.7 (4)
O3 ⁱⁱⁱ —K1—O6 ^{iv}	124.0 (3)	O10 ^{xii} —W2—O11 ^{xii}	88.9 (4)
O3 ⁱ —K1—Se ⁱⁱⁱ	95.2 (2)	O7—W2—O11 ^{xii}	84.0 (4)
O5 ⁱⁱ —K1—Se ⁱⁱⁱ	94.6 (2)	O4—W2—O3 ⁱ	172.6 (4)
O1 ⁱⁱⁱ —K1—Se ⁱⁱⁱ	29.60 (19)	O8—W2—O3 ⁱ	86.2 (4)
O5 ⁱⁱⁱ —K1—Se ⁱⁱⁱ	30.4 (2)	O10 ^{xii} —W2—O3 ⁱ	85.5 (4)
O8—K1—Se ⁱⁱⁱ	106.4 (2)	O7—W2—O3 ⁱ	79.6 (4)
O4 ^{iv} —K1—Se ⁱⁱⁱ	153.9 (2)	O11 ^{xii} —W2—O3 ⁱ	81.6 (4)
O3 ⁱⁱⁱ —K1—Se ⁱⁱⁱ	30.43 (19)	O4—W2—K2 ^{xv}	105.4 (4)
O6 ^{iv} —K1—Se ⁱⁱⁱ	153.6 (2)	O8—W2—K2 ^{xv}	48.1 (3)
O3 ⁱ —K1—Se ⁱⁱ	130.7 (3)	O10 ^{xii} —W2—K2 ^{xv}	47.6 (3)
O5 ⁱⁱ —K1—Se ⁱⁱ	24.1 (2)	O7—W2—K2 ^{xv}	133.7 (3)
O1 ⁱⁱⁱ —K1—Se ⁱⁱ	97.7 (2)	O11 ^{xii} —W2—K2 ^{xv}	134.4 (3)
O5 ⁱⁱⁱ —K1—Se ⁱⁱ	82.7 (2)	O3 ⁱ —W2—K2 ^{xv}	82.0 (3)
O8—K1—Se ⁱⁱ	74.0 (2)	O4—W2—K1	142.1 (3)
O4 ^{iv} —K1—Se ⁱⁱ	50.4 (2)	O8—W2—K1	46.7 (3)
O3 ⁱⁱⁱ —K1—Se ⁱⁱ	134.5 (2)	O10 ^{xii} —W2—K1	98.2 (3)
O6 ^{iv} —K1—Se ⁱⁱ	100.5 (2)	O7—W2—K1	73.6 (3)
Se ⁱⁱⁱ —K1—Se ⁱⁱ	105.89 (9)	O11 ^{xii} —W2—K1	120.3 (3)
O3 ⁱ —K1—Se ⁱ	23.8 (2)	O3 ⁱ —W2—K1	40.7 (3)
O5 ⁱⁱ —K1—Se ⁱ	131.1 (2)	K2 ^{xv} —W2—K1	64.86 (8)
O1 ⁱⁱⁱ —K1—Se ⁱ	98.5 (2)	O4—W2—K1 ^{xv}	40.9 (4)
O5 ⁱⁱⁱ —K1—Se ⁱ	134.1 (2)	O8—W2—K1 ^{xv}	76.3 (3)
O8—K1—Se ⁱ	75.4 (2)	O10 ^{xii} —W2—K1 ^{xv}	68.4 (3)
O4 ^{iv} —K1—Se ⁱ	100.3 (2)	O7—W2—K1 ^{xv}	127.3 (3)
O3 ⁱⁱⁱ —K1—Se ⁱ	82.19 (19)	O11 ^{xii} —W2—K1 ^{xv}	117.0 (3)
O6 ^{iv} —K1—Se ⁱ	50.05 (19)	O3 ⁱ —W2—K1 ^{xv}	146.4 (3)
Se ⁱⁱⁱ —K1—Se ⁱ	105.76 (9)	K2 ^{xv} —W2—K1 ^{xv}	64.97 (7)
Se ⁱⁱ —K1—Se ⁱ	140.87 (10)	K1—W2—K1 ^{xv}	120.66 (4)
O3 ⁱ —K1—W2	31.2 (2)	O6—W3—O11	100.1 (4)
O5 ⁱⁱ —K1—W2	81.4 (2)	O6—W3—O9	100.1 (5)
O1 ⁱⁱⁱ —K1—W2	71.7 (2)	O11—W3—O9	97.5 (5)

O5 ⁱⁱⁱ —K1—W2	122.4 (2)	O6—W3—O12 ^{xiii}	91.8 (5)
O8—K1—W2	26.7 (2)	O11—W3—O12 ^{xiii}	89.3 (4)
O4 ^{iv} —K1—W2	97.2 (2)	O9—W3—O12 ^{xiii}	165.0 (4)
O3 ⁱⁱⁱ —K1—W2	98.9 (2)	O6—W3—O8	91.8 (4)
O6 ^{iv} —K1—W2	75.8 (2)	O11—W3—O8	165.4 (4)
Se ⁱⁱⁱ —K1—W2	98.21 (8)	O9—W3—O8	88.6 (4)
Se ⁱⁱ —K1—W2	100.71 (8)	O12 ^{xiii} —W3—O8	81.8 (4)
Se ⁱ —K1—W2	52.29 (5)	O6—W3—O5 ⁱⁱ	171.1 (4)
O2 ^v —K2—O6 ^{vi}	84.1 (3)	O11—W3—O5 ⁱⁱ	86.1 (4)
O2 ^v —K2—O4 ^{vi}	82.2 (3)	O9—W3—O5 ⁱⁱ	85.3 (4)
O6 ^{vi} —K2—O4 ^{vi}	57.1 (3)	O12 ^{xiii} —W3—O5 ⁱⁱ	81.8 (4)
O2 ^v —K2—O10 ^{vii}	129.3 (4)	O8—W3—O5 ⁱⁱ	81.2 (4)
O6 ^{vi} —K2—O10 ^{vii}	81.2 (3)	O6—W3—K1	135.8 (3)
O4 ^{vi} —K2—O10 ^{vii}	126.1 (3)	O11—W3—K1	124.0 (3)
O2 ^v —K2—O8 ^{iv}	168.0 (3)	O9—W3—K1	73.4 (3)
O6 ^{vi} —K2—O8 ^{iv}	87.8 (3)	O12 ^{xiii} —W3—K1	91.6 (3)
O4 ^{vi} —K2—O8 ^{iv}	85.9 (3)	O8—W3—K1	45.4 (2)
O10 ^{vii} —K2—O8 ^{iv}	57.6 (3)	O5 ⁱⁱ —W3—K1	38.9 (3)
O2 ^v —K2—O12 ⁱ	124.7 (4)	O6—W3—K2 ^{xv}	95.1 (4)
O6 ^{vi} —K2—O12 ⁱ	126.0 (3)	O11—W3—K2 ^{xv}	129.0 (3)
O4 ^{vi} —K2—O12 ⁱ	80.6 (3)	O9—W3—K2 ^{xv}	127.2 (3)
O10 ^{vii} —K2—O12 ⁱ	102.8 (3)	O12 ^{xiii} —W3—K2 ^{xv}	41.6 (3)
O8 ^{iv} —K2—O12 ⁱ	54.6 (3)	O8—W3—K2 ^{xv}	40.4 (3)
O2 ^v —K2—O9 ^{viii}	88.4 (3)	O5 ⁱⁱ —W3—K2 ^{xv}	75.9 (3)
O6 ^{vi} —K2—O9 ^{viii}	106.9 (3)	K1—W3—K2 ^{xv}	61.03 (7)
O4 ^{vi} —K2—O9 ^{viii}	162.1 (3)	O6—W3—K2 ^{viii}	88.1 (4)
O10 ^{vii} —K2—O9 ^{viii}	51.2 (3)	O11—W3—K2 ^{viii}	54.1 (3)
O8 ^{iv} —K2—O9 ^{viii}	102.5 (3)	O9—W3—K2 ^{viii}	47.8 (3)
O12 ⁱ —K2—O9 ^{viii}	117.2 (3)	O12 ^{xiii} —W3—K2 ^{viii}	142.7 (3)
O2 ^v —K2—O7 ^{ix}	84.6 (3)	O8—W3—K2 ^{viii}	135.5 (3)
O6 ^{vi} —K2—O7 ^{ix}	161.5 (3)	O5 ⁱⁱ —W3—K2 ^{viii}	100.7 (3)
O4 ^{vi} —K2—O7 ^{ix}	106.7 (3)	K1—W3—K2 ^{viii}	113.79 (7)
O10 ^{vii} —K2—O7 ^{ix}	117.3 (3)	K2 ^{xv} —W3—K2 ^{viii}	174.68 (8)
O8 ^{iv} —K2—O7 ^{ix}	100.8 (3)	O1—Se—O5	96.1 (5)
O12 ⁱ —K2—O7 ^{ix}	51.9 (3)	O1—Se—O3	97.5 (5)
O9 ^{viii} —K2—O7 ^{ix}	87.4 (3)	O5—Se—O3	100.4 (4)
O2 ^v —K2—O11 ^{viii}	63.4 (3)	O1—Se—K1 ^x	57.7 (3)
O6 ^{vi} —K2—O11 ^{viii}	137.0 (3)	O5—Se—K1 ^x	61.4 (3)
O4 ^{vi} —K2—O11 ^{viii}	135.9 (3)	O3—Se—K1 ^x	62.7 (4)
O10 ^{vii} —K2—O11 ^{viii}	97.6 (3)	O1—Se—K1 ⁱⁱ	71.1 (3)
O8 ^{iv} —K2—O11 ^{viii}	127.9 (3)	O5—Se—K1 ⁱⁱ	40.5 (3)
O12 ⁱ —K2—O11 ^{viii}	96.4 (3)	O3—Se—K1 ⁱⁱ	133.7 (4)
O9 ^{viii} —K2—O11 ^{viii}	48.8 (3)	K1 ^x —Se—K1 ⁱⁱ	74.10 (9)
O7 ^{ix} —K2—O11 ^{viii}	46.8 (3)	O1—Se—K1 ⁱ	72.8 (3)
O2 ^v —K2—W2 ^{iv}	156.5 (3)	O5—Se—K1 ⁱ	132.1 (4)
O6 ^{vi} —K2—W2 ^{iv}	82.8 (2)	O3—Se—K1 ⁱ	39.3 (3)
O4 ^{vi} —K2—W2 ^{iv}	106.6 (2)	K1 ^x —Se—K1 ⁱ	74.24 (9)
O10 ^{vii} —K2—W2 ^{iv}	28.8 (2)	K1 ⁱⁱ —Se—K1 ⁱ	140.87 (10)

O8 ^{iv} —K2—W2 ^{iv}	28.8 (2)	Se—O1—W1	141.0 (6)
O12 ⁱ —K2—W2 ^{iv}	78.7 (2)	Se—O1—K1 ^x	92.7 (4)
O9 ^{viii} —K2—W2 ^{iv}	76.9 (2)	W1—O1—K1 ^x	125.8 (4)
O7 ^{ix} —K2—W2 ^{iv}	112.5 (2)	W1—O2—K2 ^{xiv}	136.4 (5)
O11 ^{viii} —K2—W2 ^{iv}	115.99 (18)	Se—O3—W2 ⁱ	123.4 (5)
O2 ^v —K2—W1 ⁱ	97.2 (3)	Se—O3—K1 ⁱ	116.9 (5)
O6 ^{vi} —K2—W1 ⁱ	139.0 (2)	W2 ⁱ —O3—K1 ⁱ	108.1 (4)
O4 ^{vi} —K2—W1 ⁱ	82.3 (2)	Se—O3—K1 ^x	86.8 (4)
O10 ^{vii} —K2—W1 ⁱ	124.7 (2)	W2 ⁱ —O3—K1 ^x	118.7 (4)
O8 ^{iv} —K2—W1 ⁱ	83.2 (2)	K1 ⁱ —O3—K1 ^x	99.0 (3)
O12 ⁱ —K2—W1 ⁱ	28.6 (2)	W2—O4—K2 ^{xvi}	139.1 (5)
O9 ^{viii} —K2—W1 ⁱ	114.1 (2)	W2—O4—K1 ^{xv}	117.3 (5)
O7 ^{ix} —K2—W1 ⁱ	29.32 (19)	K2 ^{xvi} —O4—K1 ^{xv}	90.3 (3)
O11 ^{viii} —K2—W1 ⁱ	76.0 (2)	Se—O5—W3 ⁱⁱ	124.5 (5)
W2 ^{iv} —K2—W1 ⁱ	105.51 (8)	Se—O5—K1 ⁱⁱ	115.3 (5)
O2 ^v —K2—W1 ⁱⁱ	101.5 (3)	W3 ⁱⁱ —O5—K1 ⁱⁱ	111.7 (4)
O6 ^{vi} —K2—W1 ⁱⁱ	81.5 (2)	Se—O5—K1 ^x	88.2 (4)
O4 ^{vi} —K2—W1 ⁱⁱ	138.0 (2)	W3 ⁱⁱ —O5—K1 ^x	112.0 (4)
O10 ^{vii} —K2—W1 ⁱⁱ	28.4 (2)	K1 ⁱⁱ —O5—K1 ^x	99.0 (3)
O8 ^{iv} —K2—W1 ⁱⁱ	85.9 (2)	W3—O6—K2 ^{xvi}	134.9 (6)
O12 ⁱ —K2—W1 ⁱⁱ	125.5 (2)	W3—O6—K1 ^{xv}	125.9 (5)
O9 ^{viii} —K2—W1 ⁱⁱ	30.0 (2)	K2 ^{xvi} —O6—K1 ^{xv}	90.0 (3)
O7 ^{ix} —K2—W1 ⁱⁱ	115.2 (2)	W1 ⁱⁱⁱ —O7—W2	146.6 (6)
O11 ^{viii} —K2—W1 ⁱⁱ	78.6 (2)	W1 ⁱⁱⁱ —O7—K2 ^{ix}	89.2 (4)
W2 ^{iv} —K2—W1 ⁱⁱ	57.20 (5)	W2—O7—K2 ^{ix}	113.7 (4)
W1 ⁱ —K2—W1 ⁱⁱ	137.13 (9)	W2—O8—W3	131.3 (5)
O2—W1—O7 ^x	96.6 (5)	W2—O8—K2 ^{xv}	103.1 (4)
O2—W1—O12	100.1 (5)	W3—O8—K2 ^{xv}	112.3 (4)
O7 ^x —W1—O12	96.1 (4)	W2—O8—K1	106.6 (4)
O2—W1—O10 ^{xi}	95.0 (5)	W3—O8—K1	106.0 (3)
O7 ^x —W1—O10 ^{xi}	166.0 (5)	K2 ^{xv} —O8—K1	89.6 (3)
O12—W1—O10 ^{xi}	89.5 (4)	W3—O9—W1 ⁱⁱⁱ	145.8 (6)
O2—W1—O9 ^x	91.8 (5)	W3—O9—K2 ^{viii}	107.3 (4)
O7 ^x —W1—O9 ^x	89.5 (4)	W1 ⁱⁱⁱ —O9—K2 ^{viii}	96.9 (4)
O12—W1—O9 ^x	166.1 (4)	W2 ^{xvii} —O10—W1 ^{xiii}	147.4 (6)
O10 ^{xi} —W1—O9 ^x	82.3 (4)	W2 ^{xvii} —O10—K2 ^{xviii}	103.6 (4)
O2—W1—O1	169.9 (4)	W1 ^{xiii} —O10—K2 ^{xviii}	109.0 (4)
O7 ^x —W1—O1	82.7 (4)	W3—O11—W2 ^{xvii}	149.4 (5)
O12—W1—O1	89.9 (4)	W3—O11—K2 ^{viii}	100.2 (4)
O10 ^{xi} —W1—O1	84.4 (4)	W2 ^{xvii} —O11—K2 ^{viii}	109.0 (4)
O9 ^x —W1—O1	78.2 (4)	W1—O12—W3 ^{xi}	146.7 (5)
O2—W1—K2 ⁱ	71.7 (4)	W1—O12—K2 ⁱ	102.4 (4)
O7 ^x —W1—K2 ⁱ	61.4 (3)	W3 ^{xi} —O12—K2 ⁱ	110.9 (4)

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