

# Crystal structure of disilver(I) dizinc(II) iron(III) tris(orthovanadate) with an alluaudite-type structure

Nour El Houda Lamsakhar,\* Mohammed Zriouil, Abderrazzak Assani, Mohamed Saadi and Lahcen El Ammari

Received 5 July 2018

Accepted 24 July 2018

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** crystal structure; transition metal vanadate; solid-state reaction; alluaudite structure type.; crystal structure.

**CCDC reference:** 1857879

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

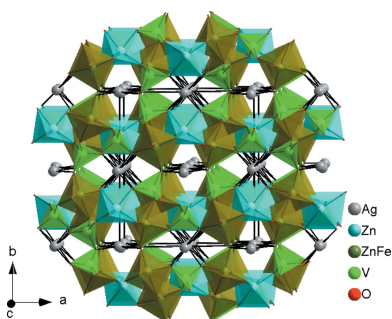
Laboratoire de Chimie Appliquée des Matériaux, Centre des Sciences des Matériaux, Faculty of Sciences, Mohammed V University in Rabat, Avenue Ibn Batouta, BP 1014, Rabat, Morocco. \*Correspondence e-mail: nlamsakhar@gmail.com

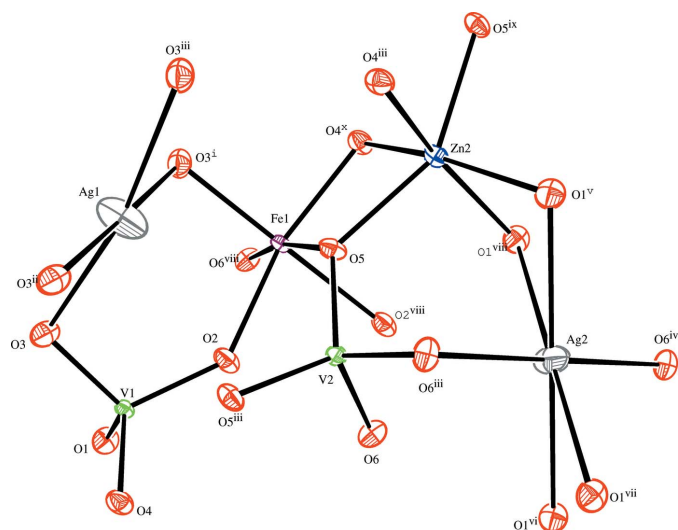
The title compound,  $\text{Ag}_2\text{Zn}_2\text{Fe}(\text{VO}_4)_3$ , has been synthesized by solid-state reactions and belongs to the alluaudite structure family. In the crystal structure, four sites are positioned at special positions. One silver site is located on an inversion centre (Wyckoff position  $4b$ ), and an additional silver site, as well as one zinc and one vanadium site, on twofold rotation axes ( $4e$ ). One site on a general position is statistically occupied by  $\text{Fe}^{\text{III}}$  and  $\text{Zn}^{\text{II}}$  cations that are octahedrally surrounded by O atoms. The three-dimensional framework structure of the title vanadate results from  $[(\text{Zn},\text{Fe})_2\text{O}_{10}]$  units of edge-sharing  $[(\text{Zn},\text{Fe})\text{O}_6]$  octahedra that alternate with  $[\text{ZnO}_6]$  octahedra so as to form infinite chains parallel to  $[10\bar{1}]$ . These chains are linked through  $\text{VO}_4$  tetrahedra by sharing vertices, giving rise to layers extending parallel to  $(010)$ . Such layers are shared by common vanadate tetrahedra. The resulting three-dimensional framework delimits two types of channels parallel to  $[001]$  in which the silver sites are located with four- and sixfold coordination by oxygen.

## 1. Chemical context

The crystal structure of the mineral alluaudite with general formula  $A(1)A(2)M(1)M(2)_2(X\text{O}_4)_3$  was determined nearly fifty years ago by Moore (1971). In the structure, the two  $A$  sites can be occupied by mono- or divalent cations of medium size, and the  $M(1)$  and  $M(2)$  sites can accommodate di- or trivalent cations, which are generally transition metals and are octahedrally surrounded. The specific feature of the alluaudite structure is the existence of two channels parallel to  $[001]$  in which the  $A$ -site cations are located. As a result, alluaudite-type compounds can exhibit electronic and/or ionic conductivity (Hatert, 2008). In addition, alluaudite-type compounds have been reported as materials for fossil energy conversion, as sensor materials and storage energy materials (Korzenski *et al.*, 1998), and as materials used in catalysis (Kacimi *et al.*, 2005).

Accordingly, the synthesis and structural characterization of new alluaudite-type phosphates and vanadates within pseudo-ternary  $A_2\text{O}/\text{MO}/\text{P}_2\text{O}_5$  or pseudo-quaternary  $A_2\text{O}/\text{MO}/\text{Fe}_2\text{O}_3/\text{P}_2\text{O}_5$  systems using hydrothermal or solid-state reactions was the focus of our current research. Obtained phases are, for example,  $\text{NaMg}_3(\text{HPO}_4)_2(\text{PO}_4)$  (Ould Saleck *et al.*, 2015),  $\text{Na}_2\text{Co}_2\text{Fe}(\text{PO}_4)_3$  (Bouraima *et al.*, 2015) or  $\text{Na}_{1.67}\text{Zn}_{1.67}\text{Fe}_{1.33}(\text{PO}_4)_3$  (Khmiyas *et al.*, 2015). We have also succeeded in preparing the first vanadate-based alluaudite-type phase  $(\text{Na}_{0.70})(\text{Na}_{0.70},\text{Mn}_{0.30})(\text{Fe}^{\text{III}},\text{Fe}^{\text{II}})_2\text{Fe}^{\text{II}}(\text{VO}_4)_3$  (Benhsina *et al.*,





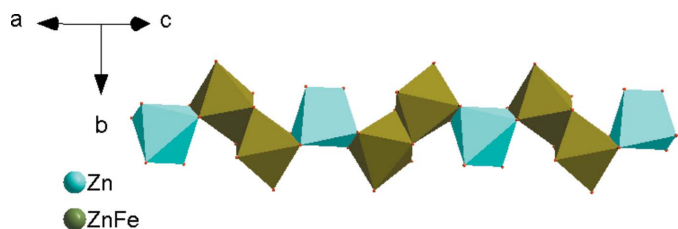
**Figure 1**  
The principal building units in the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $x, -y + 1, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $-x + 1, y, -z + \frac{3}{2}$ ; (iv)  $x, -y, z - \frac{1}{2}$ ; (v)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (vi)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (viii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (ix)  $-x + 1, y, -z + \frac{1}{2}$ ; (x)  $x, y, z - 1$ .]

2016). A second alluaudite-type vanadate with composition  $\text{Na}_2(\text{Fe}^{\text{III}}/\text{Co}^{\text{II}})_2\text{Co}^{\text{II}}(\text{VO}_4)_3$  was prepared by Hadouchi *et al.* (2016) shortly afterwards.

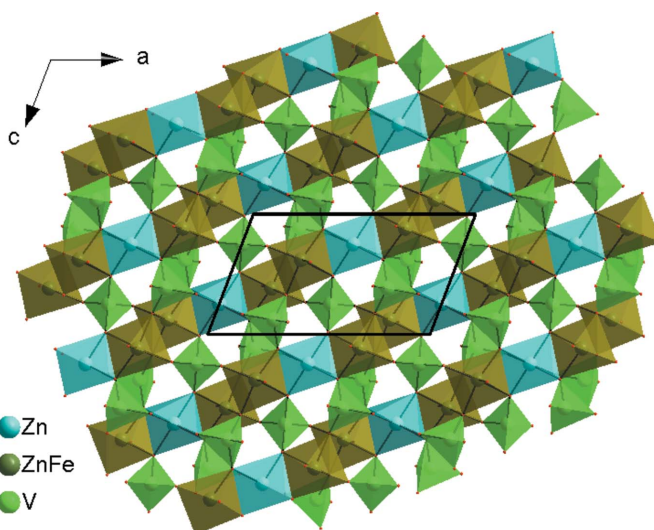
In this context, the current exploration of  $A_2\text{O}/\text{MO}/\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$  systems, where *A* is a monovalent cation and *M* a divalent cation, led to another vanadate with alluaudite-type structure, namely  $\text{Ag}_2\text{Zn}_2\text{Fe}(\text{VO}_4)_3$ . Its synthesis and crystal structure are reported in this article.

## 2. Structural commentary

The principal building units of the crystal structure of the new member of the alluaudite-type family are represented in Fig. 1. All atoms are in general positions except for four atoms that are located on special positions. Ag1 is located on an inversion centre (Wyckoff position 4*b*), and Ag2 as well as Zn2 and V2 are located on twofold rotation axes (4*e*) of space group  $C2/c$ . The M2 site is in a general position (8*f*) and statistically occupied by Fe1 and Zn1 atoms that are octahedrally surrounded by O atoms. Such a partial cationic disorder was



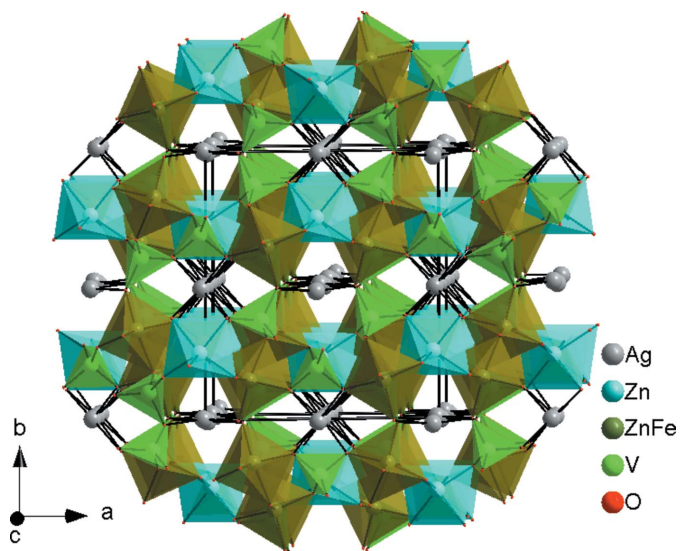
**Figure 2**  
Edge-sharing  $[(\text{Zn},\text{Fe})\text{1O}_6]$  and  $[\text{Zn}_2\text{O}_6]$  octahedra forming a kinked chain running parallel to  $[10\bar{1}]$ .



**Figure 3**  
A layer perpendicular to (010), resulting from the connection of chains via the vertices of  $\text{VO}_4$  tetrahedra and  $[\text{ZnO}_6]$  octahedra.

also reported for the cobalt homologue  $\text{Na}_2(\text{Fe}^{\text{III}}/\text{Co}^{\text{II}})_2\text{Co}^{\text{II}}(\text{VO}_4)_3$  (Hadouchi *et al.*, 2016).

The crystal structure of  $\text{Ag}_2\text{Zn}_2\text{Fe}(\text{VO}_4)_3$  is made up from  $[(\text{Zn},\text{Fe})\text{1}_2\text{O}_{10}]$  dimers, resulting from edge-sharing  $[(\text{Zn},\text{Fe})\text{1O}_6]$  octahedra, that are connected by a common edge to  $[\text{Zn}_2\text{O}_6]$  octahedra. The linkage of alternating  $[(\text{Zn},\text{Fe})\text{1}_2\text{O}_{10}]$  and  $[\text{Zn}_2\text{O}_6]$  units leads to infinite zigzag chains along  $[10\bar{1}]$  (Fig. 2). These chains are linked via the vertices of  $\text{VO}_4$  tetrahedra into layers parallel to (010), as shown in Fig. 3. Adjacent layers are linked by  $\text{V1O}_4$  tetrahedra into a three-dimensional framework structure that delimits two types of channels in which the  $\text{Ag}^{\text{I}}$  cations reside (Fig. 4). The Ag1 site is located in one channel and is surrounded by



**Figure 4**  
Polyhedral representation of  $\text{Ag}_2\text{Zn}_2\text{Fe}(\text{VO}_4)_3$  showing the channels running parallel to the  $[001]$  direction.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	Ag <sub>2</sub> Zn <sub>2</sub> Fe(VO <sub>4</sub> ) <sub>3</sub>
<i>M<sub>r</sub></i>	747.15
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.8025 (2), 12.9133 (2), 6.8000 (1)
$\beta$ (°)	110.759 (1)
<i>V</i> (Å <sup>3</sup> )	969.10 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	13.09
Crystal size (mm)	0.31 × 0.26 × 0.20
Data collection	
Diffractometer	Bruker X8 <i>APEX</i>
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.596, 0.748
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	30791, 2662, 2437
<i>R<sub>int</sub></i>	0.042
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.869
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.021, 0.048, 1.13
No. of reflections	2662
No. of parameters	95
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.36, -2.41

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

four oxygen atoms, whereas the Ag<sub>2</sub> site in the second channel is surrounded by six oxygen atoms.

The calculated bond-valences sums (Brown & Altermatt, 1985) of the atoms in the structure are in the expected ranges for Ag<sup>I</sup>, Zn<sup>II</sup>, Fe<sup>III</sup> and V<sup>V</sup> and are as follows (values in valence units): Ag<sub>1</sub> (0.83), Ag<sub>2</sub> (1.11), Zn<sub>1</sub> (1.95), Zn<sub>2</sub> (2.20), Fe<sub>1</sub> (2.67), V<sub>1</sub> (4.98) and V<sub>2</sub> (4.93); values of oxygen atoms range between 1.90 and 2.01 valence units.

### 3. Database Survey

Over the last twenty years, many synthetic alluaudite-type phosphates, arsenates, sulfates and molybdates have been reported, such as NaMnFe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> used as the positive electrode in sodium and lithium batteries (Trad *et al.*, 2010; Kim *et al.*, 2014; Huang *et al.*, 2015), Na<sub>2.44</sub>Mn<sub>1.79</sub>(SO<sub>4</sub>)<sub>3</sub> used as a potential high-voltage cathode material (*ca* 4.4 V) for sodium batteries (Dwibedi *et al.*, 2015), K<sub>0.13</sub>Na<sub>3.87</sub>Mg(MoO<sub>4</sub>)<sub>3</sub> as a promising compound for developing new materials with high ionic conductivity (Ennajeh *et al.*, 2015), or NaZn<sub>3</sub>(AsO<sub>4</sub>)(AsO<sub>3</sub>OH)<sub>2</sub> (Đorđević *et al.*, 2015).

### 4. Synthesis and crystallization

Ag<sub>2</sub>Zn<sub>2</sub>Fe(VO<sub>4</sub>)<sub>3</sub> was prepared by a solid-state reaction. A stoichiometric amount of silver nitrate (AgNO<sub>3</sub>), zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and vanadium oxide (V<sub>2</sub>O<sub>5</sub>) was employed in the molar ratio Ag:

Zn:Fe:V = 2:2:1:3 and put into a platinum crucible. After different heat treatments at lower temperatures to remove water and other volatile gaseous products, the reaction mixture was melted at 1033 K for 30 minutes, followed by slow cooling with a 5 K h<sup>-1</sup> rate to room temperature. The resulting product contained parallelepipedic orange crystals corresponding to the studied title vanadate. In addition, small block-like crystals with poor quality and unidentified by X-ray powder diffraction were present.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The remaining maximum and minimum electron density peaks in the final Fourier map are 0.40 Å away from Fe<sub>1</sub> and 0.62 Å from Ag<sub>1</sub>, respectively. Due to charge neutrality, sites Zn<sub>1</sub> and Fe<sub>2</sub> were modelled as statistically occupied, assuming a trivalent oxidation state for the iron site.

### Acknowledgements

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements.

### Funding information

The authors thank Mohammed V University, Rabat, Morocco, for financial support.

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## supporting information

*Acta Cryst.* (2018). E74, 1155-1158 [https://doi.org/10.1107/S205698901801071X]

## Crystal structure of disilver(I) dizinc(II) iron(III) tris(orthovanadate) with an alluaudite-type structure

Nour El Houda Lamsakhar, Mohammed Zriouil, Abderrazzak Assani, Mohamed Saadi and Lahcen El Ammari

### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *S SAINT* (Bruker, 2014); data reduction: *S SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Disilver(I) dizinc(II) iron(III) tris(orthovanadate)

#### Crystal data

$\text{Ag}_2\text{Zn}_2\text{Fe}(\text{VO}_4)_3$   
 $M_r = 747.15$   
 Monoclinic, *C2/c*  
 $a = 11.8025$  (2) Å  
 $b = 12.9133$  (2) Å  
 $c = 6.8000$  (1) Å  
 $\beta = 110.759$  (1)°  
 $V = 969.10$  (3) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 1380$   
 $D_x = 5.121$  Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2662 reflections  
 $\theta = 2.4\text{--}38.1^\circ$   
 $\mu = 13.09$  mm<sup>-1</sup>  
 $T = 296$  K  
 Parallelepiped, orange  
 0.31 × 0.26 × 0.20 mm

#### Data collection

Bruker X8 APEX  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Krause *et al.*, 2015)  
 $T_{\min} = 0.596$ ,  $T_{\max} = 0.748$

30791 measured reflections  
 2662 independent reflections  
 2437 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.042$   
 $\theta_{\max} = 38.1^\circ$ ,  $\theta_{\min} = 2.4^\circ$   
 $h = -18 \rightarrow 20$   
 $k = -22 \rightarrow 22$   
 $l = -11 \rightarrow 9$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.048$   
 $S = 1.13$   
 2662 reflections  
 95 parameters

0 restraints  
 $w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 4.2342P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -2.41$  e Å<sup>-3</sup>

Extinction correction: SHELXL2016  
(Sheldrick, 2015b),  
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.00163 (6)

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$	Occ. (<1)
Ag1	0.500000	0.49090 (3)	0.750000	0.02736 (7)	
Ag2	0.500000	0.000000	0.500000	0.02115 (6)	
Zn2	0.500000	0.23529 (2)	0.250000	0.00945 (6)	
Zn1	0.29222 (2)	0.34062 (2)	0.38041 (3)	0.00652 (5)	0.5
Fe1	0.29222 (2)	0.34062 (2)	0.38041 (3)	0.00652 (5)	0.5
V1	0.27045 (3)	0.38683 (2)	0.88206 (4)	0.00612 (5)	
V2	0.500000	0.20643 (3)	0.750000	0.00602 (6)	
O1	0.12116 (12)	0.39616 (11)	0.8338 (2)	0.0128 (2)	
O2	0.28524 (13)	0.31700 (11)	0.6746 (2)	0.0124 (2)	
O3	0.33803 (14)	0.50767 (11)	0.8997 (2)	0.0139 (2)	
O4	0.33926 (12)	0.32576 (11)	1.1233 (2)	0.0112 (2)	
O5	0.46319 (12)	0.27705 (11)	0.5152 (2)	0.0099 (2)	
O6	0.38484 (12)	0.12416 (10)	0.7343 (2)	0.0115 (2)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ag1	0.01209 (9)	0.05204 (18)	0.01674 (11)	0.000	0.00362 (8)	0.000
Ag2	0.03519 (13)	0.01557 (9)	0.01224 (9)	-0.01110 (8)	0.00786 (9)	-0.00296 (7)
Zn2	0.00905 (11)	0.01104 (12)	0.00942 (12)	0.000	0.00472 (9)	0.000
Zn1	0.00607 (8)	0.00863 (9)	0.00535 (9)	0.00074 (6)	0.00264 (6)	0.00062 (6)
Fe1	0.00607 (8)	0.00863 (9)	0.00535 (9)	0.00074 (6)	0.00264 (6)	0.00062 (6)
V1	0.00655 (10)	0.00709 (10)	0.00474 (10)	0.00040 (8)	0.00202 (8)	0.00021 (8)
V2	0.00649 (14)	0.00644 (14)	0.00448 (14)	0.000	0.00112 (11)	0.000
O1	0.0095 (5)	0.0130 (5)	0.0160 (6)	0.0017 (4)	0.0045 (5)	0.0008 (5)
O2	0.0140 (6)	0.0155 (6)	0.0082 (5)	0.0017 (5)	0.0046 (4)	-0.0004 (4)
O3	0.0149 (6)	0.0116 (5)	0.0158 (6)	-0.0010 (4)	0.0061 (5)	0.0017 (5)
O4	0.0123 (5)	0.0133 (5)	0.0078 (5)	0.0037 (4)	0.0034 (4)	0.0019 (4)
O5	0.0090 (5)	0.0135 (5)	0.0075 (5)	0.0019 (4)	0.0035 (4)	0.0027 (4)
O6	0.0087 (5)	0.0103 (5)	0.0136 (6)	-0.0007 (4)	0.0019 (4)	0.0016 (4)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Ag1—O3 <sup>i</sup>	2.4699 (15)	Zn2—O1 <sup>v</sup>	2.1619 (15)
Ag1—O3 <sup>ii</sup>	2.4699 (16)	Zn1—O6 <sup>viii</sup>	2.0068 (14)

Ag1—O3 <sup>iii</sup>	2.4734 (16)	Zn1—O4 <sup>x</sup>	2.0222 (14)
Ag1—O3	2.4734 (16)	Zn1—O3 <sup>i</sup>	2.0241 (15)
Ag2—O6 <sup>iv</sup>	2.4374 (14)	Zn1—O2	2.0540 (14)
Ag2—O6 <sup>iii</sup>	2.4374 (14)	Zn1—O5	2.0675 (13)
Ag2—O1 <sup>v</sup>	2.5032 (15)	Zn1—O2 <sup>viii</sup>	2.2082 (15)
Ag2—O1 <sup>vi</sup>	2.5032 (15)	V1—O1	1.6784 (14)
Ag2—O1 <sup>vii</sup>	2.5873 (14)	V1—O2	1.7343 (14)
Ag2—O1 <sup>viii</sup>	2.5873 (14)	V1—O3	1.7372 (15)
Zn2—O5 <sup>ix</sup>	2.0704 (14)	V1—O4	1.7402 (13)
Zn2—O5	2.0705 (14)	V2—O6	1.6984 (14)
Zn2—O4 <sup>iii</sup>	2.1325 (13)	V2—O6 <sup>iii</sup>	1.6984 (14)
Zn2—O4 <sup>x</sup>	2.1325 (13)	V2—O5 <sup>iii</sup>	1.7544 (13)
Zn2—O1 <sup>viii</sup>	2.1619 (15)	V2—O5	1.7544 (13)
O3 <sup>i</sup> —Ag1—O3 <sup>ii</sup>	179.15 (7)	O5—Zn2—O1 <sup>v</sup>	107.36 (5)
O3 <sup>i</sup> —Ag1—O3 <sup>iii</sup>	92.83 (5)	O4 <sup>iii</sup> —Zn2—O1 <sup>v</sup>	85.01 (5)
O3 <sup>ii</sup> —Ag1—O3 <sup>iii</sup>	87.10 (5)	O4 <sup>x</sup> —Zn2—O1 <sup>v</sup>	161.31 (5)
O3 <sup>i</sup> —Ag1—O3	87.10 (5)	O1 <sup>viii</sup> —Zn2—O1 <sup>v</sup>	76.52 (7)
O3 <sup>ii</sup> —Ag1—O3	92.83 (5)	O6 <sup>viii</sup> —Zn1—O4 <sup>x</sup>	104.63 (6)
O3 <sup>iii</sup> —Ag1—O3	169.95 (7)	O6 <sup>viii</sup> —Zn1—O3 <sup>i</sup>	91.33 (6)
O6 <sup>iv</sup> —Ag2—O6 <sup>iii</sup>	180.00 (6)	O4 <sup>x</sup> —Zn1—O3 <sup>i</sup>	89.94 (6)
O6 <sup>iv</sup> —Ag2—O1 <sup>v</sup>	105.99 (5)	O6 <sup>viii</sup> —Zn1—O2	90.95 (6)
O6 <sup>iii</sup> —Ag2—O1 <sup>v</sup>	74.01 (5)	O4 <sup>x</sup> —Zn1—O2	161.09 (6)
O6 <sup>iv</sup> —Ag2—O1 <sup>vi</sup>	74.01 (5)	O3 <sup>i</sup> —Zn1—O2	100.52 (6)
O6 <sup>iii</sup> —Ag2—O1 <sup>vi</sup>	105.99 (5)	O6 <sup>viii</sup> —Zn1—O5	168.70 (6)
O1 <sup>v</sup> —Ag2—O1 <sup>vi</sup>	180.00 (6)	O4 <sup>x</sup> —Zn1—O5	79.73 (5)
O6 <sup>iv</sup> —Ag2—O1 <sup>vii</sup>	107.39 (5)	O3 <sup>i</sup> —Zn1—O5	99.16 (6)
O6 <sup>iii</sup> —Ag2—O1 <sup>vii</sup>	72.61 (5)	O2—Zn1—O5	83.05 (5)
O1 <sup>v</sup> —Ag2—O1 <sup>vii</sup>	116.56 (6)	O6 <sup>viii</sup> —Zn1—O2 <sup>viii</sup>	80.30 (5)
O1 <sup>vi</sup> —Ag2—O1 <sup>vii</sup>	63.44 (6)	O4 <sup>x</sup> —Zn1—O2 <sup>viii</sup>	89.43 (5)
O6 <sup>iv</sup> —Ag2—O1 <sup>viii</sup>	72.61 (5)	O3 <sup>i</sup> —Zn1—O2 <sup>viii</sup>	171.16 (6)
O6 <sup>iii</sup> —Ag2—O1 <sup>viii</sup>	107.39 (5)	O2—Zn1—O2 <sup>viii</sup>	82.59 (6)
O1 <sup>v</sup> —Ag2—O1 <sup>viii</sup>	63.44 (6)	O5—Zn1—O2 <sup>viii</sup>	89.40 (5)
O1 <sup>vi</sup> —Ag2—O1 <sup>viii</sup>	116.56 (6)	O1—V1—O2	106.24 (7)
O1 <sup>vii</sup> —Ag2—O1 <sup>viii</sup>	180.0	O1—V1—O3	111.93 (7)
O5 <sup>ix</sup> —Zn2—O5	149.81 (8)	O2—V1—O3	110.32 (7)
O5 <sup>ix</sup> —Zn2—O4 <sup>iii</sup>	77.17 (5)	O1—V1—O4	108.88 (7)
O5—Zn2—O4 <sup>iii</sup>	86.37 (5)	O2—V1—O4	112.54 (7)
O5 <sup>ix</sup> —Zn2—O4 <sup>x</sup>	86.37 (5)	O3—V1—O4	107.01 (7)
O5—Zn2—O4 <sup>x</sup>	77.17 (5)	O6—V2—O6 <sup>iii</sup>	102.56 (10)
O4 <sup>iii</sup> —Zn2—O4 <sup>x</sup>	113.56 (8)	O6—V2—O5 <sup>iii</sup>	108.46 (7)
O5 <sup>ix</sup> —Zn2—O1 <sup>viii</sup>	107.36 (5)	O6 <sup>iii</sup> —V2—O5 <sup>iii</sup>	109.48 (6)
O5—Zn2—O1 <sup>viii</sup>	96.35 (6)	O6—V2—O5	109.48 (6)
O4 <sup>iii</sup> —Zn2—O1 <sup>viii</sup>	161.31 (5)	O6 <sup>iii</sup> —V2—O5	108.47 (7)

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$O4^x-Zn2-O1^{viii}$	85.01 (5)	$O5^{iii}-V2-O5$	117.36 (9)
$O5^{ix}-Zn2-O1^v$	96.35 (6)		

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