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Synthesis and characterization of the Anderson–Evans tungstoantimonate $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][SbW_6O_{24}]$

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A novel tungstoantimonate, $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][Sb^{V}W^{VI}{}_6O_{24}]$ (**SbW_6**), was synthesized from an aqueous solution and structurally characterized by single-crystal X-ray diffraction, which revealed *C*2/*c* symmetry. The structure contains two serinol $[(HOCH_2)_2CHNH_3]^+$ and five Na^+ cations, which are octahedrally surrounded by 18 water molecules, and one $[Sb^{V}W^{VI}{}_6O_{24}]^{7-}$ anion. The serinol molecules also play a critical role in the synthesis by acting as a mild buffering agent. Each of the W^{VI} and Sb^{V} ions is six-coordinated and displays a distorted octahedral motif. A three-dimensional supramolecular framework is formed *via* hydrogen-bonding interactions between the tungstoantimonates and cations. Powder X-ray diffraction, elemental analysis, thermogravimetric analysis and IR spectroscopy were performed on **SbW_6** to prove the purity, to identify the water content and to characterize the vibrational modes of the crystallized phase.

1. Introduction

Polyoxometalates (POMs) are known as early transition metal–oxygen clusters (Pope, 1983; Gumerova & Rompel, 2020). They are assembled from $\{MO_x\}$ polyhedra, with $x = 4$–7 and M being commonly $Mo^{V/VI}$, $W^{V/VI}$, $V^{IV/V}$, Nb^{V} or Ta^{V} as addenda ions, through sharing of corners and edges (Pope, 1983). POMs can be considered as either isopolyanions $[M_mO_y]^{q-}$, which feature only one metallic M ion ($Mo^{V/VI}$, $W^{V/VI}$, $V^{IV/V}$, Nb^{V} or Ta^{V}), or heteropolyanions $[X_rM_mO_y]^{q-}$, which additionally contain a heteroelement X (Pope, 1983). POMs display a wide range of crucial applications, ranging from catalysis (Wang & Yang, 2015), materials science (Cherevan *et al.*, 2020) and molecular magnetism (Clemente-Juan *et al.*, 2012), to bio- and nanotechnology (Rhule *et al.*, 1998; Bijelic *et al.*, 2018, 2019), as well as macromolecular crystallography (Bijelic & Rompel, 2015, 2017, 2018).

The Anderson–Evans polyoxoanion has the general formula $[H_y(XO_6)M_6O_{18}]^{n-}$, where $y = 0$–6, $n = 2$–8, M = addenda ion (Mo^{VI} or W^{VI}) and X = central heteroion in oxidation states from +2 to +7 (Blazevic & Rompel, 2016). Its structure consists of six corner- and edge-shared $\{MoO_6\}$ or $\{WO_6\}$ octahedra, which surround the $\{XO\}_6$ octahedron (Evans, 1948). In the structure, there exist three differently coordinated oxygen ions (Fig. 1): six triple-bridged oxygen ions (μ_3-O) that connect the heteroion and two addenda ions, six double-bridged oxygen ions (μ_2-O) that connect two addenda ions and lastly two terminal oxygen ions (O_t) per addenda ion (Evans, 1948; Pope, 1983). The oxidation state of a heteroion plays a significant role in the protonation mode of the triple-bridged oxygen ions (μ_3-O) in the Anderson–Evans arche-

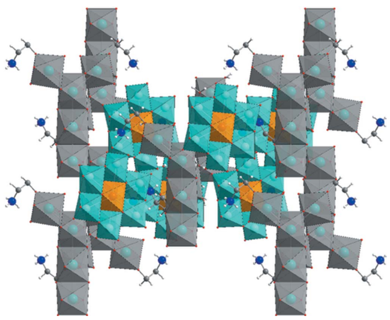


Table 1
POTs with $Sb^{III/V}$ as the only heteroion [based on the Inorganic Crystal Structure Database (FIZ, Karlsruhe; http://www.fiz-informationsdienste.de/DB/icsd/www-recherche.htm) and the Cambridge Structural Database (CSD; Groom *et al.*, 2016) in April 2021].

POT	Type	References
$K_5Na_2[Sb^{V}W^{VI}{}_6O_{24}]$	Anderson	Lee & Sasaki (1987)
$K_{5.5}H_{1.5}[Sb^{V}W^{VI}{}_6O_{24}]$	Anderson	Naruke & Yamase (1992)
$Na_7[Sb^{V}W^{VI}{}_6O_{24}]$	Anderson	Mukhacheva *et al.* (2017)
$K_6[H_{12}Sb^{V}{}_6W^{VI}{}_4O_{36}]$	Pseudo-Anderson–Evans dimer	Park *et al.* (1994)
$(NH_4)_9[Sb^{V}W^{VI}{}_{18}O_{60}(OH)_2]$	Dawson	Zhang *et al.* (2010)
$Na_9[Sb^{III}W^{VI}{}_9O_{33}]$	Keggin	Bösing *et al.* (1997)
$K_{12}[Sb^{III}{}_2W^{VI}{}_{22}O_{74}(OH)_2]$	Krebs	Bösing *et al.* (1997)
$[N(CH_3)_4]_{10}Na_{12}[Na_2Sb^{III}{}_8W^{VI}{}_{36}O_{132}(H_2O)_4]$	Trimer based on lacunary Keggin	Bösing *et al.* (1997)
$(H_2en)_8H_6\{[Sb^{III}{}_2(W^{VI}O_2)_2(B\text{-}\beta\text{-}Sb^{III}W^{VI}{}_9O_{33})_2][(W^{VI}O_2)_2\text{-}(W^{VI}O_3)_2(B\text{-}\beta\text{-}Sb^{III}W^{VI}{}_9O_{33})_2]\}$ (en = ethylenediamine)	Krebs	Xin *et al.* (2019)
$K_{11}Na_{16}[H_2(Sb^{III}W^{VI}{}_9O_{33})(W^{VI}{}_5O_{12})(Sb^{III}{}_2W^{VI}{}_{29}O_{103})]$	Trimer based on lacunary Keggin	Tanuhadi *et al.* (2021)

type, according to which they can be divided into three groups. The first, *i.e.* $[X^{n+}M_6O_{24}]^{(12-n)-}$ (n = 5–7), referred to as 'type A', is a deprotonated structure that exists when it contains heteroions with a high oxidation state (*e.g.* Te^{VI} or I^{VII}). The second, *i.e.* $[X^{n+}(OH)_6M_6O_{18}]^{(6-n)-}$ (n = 2–4), referred to as 'type B', is protonated on the six μ_3-O ions, with each side having three protons. The B-type POMs are usually present when the heteroion has a low oxidation state (*e.g.* Ni^{II} or Co^{II}) (Blazevic & Rompel, 2016). The third group, called 'mixed type', is a combination of the two types mentioned above, as it has protonated μ_3-O ions only on one side (Gumerova *et al.*, 2019). Therefore, it is referred to as one-side protonated with one known polyoxotungstate example, $[Cr^{III}(OH)_3W^{VI}{}_6O_{21}]^{6-}$, so far (Gumerova *et al.*, 2019). Interestingly, there are some platinum-based compounds, with the general formula $[H_nPt^{IV}M^{VI}{}_6O_{24}]^{(8-n)-}$ (M = W or Mo, where $1 < n < 6$; Lee *et al.*, 2004), which exhibit protonation degrees of their μ_3-O ions ranging from 1 to 6 and n is not necessarily an integer.

The majority of Anderson–Evans-type clusters have a planar hexagonal configuration with $\overline{3}m$ (D_{3d}) point symmetry, which is known as the α-isomer (Anderson, 1937). Another configuration of the Anderson–Evans-type cluster shows a bent structure of $2mm$ (C_{2v}) point symmetry and is called the β-isomer (Lindqvist, 1959). An example of the β-isomer was presented by the Ogawa group (Ogawa *et al.*, 1988), *i.e.* $[Sb^{V}(OH)_2Mo^{VI}{}_6O_{22}]^{5-}$ and is one of the few reported structures to date (Lee & Sasaki, 1994; Zhang *et al.*, 2017; Li & Wei, 2021). The Anderson–Evans compounds can be modified in several ways: (i) by variation of the heteroion in the central position; (ii) by combination with various inorganic and organic cations, and (iii) by covalent attachment of one or two alkoxo ligands.

In recent decades, some unsubstituted tungstoantimonates, which have only one heteroion, $Sb^{III/V}$, have been synthesized and structurally characterized (Table 1), but the majority of Sb-containing polyoxotungstates (POTs) contain additional heteroions, such as 3*d* or 4*f* metals (Tanuhadi *et al.*, 2018, 2020). Only three Sb-POTs of the Anderson–Evans archetype, namely, $K_5Na_2[Sb^{V}W^{VI}{}_6O_{24}]\cdot 12H_2O$ (Lee & Sasaki, 1987), $K_{5.5}H_{1.5}[Sb^{V}W^{VI}{}_6O_{24}]\cdot 6H_2O$ (Naruke & Yamase, 1992) and $Na_7[Sb^{V}W^{VI}{}_6O_{24}]\cdot 24H_2O$ (Mukhacheva *et al.*, 2017), have been reported so far. Interestingly, the relative luminescence yield from the O→W LCMT transition of $K_{5.5}H_{1.5}[Sb^{V}W^{VI}{}_6O_{24}]\cdot 6H_2O$ was higher than that of Ln-containing $Na_9[Gd^{III}(W^{VI}{}_5O_{18})_2]\cdot 18H_2O$ under the same conditions (Naruke & Yamase, 1992). The high luminescence yield of $[Sb^{V}W^{VI}{}_6O_{24}]^{7-}$ is attractive for potential photochemical applications in the future.

Serinol ($C_3H_9NO_2$, 2-aminopropane-1,3-diol) is a very stable, highly water soluble, nontoxic, odourless, biodegradable compound which is widely used as a versatile starting material in organic synthesis and as an additive for materials applications, such as composite materials (Barbera *et al.*, 2020; Andreessen & Steinbüchel, 2011). In POM synthesis, serinol can be seen as an alkoxylation ligand or a counter-cation or buffering agent due to the presence of an amino group. Considering that the Sb-centred Anderson–Evans POT has not yet been reported with organic counter-cations, we expand the compound class by applying serinol, which can coordinate in different ways to metals through the $-NH_2$ and $-HOCH_2$ groups and thus significantly affects both the structure and properties, in the synthesis in Sb^{5+}–$WO_4{}^{2-}$ (with an Sb:W ratio of 1:6) systems. Here we report a novel Anderson–Evans Sb-centred POT, $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][Sb^{V}W^{VI}{}_6O_{24}]$ (**SbW$_6$**), being the first example of $[Sb^{V}W^{VI}{}_6O_{24}]^{7-}$ crystallized with an organic counter-cation, which was synthesized from aqueous solution and has been fully characterized.

2. Experimental

2.1. Synthesis and crystallization

The reagents were used as purchased from Merck (Austria) and VWR (Austria) without further purification.

2.1.1. Synthesis of $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][SbW_6O_{24}]$ (SbW$_6$). $Na_2WO_4\cdot 2H_2O$ (0.99 g, 3 mmol) and $KSb^{V}(OH)_6$ (0.13 g, 0.5 mmol) were mixed in a 6:1 ratio in H_2O (12 ml), yielding a turbid solution. The solution was then acidified with aqueous HCl (1 *M*, 4.4 ml) and the pH was set at 4.0. Serinol [$(HOCH_2)_2CHNH_2$; 0.18 g, 2 mmol] was then added and the pH was altered to 7.1. Under stirring and heating for 1 h, at 75 °C, the precipitate was dissolved, and the final solution was colourless. The pH after the reaction was 7.0. The solution was left for evaporation at room temperature,

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Na_5(H_2O)_{18}(C_3H_{10}NO_2)_2]$-$[SbW_6O_{24}]$
M_r	2232.32
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	200
a, *b*, *c* (Å)	21.9761 (14), 13.9179 (9), 16.209 (1)
β (°)	111.189 (2)
V (Å^3)	4622.5 (5)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	15.61
Crystal size (mm)	0.1 × 0.08 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.542, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	100214, 8841, 8213
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.025, 1.15
No. of reflections	8841
No. of parameters	390
No. of restraints	23
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.69

Computer programs: *APEX3* (Bruker, 2015), *SAINT* (Bruker, 2016), *SHELXT2018* (Sheldrick, 2015*a*), *shelXle* (Hübschle *et al.*, 2011), *SHELXL2018* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *DIAMOND* (Brandenburg, 2006), *OLEX2* (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2020).

leading to colourless crystals suitable for single-crystal X-ray diffraction within 1 d (yield: 0.4 g, 60%, based on W). The pH of the Sb^{5+}–WO_4^{2-} solution was varied from 3.7 to 5.0; however, after the addition of serinol (0.18 g, 2 mmol), the final pH was in the range from 7.0 to 7.7 and, in all cases, crystals with the same unit cell were obtained. Other synthetic routes, such as reflux reaction and hydrothermal synthesis at 120 °C, for the same reaction mixture led to the same product. Elemental analysis found (calculated) for $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][Sb^VW^{VI}_6O_{24}]$ (%): C 3.18 (3.23), H 2.56 (2.53), N 1.29 (1.25), O 32.89 (32.97). FT–IR (cm^{-1}): 3357 (*s*), 2952 (*sh*), 1610 (*s*), 1498 (*s*), 1464 (*sh*), 1373 (*w*), 1256 (*w*), 1099 (*w*), 1037 (*s*), 1018 (*sh*), 927 (*s*), 850 (*s*), 703 (*sh*), 632 (*w*), 640 (*w*), 563 (*w*), 420 (*s*), 349 (*s*), 310 (*s*).

2.2. IR spectroscopy

SbW_6 was characterized by IR spectroscopy on a Bruker Vertex70 IR Spectrometer equipped with a single-reflection diamond-ATR unit in the range 4000–300 cm^{-1}.

2.3. TGA measurements

Thermogravimetric analysis (TGA) was performed on a Mettler SDTA851e Thermogravimetric Analyzer under a nitrogen flow with a heating rate of 5 K min^{-1} in the region from 303 to 873 K.

2.4. Elemental analysis

The determination of C/H/N/O was carried out using an ‘EA 1108 CHNS-O’ elemental analyzer by Carlo Erba Instruments at the Mikroanalytisches Laboratorium, Faculty of Chemistry, University of Vienna.

2.5. Powder X-ray diffraction (PXRD)

PXRD was performed on a Bruker D8 Advance diffractometer, with Cu *K*α radiation (λ = 1.54056 Å), a Lynxeye silicon strip detector and a SolX energy dispersive detector (variable slit aperture with 12 mm, $10° \leq 2\theta \leq 50°$).

2.6. Refinement

In Table 2, the crystallographic characteristics of **SbW_6** and the experimental conditions of data collection and refinement are reported. The positions of the H atoms of the water molecules were obtained by difference Fourier techniques and were refined with free isotropic displacement parameters and O—H distances restrained to 0.95 (2) Å. The disordered water molecule in the coordination sphere of atom Na1 was refined with two positions (O23 and O24), with free occupancy factors to a total of 100%. The H atoms of this disordered group had U_{iso}(H) values set to $1.5U_{eq}$(O) of the parent atom. H atoms bound to N or C atoms were placed in idealized positions (N—H = 0.91 Å and C—H = 0.99 or 1.00 Å for CH_2 and CH groups, respectively) and refined in riding modes, with U_{iso}(H) values set to $1.5U_{eq}$(N) or to $1.2U_{eq}$(C).

3. Results and discussion

The preparation of **SbW_6** was carried out at a W^{VI} to Sb^V ratio of 6:1 and at a pH of 7.1. In the absence of serinol, at pH 7.5, protonated $K_{5.5}H_{1.5}[Sb^VW^{VI}_6O_{24}]\cdot6H_2O$ (Naruke & Yamase, 1992), and at pH 4.5, unprotonated $K_5Na_2[Sb^VW^{VI}_6O_{24}]\cdot12H_2O$ (Lee & Sasaki, 1987), were obtained.

The main structural elements of **SbW_6** are the Anderson–Evans $[Sb^VW^{VI}_6O_{24}]^{7-}$ anion and the complex $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2]^{7+}$ cation, which are connected *via* hydrogen bonds between terminal (O_t) and bridging O atoms (μ_2-O) of the polyanion and protons from the cationic complex (Fig. 1). Crystallographically centrosymmetric $[Sb^VW^{VI}_6O_{24}]^{7-}$ shows the characteristic Anderson–Evans A-type structure with a central $\{SbO_6\}$ octahedron surrounded by six edge-shared $\{WO_6\}$ octahedra that form a planar array of distorted octahedra (Fig. 1). The average W—Sb bond length is 3.26 Å. As is typical for all Anderson–Evans A-type structures, three different coordination modes of the O atoms are present in the structure: six triple-bridged oxygen ions (μ_3-O) connect the heteroion and two W ions, six double-bridged oxygen ions (μ_2-O) connect two W ions and two terminal oxygen (O_t) ions are connected to each of the six W ions (Fig. 1). The average distance for Sb—μ_3-O is 1.98 Å, for W—μ_3-O is 2.27 Å, for W—μ_2-O is 1.94 Å and for W—O_t is

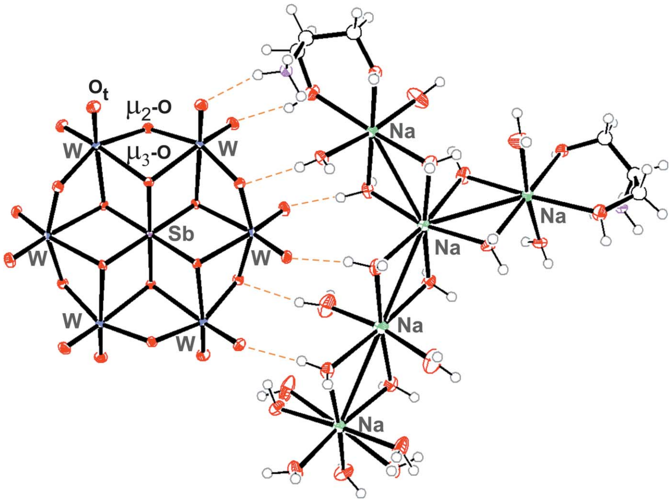


Figure 1
Displacement ellipsoid plot of **SbW$_6$** with the hydrogen-bond interactions between the anion and the counter-cation complex highlighted (orange dashed line). Displacement ellipsoids are displayed at the 50% probability level. Colour code: W blue, Sb pink, Na green, C grey, N purple, O red and H white.

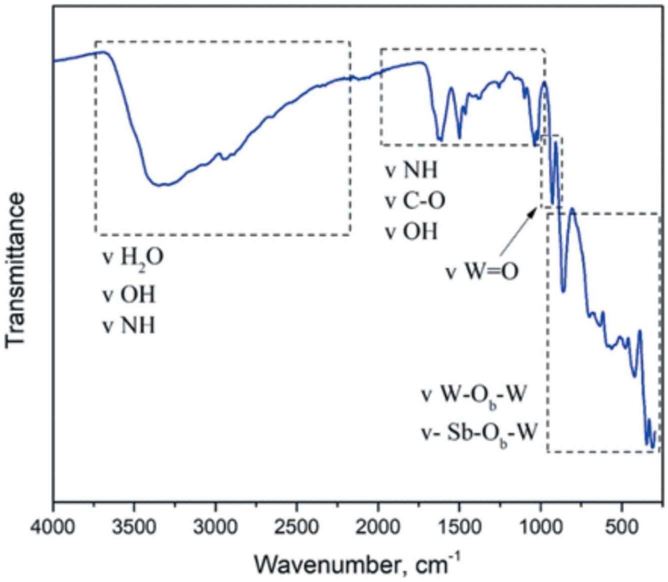


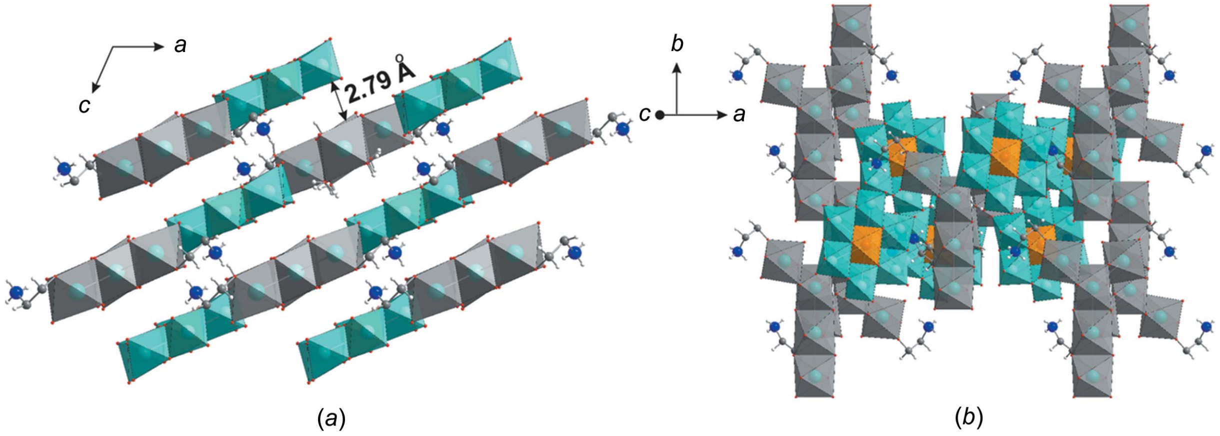
Figure 3
IR spectrum of **SbW$_6$** in the region from 4000 to 300 cm^{-1}.

1.74 Å. The values are comparable with those of $K_{5.5}H_{1.5}[Sb^{V}W^{VI}{}_6O_{24}]$ (Naruke & Yamase, 1992). For instance, the Sb—μ_3-O bond length (1.98 Å) differs by only 0.03 Å from the others reported by Naruke & Yamase (1992) (2.01 Å). Applying bond valence sum (BVS) calculations (Brown & Altermatt, 1985), all the W ions in $[Sb^{V}W^{VI}{}_6O_{24}]^{7-}$ exhibit the +VI oxidation state (average calculated value of 6.01) and Sb shows the +V oxidation state (5.37). Based on BVS analysis and the number of counter-cations, it was concluded that the Anderson–Evans anion is not protonated and belongs to type A.

The counter-cation is composed of five octahedrally coordinated Na^+ ions, which assemble in an elevated T-shape form, and two protonated serinol molecules that are coordinated to two Na^+ ions *via* –$HOCH_2$ groups. This group has crystallographically imposed twofold symmetry. One serinol ligand interacts through the –NH_3 group with the terminal O atom of the POT anion, and the second interacts with the adjacent O atom in $\{NaO_6\}$ (Fig. 1).

The three-dimensional (3D) structure of **SbW$_6$** consists of two-dimensional (2D) sheets formed of $[Sb^{V}W^{VI}{}_6O_{24}]^{7-}$ anions and complex $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2]^{7+}$, cations connected *via* hydrogen bonds (Figs. 1 and 2). The distances between 2D layers are approximately 2.79 Å, which allows the formation of hydrogen bonds between the layers and creates cavities along the *b* axis (Fig. 2*a*). This packing is different to that observed in $K_{5.5}H_{1.5}[Sb^{V}W^{VI}{}_6O_{24}]\cdot 6H_2O$ and $K_5Na_2[Sb^{V}W^{VI}{}_6O_{24}]\cdot 12H_2O$, where the layers of anions alternate with layers or single polyhedra of counter-cations.

The IR spectrum of **SbW$_6$** (Fig. 3) is characteristic for Anderson–Evans POMs (Liu *et al.*, 2015; Qu *et al.*, 2012). The broad bands in the region between 2300 to 3750 cm^{-1} represent the vibrations of the –OH groups of H_2O and the N—H bonds of the amine groups of serinol. In the area between 1610



(*a*) (*b*)

Figure 2
The crystal packing of **SbW$_6$**, (*a*) viewed along the *b* axis and (*b*) viewed along the *z* axis. Colour code: $\{WO_6\}$ turquoise, $\{SbO_6\}$ orange, $\{Na(H_2O)_6\}$ grey, C grey, N blue, O red and H black.

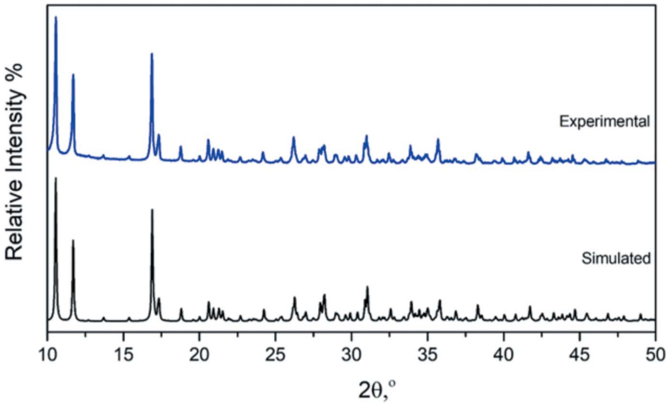


Figure 4
Experimental (blue colour) and simulated (black colour) powder XRD pattern of $\mathbf{SbW_6}$.

and 1018 cm^{-1}, the bands are attributed to the vibrations of C—H, C—O and again N—H in serinol. The bands at about 930 and 880 cm^{-1} are attributed to antisymmetric stretching vibrations of the terminal W=O bonds and Sb—O—W bridges (O$_b$), respectively. The bands at 640 and 563 cm^{-1} are associated with the asymmetric stretching of W—O—W bridges (O$_b$) and the bending vibrations of W—O—W, respectively. Lastly, the bands between 750 and 300 cm^{-1} are contributed by Sb—O—W vibrations (Liu *et al.*, 2015).

The powder XRD pattern of $\mathbf{SbW_6}$ (Fig. 4) was investigated at room temperature. The simulated powder diffraction pattern was based on the single-crystal structural data. The observed peak positions are in good alignment with the simulated patterns, which confirms that the POT structure had been solved accurately and that $\mathbf{SbW_6}$ consists of a single phase.

The exact number of water molecules was determined using TGA. The curve (Fig. 5) shows three weight-loss steps during the heating process from 30 to 600 °C. The first weight loss of 14.7% in the temperature range 30–200 °C corresponds to all water molecules from the Na$^+$ coordinating spheres. The second and third step correspond in total to 8.4% and the loss of two serinol molecules.

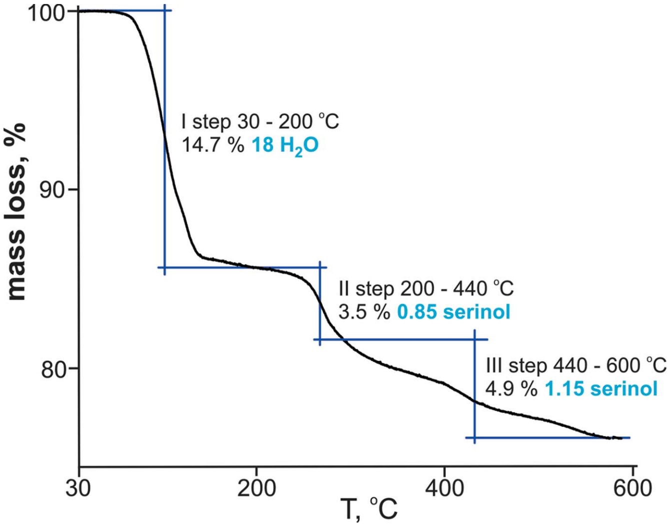


Figure 5
Thermogravimetric curve of $\mathbf{SbW_6}$.

The composition of the counter-cation has remarkable effects on the crystal packing and thus on the physical properties of Anderson–Evans POMs (Blazevic & Rompel, 2016). The success in synthesizing $\mathbf{SbW_6}$ shows that the Sb-centred Anderson–Evans POT is a versatile building block, which can be modified by organic counter-cations into high-dimensional architectures. $\mathbf{SbW_6}$ is the first reported K$^+$-free salt with an organic counter-cation, and it has much higher water solubility and can expand the areas of its application in aqueous solution.

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Synthesis and characterization of the Anderson–Evans tungstoantimonate $[Na_5(H_2O)_{18}\{(HOCH_2)_2CHNH_3\}_2][SbW_6O_{24}]$

Kleanthi Sifaki, Nadiia I. Gumerova, Gerald Giester and Annette Rompel

Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a) and *shelXle* (Hübschle *et al.*, 2011); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2020).

Sodium-serinol hexatungstoanitimonate

Crystal data

$[Na_5(H_2O)_{18}(C_3H_{10}NO_2)_2][SbW_6O_{24}]$
$M_r = 2232.32$
Monoclinic, $C2/c$
$a = 21.9761\ (14)$ Å
$b = 13.9179\ (9)$ Å
$c = 16.209\ (1)$ Å
$\beta = 111.189\ (2)°$
$V = 4622.5\ (5)$ Å^3
$Z = 4$
$F(000) = 4096$
$D_x = 3.208$ Mg m$^{-3$}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9051 reflections
$\theta = 2.4–33.2°$
$\mu = 15.61$ mm^{-1}
$T = 200$ K
Block, clear colourless
0.1 × 0.08 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min} = 0.542$, $T_{max} = 0.747$
100214 measured reflections
8841 independent reflections
8213 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 33.2°$, $\theta_{min} = 2.0°$
$h = -33 \rightarrow 33$
$k = -21 \rightarrow 21$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.013$
$wR(F^2) = 0.025$
$S = 1.15$
8841 reflections
390 parameters
23 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0049P)^2 + 8.8181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Extinction correction: SHELXL2018 (Sheldrick, 2015b), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000087 (2)

Special details

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

Refinement. Olex2_refinement_description 1. Fixed U_{iso} At 1.2 times of: All C(H) groups, All C(H,H) groups At 1.5 times of: All N(H,H,H) groups, All O(H,H) groups 2. Restrained distances O24—H24B = O24—H24A = O23—H23A = O23—H23B = O22—H22A = O22—H22B = O21—H21A = O21—H21B = O20—H20A = O20—H20B = O19—H19A = O19—H19B = O18—H18B = O18—H18A = O16—H16B = O16—H16A = O17—H17B = O17—H17A = O15—H15B = O15—H15A = O14—H14 = O13—H13 0.95 with σ of 0.03 Na1—H24A ~ Na1—H24B with σ of 0.02 3. Others Sof(O24)=Sof(H24A)=Sof(H24B)=FVAR(1) Sof(O23)=Sof(H23A)=Sof(H23B)=FVAR(2) 4.a Free rotating group: O24(H24A,H24B) 4.b Rotating group: O23(H23A,H23B) 4.c Ternary CH refined with riding coordinates: C2(H2) 4.d Secondary CH2 refined with riding coordinates: C1(H1D,H1E), C3(H3A,H3B) 4.e Idealized Me refined as rotating group: N1(H1A,H1B,H1C)

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
W1	0.23646 (2)	0.98310 (2)	0.50967 (2)	0.00915 (2)	
W2	0.33638 (2)	0.89214 (2)	0.42377 (2)	0.00926 (2)	
W3	0.34950 (2)	0.65895 (2)	0.41500 (2)	0.00910 (2)	
Sb1	0.250000	0.750000	0.500000	0.00687 (3)	
O1	0.19305 (6)	0.63497 (9)	0.46152 (8)	0.0092 (2)	
O2	0.32045 (6)	0.65301 (9)	0.53084 (8)	0.0093 (2)	
O3	0.26877 (6)	0.76387 (9)	0.38977 (8)	0.0088 (2)	
O4	0.29370 (7)	1.06930 (10)	0.56698 (9)	0.0160 (3)	
O5	0.16585 (7)	1.05002 (10)	0.45722 (9)	0.0164 (3)	
O6	0.21773 (6)	0.93907 (9)	0.61149 (8)	0.0116 (2)	
O7	0.39611 (7)	0.97551 (10)	0.48078 (9)	0.0174 (3)	
O8	0.25818 (6)	0.96747 (9)	0.40414 (8)	0.0115 (2)	
O9	0.33570 (7)	0.89690 (10)	0.31671 (9)	0.0160 (3)	
O10	0.39142 (6)	0.77917 (9)	0.46445 (8)	0.0122 (2)	
O11	0.34480 (7)	0.67242 (10)	0.30582 (9)	0.0143 (3)	
O12	0.41832 (7)	0.58827 (10)	0.46496 (9)	0.0168 (3)	
Na1	0.500000	0.99629 (9)	0.250000	0.0197 (2)	
Na2	0.500000	0.74736 (9)	0.250000	0.0239 (3)	
Na3	0.500000	0.49315 (9)	0.250000	0.0192 (2)	
Na4	0.41110 (4)	0.34118 (6)	0.32760 (5)	0.01762 (16)	
O13	0.33515 (7)	0.21655 (10)	0.26482 (9)	0.0161 (3)	
H13	0.3018 (12)	0.232 (2)	0.2144 (16)	0.039 (8)*	
O14	0.37746 (8)	0.31336 (12)	0.45147 (10)	0.0228 (3)	
H14	0.370 (2)	0.366 (2)	0.479 (3)	0.086 (14)*	
O15	0.31493 (7)	0.43482 (11)	0.27597 (10)	0.0175 (3)	
H15A	0.2958 (12)	0.4493 (19)	0.2199 (14)	0.026 (7)*	
H15B	0.3004 (14)	0.4779 (19)	0.3006 (19)	0.041 (9)*	

O16	0.49851 (9)	0.23264 (14)	0.37966 (13)	0.0348 (4)	
H16A	0.504 (3)	0.179 (3)	0.352 (3)	0.13 (2)*	
H16B	0.5299 (14)	0.230 (2)	0.4319 (17)	0.051 (10)*	
O17	0.42545 (8)	0.35821 (12)	0.19100 (10)	0.0222 (3)	
H17A	0.3901 (13)	0.364 (2)	0.1394 (17)	0.044 (9)*	
H17B	0.4492 (15)	0.316 (2)	0.175 (2)	0.053 (10)*	
O18	0.48239 (7)	0.47272 (12)	0.38301 (10)	0.0198 (3)	
H18A	0.5179 (12)	0.455 (2)	0.4319 (15)	0.031 (7)*	
H18B	0.4610 (15)	0.513 (2)	0.407 (2)	0.053 (10)*	
O19	0.57928 (7)	0.61738 (12)	0.29274 (10)	0.0206 (3)	
H19A	0.6093 (13)	0.603 (2)	0.3462 (16)	0.043 (9)*	
H19B	0.6047 (14)	0.629 (2)	0.262 (2)	0.046 (9)*	
O20	0.50365 (10)	0.76172 (17)	0.39592 (13)	0.0405 (5)	
H20A	0.471 (2)	0.777 (4)	0.416 (4)	0.15 (2)*	
H20B	0.5370 (18)	0.742 (3)	0.445 (2)	0.103 (17)*	
O21	0.58506 (8)	0.87360 (12)	0.28898 (11)	0.0218 (3)	
H21A	0.6135 (13)	0.893 (2)	0.3411 (16)	0.042 (9)*	
H21B	0.601 (2)	0.878 (3)	0.246 (2)	0.094 (15)*	
O22	0.58231 (8)	1.11103 (13)	0.30761 (11)	0.0274 (4)	
H22A	0.6160 (12)	1.114 (2)	0.3604 (16)	0.036 (8)*	
H22B	0.6034 (15)	1.141 (2)	0.277 (2)	0.053 (10)*	
O23	0.4836 (2)	1.0261 (7)	0.3845 (3)	0.0214 (16)	0.49 (3)
H23A	0.520517	1.019846	0.429088	0.032*	0.49 (3)
H23B	0.458680	0.981153	0.392879	0.032*	0.49 (3)
N1	0.24448 (8)	0.28660 (12)	0.33045 (11)	0.0151 (3)	
H1A	0.209963	0.263685	0.284205	0.023*	
H1B	0.268602	0.326406	0.309808	0.023*	
H1C	0.229658	0.319666	0.367847	0.023*	
C1	0.31201 (10)	0.15213 (14)	0.31546 (13)	0.0170 (4)	
H1D	0.348055	0.108998	0.349921	0.020*	
H1E	0.276807	0.111847	0.274682	0.020*	
C2	0.28596 (10)	0.20445 (14)	0.37896 (13)	0.0151 (3)	
H2	0.256858	0.158600	0.394736	0.018*	
C3	0.33729 (10)	0.23864 (15)	0.46485 (13)	0.0192 (4)	
H3A	0.315385	0.262462	0.504576	0.023*	
H3B	0.365219	0.183629	0.494426	0.023*	
O24	0.4901 (3)	0.9763 (14)	0.3884 (4)	0.041 (3)	0.51 (3)
H24A	0.525636	0.986172	0.433912	0.061*	0.51 (3)
H24B	0.460889	1.011938	0.398180	0.061*	0.51 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01187 (3)	0.00678 (3)	0.00937 (3)	0.00066 (2)	0.00455 (2)	−0.00038 (2)
W2	0.00935 (3)	0.00934 (3)	0.00992 (3)	−0.00122 (2)	0.00449 (2)	0.00009 (2)
W3	0.00888 (3)	0.01020 (3)	0.00925 (3)	0.00212 (2)	0.00452 (2)	0.00001 (2)
Sb1	0.00750 (6)	0.00630 (6)	0.00766 (6)	0.00040 (5)	0.00376 (5)	−0.00023 (5)
O1	0.0100 (5)	0.0090 (6)	0.0085 (5)	−0.0005 (4)	0.0033 (4)	−0.0006 (4)

O2	0.0098 (5)	0.0092 (6)	0.0092 (5)	0.0025 (4)	0.0038 (4)	0.0000 (4)
O3	0.0092 (5)	0.0098 (6)	0.0083 (5)	0.0002 (4)	0.0041 (4)	0.0001 (4)
O4	0.0205 (7)	0.0128 (6)	0.0155 (6)	−0.0032 (5)	0.0075 (5)	−0.0029 (5)
O5	0.0191 (7)	0.0136 (6)	0.0168 (6)	0.0060 (5)	0.0066 (5)	0.0035 (5)
O6	0.0136 (6)	0.0114 (6)	0.0101 (6)	−0.0010 (5)	0.0047 (5)	−0.0021 (5)
O7	0.0144 (6)	0.0168 (7)	0.0200 (7)	−0.0046 (5)	0.0050 (5)	−0.0026 (5)
O8	0.0140 (6)	0.0103 (6)	0.0104 (6)	0.0010 (5)	0.0046 (5)	0.0010 (5)
O9	0.0189 (7)	0.0175 (7)	0.0141 (6)	−0.0001 (5)	0.0090 (5)	0.0018 (5)
O10	0.0096 (5)	0.0134 (6)	0.0129 (6)	−0.0002 (5)	0.0031 (5)	−0.0002 (5)
O11	0.0165 (6)	0.0163 (7)	0.0125 (6)	0.0016 (5)	0.0080 (5)	0.0002 (5)
O12	0.0140 (6)	0.0187 (7)	0.0173 (7)	0.0064 (5)	0.0052 (5)	0.0008 (5)
Na1	0.0167 (5)	0.0227 (6)	0.0192 (6)	0.000	0.0059 (5)	0.000
Na2	0.0221 (6)	0.0230 (6)	0.0256 (6)	0.000	0.0073 (5)	0.000
Na3	0.0205 (6)	0.0199 (6)	0.0193 (6)	0.000	0.0095 (5)	0.000
Na4	0.0149 (4)	0.0206 (4)	0.0174 (4)	−0.0004 (3)	0.0060 (3)	0.0009 (3)
O13	0.0179 (7)	0.0170 (7)	0.0126 (6)	0.0008 (5)	0.0045 (5)	−0.0001 (5)
O14	0.0220 (7)	0.0267 (8)	0.0204 (7)	−0.0071 (6)	0.0086 (6)	−0.0050 (6)
O15	0.0201 (7)	0.0148 (7)	0.0157 (7)	0.0036 (5)	0.0043 (6)	−0.0012 (5)
O16	0.0290 (9)	0.0278 (10)	0.0314 (10)	0.0090 (7)	−0.0085 (7)	−0.0045 (8)
O17	0.0177 (7)	0.0324 (9)	0.0142 (7)	−0.0026 (6)	0.0031 (6)	−0.0011 (6)
O18	0.0187 (7)	0.0248 (8)	0.0148 (7)	0.0074 (6)	0.0047 (6)	−0.0018 (6)
O19	0.0177 (7)	0.0266 (8)	0.0182 (7)	0.0008 (6)	0.0075 (6)	0.0056 (6)
O20	0.0266 (9)	0.0643 (14)	0.0300 (10)	0.0032 (9)	0.0094 (8)	0.0026 (10)
O21	0.0191 (7)	0.0265 (8)	0.0214 (8)	−0.0021 (6)	0.0091 (6)	0.0001 (6)
O22	0.0201 (8)	0.0370 (10)	0.0200 (8)	−0.0105 (7)	0.0010 (6)	0.0034 (7)
O23	0.0177 (17)	0.027 (4)	0.0190 (17)	−0.0030 (17)	0.0059 (13)	0.0033 (17)
N1	0.0150 (7)	0.0143 (7)	0.0156 (7)	0.0007 (6)	0.0052 (6)	−0.0007 (6)
C1	0.0209 (9)	0.0105 (8)	0.0184 (9)	0.0016 (7)	0.0055 (7)	0.0002 (7)
C2	0.0184 (9)	0.0110 (8)	0.0150 (8)	−0.0004 (7)	0.0049 (7)	0.0025 (6)
C3	0.0209 (9)	0.0211 (10)	0.0135 (8)	−0.0014 (8)	0.0038 (7)	0.0009 (7)
O24	0.023 (2)	0.080 (9)	0.022 (2)	−0.016 (3)	0.0111 (17)	−0.017 (3)

Geometric parameters (Å, º)

W1—Sb1	3.2668 (2)	Na3—O17	2.4480 (19)
W1—O1^{i}	2.1899 (12)	Na3—O18	2.3414 (15)
W1—O2^{i}	2.2339 (13)	Na3—O18^{ii}	2.3414 (15)
W1—O4	1.7435 (14)	Na3—O19	2.3733 (18)
W1—O5	1.7449 (13)	Na3—O19^{ii}	2.3733 (18)
W1—O6	1.9391 (13)	Na4—O13	2.3669 (17)
W1—O8	1.9471 (13)	Na4—O14	2.4085 (17)
W2—Sb1	3.2772 (1)	Na4—O15	2.3636 (17)
W2—O1^{i}	2.2106 (12)	Na4—O16	2.3479 (19)
W2—O3	2.2599 (12)	Na4—O17	2.3585 (17)
W2—O7	1.7455 (14)	Na4—O18	2.3655 (18)
W2—O8	1.9387 (13)	O13—H13	0.90 (2)
W2—O9	1.7312 (13)	O13—C1	1.428 (2)
W2—O10	1.9477 (13)	O14—H14	0.91 (2)

W3—Sb1	3.2348 (1)	O14—C3	1.431 (3)
W3—O2	2.1925 (12)	O15—H15A	0.88 (2)
W3—O3	2.2189 (12)	O15—H15B	0.84 (2)
W3—O6^{i}	1.9416 (13)	O16—H16A	0.90 (3)
W3—O10	1.9383 (13)	O16—H16B	0.88 (2)
W3—O11	1.7452 (13)	O17—H17A	0.92 (2)
W3—O12	1.7394 (13)	O17—H17B	0.88 (2)
Sb1—O1	1.9885 (12)	O18—H18A	0.92 (2)
Sb1—O1^{i}	1.9885 (12)	O18—H18B	0.91 (2)
Sb1—O2^{i}	1.9773 (12)	O19—H19A	0.90 (2)
Sb1—O2	1.9773 (12)	O19—H19B	0.88 (2)
Sb1—O3	1.9830 (12)	O20—H20A	0.92 (3)
Sb1—O3^{i}	1.9830 (12)	O20—H20B	0.91 (3)
Na1—Na2	3.4647 (18)	O21—H21A	0.89 (2)
Na1—O21	2.4404 (18)	O21—H21B	0.89 (3)
Na1—O21^{ii}	2.4405 (18)	O22—H22A	0.91 (2)
Na1—O22^{ii}	2.3394 (18)	O22—H22B	0.89 (2)
Na1—O22	2.3394 (18)	O23—H23A	0.8740
Na1—O23^{ii}	2.371 (6)	O23—H23B	0.8741
Na1—O23	2.371 (6)	N1—H1A	0.9100
Na1—O24	2.346 (6)	N1—H1B	0.9100
Na1—O24^{ii}	2.346 (6)	N1—H1C	0.9100
Na2—Na3	3.5381 (18)	N1—C2	1.496 (2)
Na2—O19	2.4322 (19)	C1—H1D	0.9900
Na2—O19^{ii}	2.4322 (19)	C1—H1E	0.9900
Na2—O20	2.346 (2)	C1—C2	1.531 (3)
Na2—O20^{ii}	2.346 (2)	C2—H2	1.0000
Na2—O21^{ii}	2.4752 (19)	C2—C3	1.517 (3)
Na2—O21	2.4752 (19)	C3—H3A	0.9900
Na3—Na4	3.4130 (11)	C3—H3B	0.9900
Na3—Na4^{ii}	3.4130 (11)	O24—H24A	0.8699
Na3—O17^{ii}	2.4480 (19)	O24—H24B	0.8705

O1^{i}—W1—Sb1	36.42 (3)	O24—Na1—Na2	83.2 (5)
O1^{i}—W1—O2^{i}	72.79 (4)	O24^{ii}—Na1—O21	80.7 (3)
O2^{i}—W1—Sb1	36.37 (3)	O24^{ii}—Na1—O21^{ii}	89.8 (4)
O4—W1—Sb1	130.41 (5)	O24—Na1—O21^{ii}	80.7 (3)
O4—W1—O1^{i}	94.83 (6)	O24—Na1—O21	89.8 (4)
O4—W1—O2^{i}	163.66 (6)	O24^{ii}—Na1—O23^{ii}	17.2 (3)
O4—W1—O5	103.63 (7)	O24—Na1—O23^{ii}	175.4 (5)
O4—W1—O6	95.64 (6)	O24—Na1—O24^{ii}	166.4 (9)
O4—W1—O8	100.73 (6)	Na1—Na2—Na3	180.0
O5—W1—Sb1	125.95 (5)	O19—Na2—Na1	138.05 (4)
O5—W1—O1^{i}	160.13 (6)	O19^{ii}—Na2—Na1	138.06 (4)
O5—W1—O2^{i}	90.26 (6)	O19—Na2—Na3	41.95 (4)
O5—W1—O6	99.11 (6)	O19^{ii}—Na2—Na3	41.94 (4)
O5—W1—O8	95.10 (6)	O19^{ii}—Na2—O19	83.89 (9)
O6—W1—Sb1	77.17 (4)	O19^{ii}—Na2—O21	176.21 (6)

O6—W1—O1^{i}	86.15 (5)
O6—W1—O2^{i}	73.36 (5)
O6—W1—O8	155.13 (5)
O8—W1—Sb1	77.96 (4)
O8—W1—O1^{i}	74.00 (5)
O8—W1—O2^{i}	86.33 (5)
O1^{i}—W2—Sb1	36.33 (3)
O1^{i}—W2—O3	72.77 (4)
O3—W2—Sb1	36.45 (3)
O7—W2—Sb1	128.97 (5)
O7—W2—O1^{i}	93.49 (6)
O7—W2—O3	163.07 (6)
O7—W2—O8	100.36 (6)
O7—W2—O10	95.81 (6)
O8—W2—Sb1	77.78 (4)
O8—W2—O1^{i}	73.67 (5)
O8—W2—O3	85.49 (5)
O8—W2—O10	153.80 (5)
O9—W2—Sb1	127.21 (5)
O9—W2—O1^{i}	161.88 (6)
O9—W2—O3	91.10 (6)
O9—W2—O7	103.75 (7)
O9—W2—O8	97.40 (6)
O9—W2—O10	98.60 (6)
O10—W2—Sb1	76.02 (4)
O10—W2—O1^{i}	84.96 (5)
O10—W2—O3	73.62 (5)
O2—W3—Sb1	36.78 (3)
O2—W3—O3	73.84 (4)
O3—W3—Sb1	37.06 (3)
O6^{i}—W3—Sb1	77.99 (4)
O6^{i}—W3—O2	74.28 (5)
O6^{i}—W3—O3	85.85 (5)
O10—W3—Sb1	77.24 (4)
O10—W3—O2	85.43 (5)
O10—W3—O3	74.75 (5)
O10—W3—O6^{i}	155.22 (5)
O11—W3—Sb1	126.05 (4)
O11—W3—O2	160.69 (5)
O11—W3—O3	89.55 (5)
O11—W3—O6^{i}	95.15 (6)
O11—W3—O10	99.89 (6)
O12—W3—Sb1	129.14 (5)
O12—W3—O2	93.06 (6)
O12—W3—O3	163.91 (6)
O12—W3—O6^{i}	99.77 (6)
O12—W3—O10	95.30 (6)
O12—W3—O11	104.81 (6)
O19—Na2—O21	93.33 (5)
O19—Na2—O21^{ii}	176.21 (6)
O19^{ii}—Na2—O21^{ii}	93.33 (5)
O20^{ii}—Na2—Na1	85.11 (7)
O20—Na2—Na1	85.11 (7)
O20^{ii}—Na2—Na3	94.89 (7)
O20—Na2—Na3	94.89 (7)
O20—Na2—O19	90.93 (7)
O20—Na2—O19^{ii}	96.34 (7)
O20^{ii}—Na2—O19^{ii}	90.93 (7)
O20^{ii}—Na2—O19	96.34 (7)
O20—Na2—O20^{ii}	170.23 (13)
O20—Na2—O21	86.25 (7)
O20^{ii}—Na2—O21^{ii}	86.26 (7)
O20^{ii}—Na2—O21	86.81 (7)
O20—Na2—O21^{ii}	86.81 (7)
O21^{ii}—Na2—Na1	44.78 (4)
O21—Na2—Na1	44.78 (4)
O21^{ii}—Na2—Na3	135.22 (4)
O21—Na2—Na3	135.22 (4)
O21^{ii}—Na2—O21	89.56 (9)
Na4^{ii}—Na3—Na2	128.30 (2)
Na4—Na3—Na2	128.29 (2)
Na4^{ii}—Na3—Na4	103.41 (4)
O17—Na3—Na2	140.10 (4)
O17^{ii}—Na3—Na2	140.10 (4)
O17^{ii}—Na3—Na4^{ii}	43.71 (4)
O17—Na3—Na4	43.71 (4)
O17^{ii}—Na3—Na4	76.82 (5)
O17—Na3—Na4^{ii}	76.82 (5)
O17^{ii}—Na3—O17	79.80 (9)
O18^{ii}—Na3—Na2	96.98 (5)
O18—Na3—Na2	96.98 (5)
O18^{ii}—Na3—Na4^{ii}	43.80 (4)
O18^{ii}—Na3—Na4	124.83 (5)
O18—Na3—Na4^{ii}	124.84 (5)
O18—Na3—Na4	43.80 (4)
O18—Na3—O17	87.51 (6)
O18^{ii}—Na3—O17^{ii}	87.51 (6)
O18^{ii}—Na3—O17	81.79 (6)
O18—Na3—O17^{ii}	81.79 (6)
O18—Na3—O18^{ii}	166.05 (10)
O18^{ii}—Na3—O19	90.52 (6)
O18^{ii}—Na3—O19^{ii}	99.67 (6)
O18—Na3—O19	99.67 (6)
O18—Na3—O19^{ii}	90.52 (6)
O19—Na3—Na2	43.24 (4)
O19^{ii}—Na3—Na2	43.24 (4)

W1—Sb1—W1^{i}	180.0	O19—Na3—Na4	143.27 (4)
W1^{i}—Sb1—W2^{i}	59.590 (4)	O19—Na3—Na4^{ii}	95.82 (4)
W1—Sb1—W2	59.590 (4)	O19^{ii}—Na3—Na4^{ii}	143.27 (4)
W1^{i}—Sb1—W2	120.410 (3)	O19^{ii}—Na3—Na4	95.82 (4)
W1—Sb1—W2^{i}	120.411 (3)	O19^{ii}—Na3—O17	97.35 (6)
W2—Sb1—W2^{i}	180.0	O19^{ii}—Na3—O17^{ii}	171.87 (6)
W3^{i}—Sb1—W1^{i}	119.789 (2)	O19—Na3—O17	171.87 (6)
W3—Sb1—W1^{i}	60.211 (2)	O19—Na3—O17^{ii}	97.35 (6)
W3^{i}—Sb1—W1	60.211 (2)	O19^{ii}—Na3—O19	86.47 (9)
W3—Sb1—W1	119.789 (2)	O13—Na4—Na3	134.78 (5)
W3—Sb1—W2	60.200 (4)	O13—Na4—O14	81.91 (6)
W3—Sb1—W2^{i}	119.800 (5)	O14—Na4—Na3	142.74 (5)
W3^{i}—Sb1—W2^{i}	60.200 (4)	O15—Na4—Na3	94.91 (5)
W3^{i}—Sb1—W2	119.801 (5)	O15—Na4—O13	81.40 (6)
W3—Sb1—W3^{i}	180.0	O15—Na4—O14	83.06 (6)
O1—Sb1—W1	139.17 (4)	O15—Na4—O18	95.30 (6)
O1—Sb1—W1^{i}	40.83 (4)	O16—Na4—Na3	91.62 (6)
O1^{i}—Sb1—W1	40.83 (4)	O16—Na4—O13	92.36 (7)
O1^{i}—Sb1—W1^{i}	139.17 (4)	O16—Na4—O14	93.13 (7)
O1—Sb1—W2	138.80 (4)	O16—Na4—O15	173.08 (7)
O1^{i}—Sb1—W2^{i}	138.80 (3)	O16—Na4—O17	91.86 (7)
O1—Sb1—W2^{i}	41.20 (4)	O16—Na4—O18	91.03 (7)
O1^{i}—Sb1—W2	41.19 (3)	O17—Na4—Na3	45.83 (4)
O1—Sb1—W3^{i}	90.19 (4)	O17—Na4—O13	89.02 (6)
O1^{i}—Sb1—W3^{i}	89.82 (4)	O17—Na4—O14	169.82 (6)
O1^{i}—Sb1—W3	90.18 (4)	O17—Na4—O15	91.04 (6)
O1—Sb1—W3	89.81 (4)	O17—Na4—O18	89.07 (6)
O1—Sb1—O1^{i}	180.0	O18—Na4—Na3	43.24 (4)
O2^{i}—Sb1—W1	42.06 (4)	O18—Na4—O13	176.16 (6)
O2^{i}—Sb1—W1^{i}	137.94 (4)	O18—Na4—O14	99.71 (6)
O2—Sb1—W1	137.94 (4)	Na4—O13—H13	115.7 (19)
O2—Sb1—W1^{i}	42.06 (4)	C1—O13—Na4	123.74 (12)
O2—Sb1—W2	90.01 (4)	C1—O13—H13	109.0 (19)
O2^{i}—Sb1—W2	89.99 (4)	Na4—O14—H14	117 (3)
O2—Sb1—W2^{i}	89.99 (4)	C3—O14—Na4	129.46 (12)
O2^{i}—Sb1—W2^{i}	90.01 (4)	C3—O14—H14	106 (3)
O2^{i}—Sb1—W3^{i}	41.59 (4)	Na4—O15—H15A	121.8 (17)
O2—Sb1—W3^{i}	138.40 (4)	Na4—O15—H15B	132 (2)
O2^{i}—Sb1—W3	138.41 (4)	H15A—O15—H15B	102 (3)
O2—Sb1—W3	41.60 (4)	Na4—O16—H16A	126 (4)
O2^{i}—Sb1—O1	97.11 (5)	Na4—O16—H16B	129 (2)
O2^{i}—Sb1—O1^{i}	82.89 (5)	H16A—O16—H16B	104 (4)
O2—Sb1—O1	82.89 (5)	Na3—O17—H17A	121 (2)
O2—Sb1—O1^{i}	97.11 (5)	Na3—O17—H17B	104 (2)
O2—Sb1—O2^{i}	180.0	Na4—O17—Na3	90.46 (6)
O2^{i}—Sb1—O3^{i}	84.00 (5)	Na4—O17—H17A	121 (2)
O2^{i}—Sb1—O3	96.00 (5)	Na4—O17—H17B	120 (2)
O2—Sb1—O3	84.00 (5)	H17A—O17—H17B	101 (3)

O2—Sb1—O3^{i}	96.00 (5)	Na3—O18—Na4	92.96 (6)
O3—Sb1—W1^{i}	90.07 (4)	Na3—O18—H18A	117.0 (17)
O3—Sb1—W1	89.93 (4)	Na3—O18—H18B	127 (2)
O3^{i}—Sb1—W1^{i}	89.93 (4)	Na4—O18—H18A	111.3 (17)
O3^{i}—Sb1—W1	90.07 (4)	Na4—O18—H18B	106 (2)
O3^{i}—Sb1—W2	137.39 (4)	H18A—O18—H18B	101 (3)
O3—Sb1—W2	42.61 (4)	Na2—O19—H19A	130 (2)
O3—Sb1—W2^{i}	137.39 (4)	Na2—O19—H19B	104 (2)
O3^{i}—Sb1—W2^{i}	42.61 (4)	Na3—O19—Na2	94.82 (6)
O3—Sb1—W3	42.41 (3)	Na3—O19—H19A	109 (2)
O3—Sb1—W3^{i}	137.59 (3)	Na3—O19—H19B	121 (2)
O3^{i}—Sb1—W3^{i}	42.41 (3)	H19A—O19—H19B	101 (3)
O3^{i}—Sb1—W3	137.59 (4)	Na2—O20—H20A	130 (4)
O3^{i}—Sb1—O1	83.80 (5)	Na2—O20—H20B	126 (3)
O3^{i}—Sb1—O1^{i}	96.21 (5)	H20A—O20—H20B	104 (4)
O3—Sb1—O1^{i}	83.79 (5)	Na1—O21—Na2	89.63 (6)
O3—Sb1—O1	96.20 (5)	Na1—O21—H21A	104 (2)
O3—Sb1—O3^{i}	180.00 (6)	Na1—O21—H21B	103 (3)
W1^{i}—O1—W2^{i}	95.28 (5)	Na2—O21—H21A	132 (2)
Sb1—O1—W1^{i}	102.75 (5)	Na2—O21—H21B	109 (3)
Sb1—O1—W2^{i}	102.47 (5)	H21A—O21—H21B	113 (3)
W3—O2—W1^{i}	94.91 (5)	Na1—O22—H22A	131.2 (19)
Sb1—O2—W1^{i}	101.57 (5)	Na1—O22—H22B	125 (2)
Sb1—O2—W3	101.63 (5)	H22A—O22—H22B	95 (3)
W3—O3—W2	93.64 (5)	Na1—O23—H23A	109.8
Sb1—O3—W2	100.94 (5)	Na1—O23—H23B	109.3
Sb1—O3—W3	100.53 (5)	H23A—O23—H23B	104.3
W1—O6—W3^{i}	114.36 (6)	H1A—N1—H1B	109.5
W2—O8—W1	113.61 (6)	H1A—N1—H1C	109.5
W3—O10—W2	114.38 (6)	H1B—N1—H1C	109.5
O21—Na1—Na2	45.59 (4)	C2—N1—H1A	109.5
O21^{ii}—Na1—Na2	45.59 (4)	C2—N1—H1B	109.5
O21—Na1—O21^{ii}	91.19 (9)	C2—N1—H1C	109.5
O22—Na1—Na2	133.05 (5)	O13—C1—H1D	109.1
O22^{ii}—Na1—Na2	133.05 (5)	O13—C1—H1E	109.1
O22—Na1—O21	87.99 (6)	O13—C1—C2	112.67 (15)
O22^{ii}—Na1—O21^{ii}	87.99 (6)	H1D—C1—H1E	107.8
O22—Na1—O21^{ii}	172.04 (6)	C2—C1—H1D	109.1
O22^{ii}—Na1—O21	172.04 (6)	C2—C1—H1E	109.1
O22^{ii}—Na1—O22	93.90 (10)	N1—C2—C1	108.36 (15)
O22^{ii}—Na1—O23	84.0 (2)	N1—C2—H2	107.3
O22—Na1—O23	82.30 (18)	N1—C2—C3	110.62 (16)
O22—Na1—O23^{ii}	84.0 (2)	C1—C2—H2	107.3
O22^{ii}—Na1—O23^{ii}	82.30 (18)	C3—C2—C1	115.57 (17)
O22—Na1—O24^{ii}	97.9 (4)	C3—C2—H2	107.3
O22^{ii}—Na1—O24^{ii}	91.4 (3)	O14—C3—C2	112.56 (16)
O22—Na1—O24	91.4 (3)	O14—C3—H3A	109.1
O22^{ii}—Na1—O24	97.9 (4)	O14—C3—H3B	109.1

O23^{ii}—Na1—Na2	100.1 (2)	C2—C3—H3A	109.1
O23—Na1—Na2	100.1 (2)	C2—C3—H3B	109.1
O23—Na1—O21	103.9 (2)	H3A—C3—H3B	107.8
O23^{ii}—Na1—O21	90.22 (18)	Na1—O24—H24A	115.3
O23^{ii}—Na1—O23	159.8 (5)	Na1—O24—H24B	115.9
O24^{ii}—Na1—Na2	83.2 (5)	H24A—O24—H24B	104.5
Na4—O13—C1—C2	51.8 (2)	O13—C1—C2—C3	−80.5 (2)
Na4—O14—C3—C2	−31.5 (2)	N1—C2—C3—O14	−56.4 (2)
O13—C1—C2—N1	44.2 (2)	C1—C2—C3—O14	67.2 (2)

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