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$K_2V_2O_2(AsO_4)_2$

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Key indicators: single-crystal X-ray study; T = 150 K; mean σ(As–O) = 0.002 Å; R factor = 0.028; wR factor = 0.034; data-to-parameter ratio = 30.0.

The vanadium oxide arsenate with formula $K_2V_2O_2(AsO_4)_2$, dipotassium divanadium(IV) dioxide diarsenate, has been synthesized by solid-state reaction in an evacuated silica ampoule. Its structure is isotypic with $K_2V_2O_2(PO_4)_2$. The framework is built up from corner-sharing VO_6 octahedra and AsO_4 tetrahedra, creating an infinite $[VAsO_8]_\infty$ chain running along the a- and c-axis directions. The K^+ cations are located in hexagonal tunnels, which are delimited by the connection of the $[VAsO_8]_\infty$ chains.

Related literature

For the properties of the potassium titanyl phosphate $KTiOPO_4$ (KTP) family, see: El Haidouri *et al.* (1990); Harrison & Phillips (1999); Phillips *et al.* (1990). For the structures of $AMOXO_4$ compounds (A = K, Na, Li, M = transition metal and X = P, As) of the KTP family, see: Phillips *et al.* (1990); Harrison & Phillips (1999); El Haidouri *et al.* (1990). For the synthesis of $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$, see: Belkhiri *et al.* (2009). For the synthesis and structure of isotypic $K_2V_2O_2(PO_4)_2$, see: Benhamada *et al.* (1991). For the effect on the electron transport properties caused by the distortion of the $V^{IV}O_6$ octahedra, see: El Haidouri *et al.* (1990); El Brahimi & Durand (1986); Nakagawa *et al.* (1999). For the hexagonal tungsten bronze structure, see: Magnéli (1953).

Experimental

Crystal data

$K_2V_2O_2(AsO_4)_2$
M_r = 489.9
Orthorhombic, $Pc2_1n$
a = 6.5368 (2) Å
b = 10.7228 (5) Å
c = 13.0666 (4) Å
V = 915.87 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.16 mm^{-1}
T = 150 K
0.30 × 0.25 × 0.22 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.073, T_{max} = 0.107
11866 measured reflections
4169 independent reflections
3805 reflections with $I > 3\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.034
S = 1.60
4169 reflections
139 parameters
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), 1256 Friedel pairs
Flack parameter: 0.387 (8)

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SuperFlip* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *ATOMS* (Dowty, 1994) and *GRETEP* (Laugier & Bochu, 2002); software used to prepare material for publication: *JANA2006*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2035).

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supplementary materials

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$K_2V_2O_2(AsO_4)_2$

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Comment

The compounds belonging to the potassium titanyl phosphate $KTiOPO_4$ (KTP) family have been widely studied for their outstanding non linear optical property (NLO)(Phillips *et al.*, 1990; Harrison *et al.*, 1999; El Haidouri *et al.*, 1990).

These materials are characterized by their high laser damage threshold, high electrooptic coefficient and an excellent thermal stability (Phillips *et al.*, 1990; Harrison *et al.*, 1999; El Haidouri *et al.*, 1990)).

The KTP compound is generaly used in a laser system such as second harmonic generation (SGH) for doubling laser light for example in the Nd Yag laser equipement.

The framework of $AMOXO_4$ (A: K, Na, Li..), (*M*: tansition metal) and (*X*: P, As) is built up from MO_6 octahedra and AsO_4 tetrahedra sharing their corners.

The structure of $AMOXO_4$ of KTP family shows an irregular octahedra MO_6 with one short bond (1.653 (5) Å to 1.851 (5) Å)) (Phillips *et al.*, 1990; Harrison *et al.*, 1999; El Haidouri *et al.*, 1990). In two years later we synthetized a new compound $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ (Belkhiri *et al.*, 2009) of KTP family, It presents an irregular MO_6 octahedra with (*M*=V+W). The MO_6 polyhedra consist of two abnormal short bonds M—O (1.774 (7) Å) and(1.824 (8) Å) which suggest that the NLO property could be more important in this compound, because the most physical related to structural studies showed that the non linear optical property is due to the short bond in the octahedral polyhedra.

We are interested on $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ for these two short bonds, we substituted the tungsten by the vanadium element in order to show the influence of the tungsten and vanadium on the distortion of the MO_6 octahedra.

We synthetized and studied the structure of new single-crystal $K_2V_2O_2(AsO_4)_2$ isotype to $KVOPO_4$ (Benhamada *et al.*, 1991), we describe here the structure of $K_2V_2O_2(AsO_4)_2$.

The framework $[VAsO_5]_\infty$ is built up from single VO_6 octahedra sharing corners with AsO_4 tetrahedra. The projection of $K_2V_2O_2(AsO_4)_2$ structure along *a* and *c* directions (Fig. 1) and (Fig. 2) respectively shows the existence of infinite $[VAsO_8]_\infty$ chains running along *a* and *c* directions.

Two infinite $[VAsO_8]_\infty$ chains oriented along *a* are linked *via* infinite $[VAsO_8]_\infty$ chains running along *c* and *vice versa*. The AsO_4 tetrahedra share their corners with four VO_6 octahedra, and the VO_6 octahedra share their corners with four AsO_4 tetrahedra and two VO_6 octahedra.

This arrangement creates an octahedral infinite $[VO_3]_\infty$ chains running along [011] direction (Fig. 3) and (Fig. 4). The existence of one dimensional octahedral infinite $[VO_3]_\infty$ chains pretends the possibility of electronic transport properties. These properties can be accentuated by the distortion of the octahedral polyhedra occupied by V(IV) with the d1 configuration (El Haidouri *et al.*, 1990; Nakagawa *et al.*, 1999; El Brahimi & Durand, 1986).

The framework $[VAsO_5]_\infty$ delimits two sorts of hexagonal tunnels running along *a* and *c* directions, where the potassium ions are located. The first tunnel (Fig. 1) results from junction of three VO_6 octahedra and three AsO_4 tetrahedra linked by their corners. Whereas the second type of tunnel (Fig. 2) is formed of rings of four VO_6 octahedra and two AsO_4 tetrahedra linked by their corners.

The great similarity of the framework $[VAsO_5]_\infty$ with hexagonal tungsten bronze structure (HTB) described by Magnéli (1953) concerns necessary the hexagonal tunnel which can be deduced from HTB tunnels by replacing two octahedra out of six in an ordered way by two AsO_4 tetrahedra (Fig. 5).

As a result, the remplacement of tungsten by the vanadium element in the structure of $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ led to irregular octahedra VO_6 with one short (1.6551 (18) Å) and one long bond V—O (2.2301 (18) Å). Whereas in the case of $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$, the presence of the tungsten element in MO_6 with (*M*=V+W) creates an irregular octahedra MO_6 with two short bonds M—O (1.774 (7) Å) and(1.824 (8) Å).

The comparaison between the MO_6 octahedra of $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ and VO_6 octahedra of $K_2V_2O_2(AsO_4)_2$ (Fig. 6) shows clearly that the distortion is more important in MO_6 than in VO_6 due to the mixed occupation of the MO_6 by the tungsten and vanadium simultaneously. Furthermore the mixed occupation creates two short bonds which can have an impact on the non linear optical property.

Among our perspectives is to realise the non linear optical property for $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ and $K_2V_2O_2(AsO_4)_2$ and to show the influence of the vanadium and the tungsten on the second harmonic generation.

Experimental

The growth of the single-crystal $K_2V_2O_2(AsO_4)_2$ was performed in two steps: firstly, the stoechiometric mixture of K_2CO_3, V_2O_5, and As_2O_5 was heated in platinium crucible for 24 h at 573 K in order to decompose the potassium carbonate. Secondly the appropriate amount of vanadium was added into the mixture and then heated at 973 K for 7 days in evacuated silica ampoule. From the resulting mixture some dark single crystals were extracted.

Refinement

Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > n*\sigma(F^2)$ is used only for calculating *R*-factors *etc*. and is not relevant to the choice of reflections for refinement.

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: (*SuperFlip* Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *ATOMS* (Dowty, 1994) and GRETEP (Laugier & Bochu, 2002); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2006).

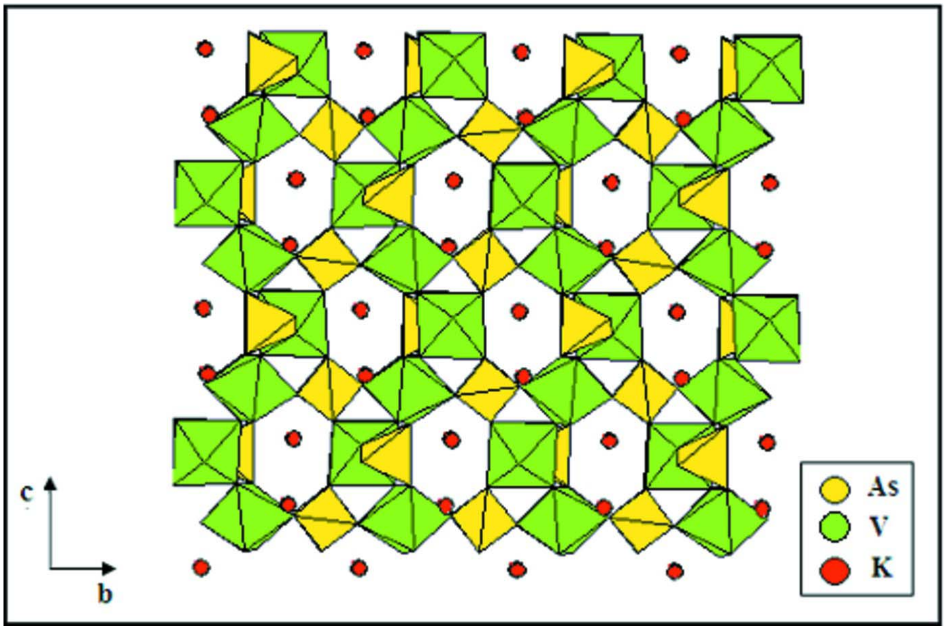

Figure 1

The projection of $K_2V_2O_2(AsO_4)_2$ along *a*.

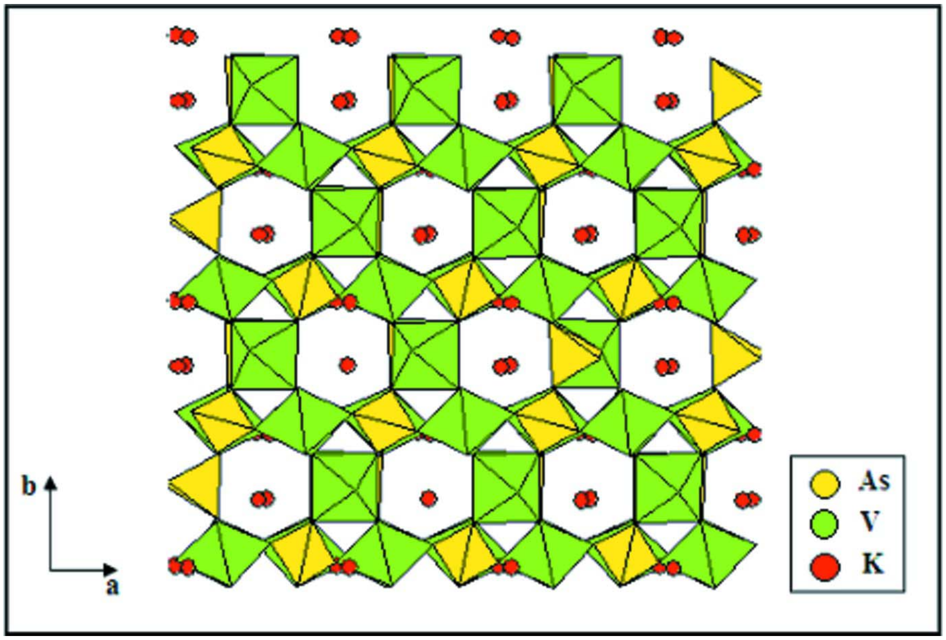

Figure 2

The projection of $K_2V_2O_2(AsO_4)_2$ along *c*.

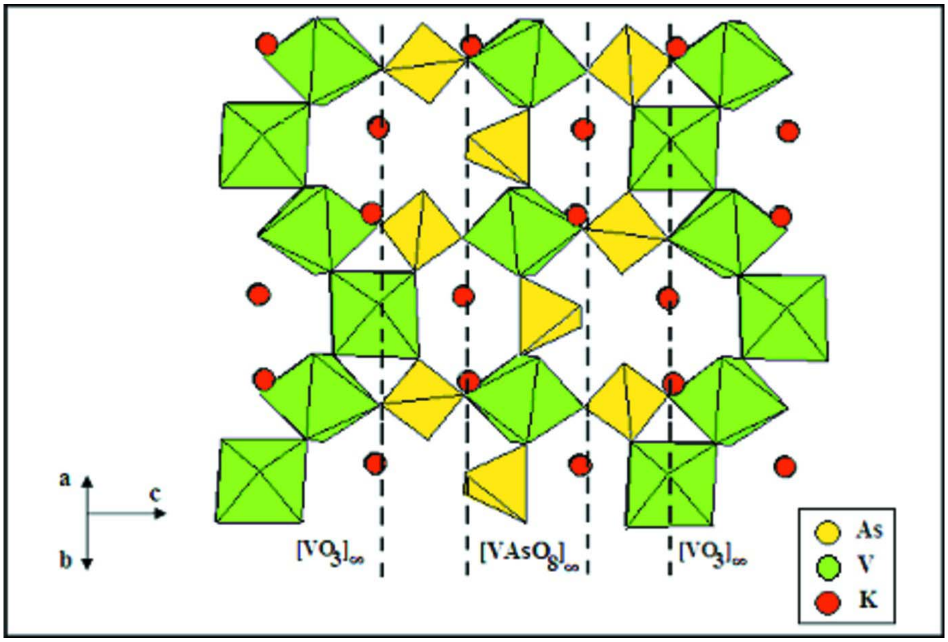

Figure 3

The projection of $K_2V_2O_2(AsO_4)_2$ along (011).

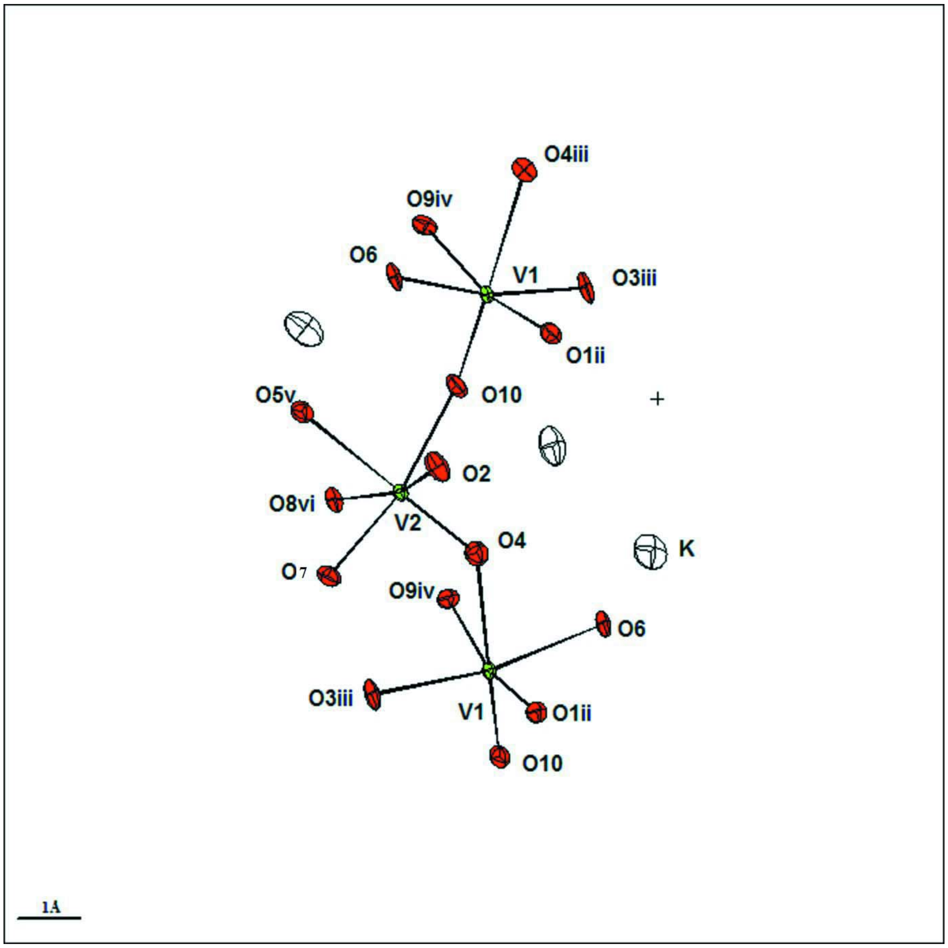

Figure 4

octahedral infinite $[VO_3]_\infty$ chains running along [011] direction with [Symmetry codes: (i) ?*x* + 1/2, *y*, *z*?1/2; (ii) *x* + 1, *y*, *z*; (iii) ?*x* + 1/2, *y*, *z* + 1/2; (iv) ?*x* + 1, *y* + 1/2, ?*z*; (v) ?*x* + 1, *y*?1/2, ?*z*; (vi) *x*?1, *y*, *z*].

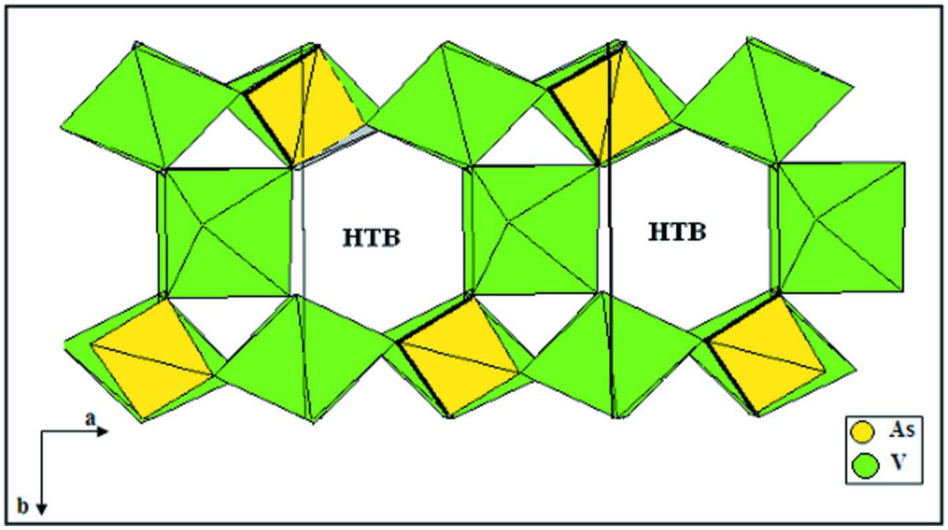

Figure 5

The comparison between $K_2V_2O_2(AsO_4)_2$ and HTB structures.

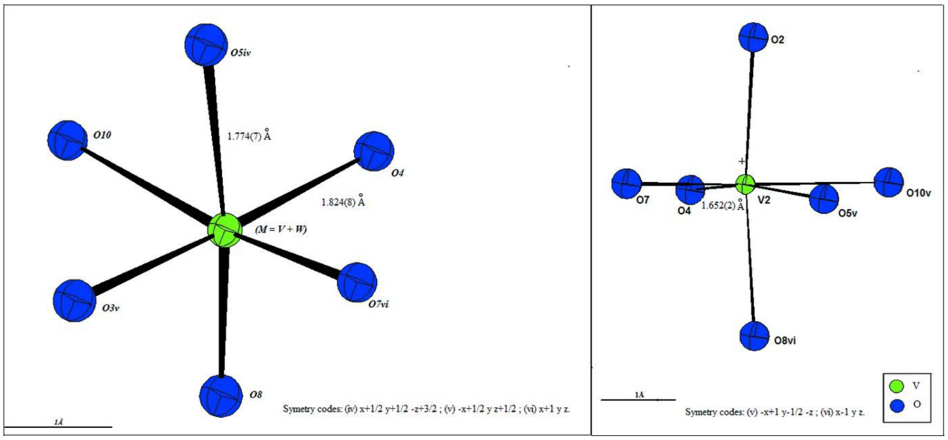

Figure 6

MO_6 and VO_6 octahedra of $K_{1.65}V_{1.78}W_{0.22}O_2(AsO_4)_2$ and $K_2V_2O_2(AsO_4)_2$ respectively.

dipotassium divanadium dioxide diarsenate

Crystal data

$K_2V_2O_2(AsO_4)_2$
$M_r = 489.9$
Orthorhombic, $Pc2_1n$
Hall symbol: P -2n -2ac
$a = 6.5368$ (2) Å
$b = 10.7228$ (5) Å
$c = 13.0666$ (4) Å
$V = 915.87$ (6) Å^3
$Z = 4$
$F(000) = 920$
$D_x = 3.552$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 5952 reflections
$\theta = 3.5$–$40.2°$
$\mu = 10.16$ mm^{-1}
$T = 150$ K
Prism, black
0.3 × 0.25 × 0.22 mm

Data collection

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD rotation images, thin slices scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.073$, $T_{\max} = 0.107$
11866 measured reflections
4169 independent reflections
3805 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 40.2°$, $\theta_{\min} = 3.5°$
$h = -23 \rightarrow 23$
$k = -11 \rightarrow 10$
$l = -19 \rightarrow 15$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.034$
$S = 1.60$
4169 reflections
139 parameters
0 restraints
0 constraints
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(F) + 0.000049F^2)$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.77$ e Å^{-3}
Extinction correction: B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 970 (110)
Absolute structure: Flack (1983), 1256 Friedel pairs
Flack parameter: 0.387 (8)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
As2	0.99887 (4)	0.333103	−0.18131 (2)	0.00293 (5)
V1	0.27644 (5)	0.59847 (6)	0.25107 (3)	0.00255 (8)
V2	0.49984 (6)	0.34895 (5)	−0.12277 (3)	0.00271 (8)
K1	−0.22511 (9)	0.53150 (8)	0.12103 (6)	0.01172 (15)
K2	0.79227 (10)	0.77688 (8)	−0.10496 (5)	0.01127 (15)
O1	−0.5484 (3)	0.4499 (2)	0.23637 (18)	0.0058 (5)
O2	0.7996 (3)	0.3653 (2)	−0.10470 (17)	0.0060 (3)
O3	0.1652 (3)	0.6001 (3)	−0.09922 (15)	0.0060 (4)
O4	0.4565 (3)	0.4521 (2)	−0.21415 (18)	0.0060 (5)
O5	0.4859 (3)	0.7051 (2)	0.01550 (19)	0.0061 (5)
O6	0.1747 (3)	0.5671 (2)	0.10771 (16)	0.0053 (4)
O7	0.4687 (4)	0.4564 (2)	−0.00520 (17)	0.0063 (5)
O8	1.2015 (3)	0.2971 (2)	−0.10749 (17)	0.0060 (3)
O9	0.9597 (3)	0.2103 (2)	−0.26290 (18)	0.0062 (5)
O10	0.4516 (3)	0.7042 (2)	0.22272 (18)	0.0061 (5)
As1	0.32206 (3)	0.58763 (5)	0.00215 (2)	0.00258 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As2	0.00216 (8)	0.00404 (10)	0.00258 (10)	−0.00032 (7)	−0.00002 (9)	0.00035 (10)
V1	0.00278 (13)	0.00322 (15)	0.00164 (15)	0.00008 (15)	0.00028 (13)	0.00010 (14)
V2	0.00261 (13)	0.00336 (17)	0.00216 (15)	0.00019 (13)	−0.00004 (13)	0.00031 (14)
K1	0.0052 (2)	0.0156 (3)	0.0144 (3)	−0.0015 (2)	−0.0016 (2)	0.0047 (3)
K2	0.0104 (2)	0.0171 (3)	0.0063 (2)	−0.0012 (2)	0.00160 (19)	−0.0001 (3)
O1	0.0065 (7)	0.0053 (8)	0.0057 (9)	0.0026 (6)	0.0020 (7)	0.0030 (7)
O2	0.0028 (4)	0.0093 (5)	0.0060 (5)	−0.0001 (4)	−0.0006 (5)	0.0005 (6)
O3	0.0046 (6)	0.0114 (9)	0.0020 (7)	0.0014 (7)	−0.0015 (5)	0.0004 (8)
O4	0.0046 (7)	0.0073 (8)	0.0063 (9)	0.0009 (6)	−0.0009 (6)	0.0011 (7)
O5	0.0062 (8)	0.0071 (8)	0.0049 (9)	−0.0031 (7)	0.0010 (6)	−0.0017 (7)
O6	0.0044 (7)	0.0088 (9)	0.0026 (7)	0.0013 (6)	0.0005 (6)	0.0012 (7)
O7	0.0069 (8)	0.0079 (8)	0.0043 (9)	0.0035 (7)	−0.0020 (6)	−0.0017 (7)
O8	0.0028 (4)	0.0093 (5)	0.0060 (5)	−0.0001 (4)	−0.0006 (5)	0.0005 (6)
O9	0.0066 (7)	0.0067 (8)	0.0052 (9)	−0.0025 (7)	0.0018 (7)	−0.0018 (8)
O10	0.0075 (8)	0.0070 (8)	0.0039 (8)	−0.0012 (7)	0.0011 (7)	0.0012 (7)
As1	0.00244 (8)	0.00385 (9)	0.00144 (9)	−0.00024 (9)	−0.00003 (8)	−0.00044 (9)

Geometric parameters (Å, º)

As2—O1^{i}	1.682 (2)	V2—O2	1.9811 (19)
As2—O2	1.679 (2)	V2—O4	1.652 (2)
As2—O8	1.684 (2)	V2—O5^{v}	2.087 (2)
As2—O9	1.714 (2)	V2—O7	1.931 (2)
V1—O1^{ii}	1.971 (2)	V2—O8^{vi}	2.0375 (19)
V1—O3^{iii}	1.993 (2)	V2—O10^{v}	2.053 (2)
V1—O4^{iii}	2.234 (2)	O3—As1	1.6805 (19)
V1—O6	2.016 (2)	O5—As1	1.662 (2)

V1—O9^{iv}	1.960 (2)	O6—As1	1.697 (2)
V1—O10	1.654 (2)	O7—As1	1.705 (2)

O1^{i}—As2—O2	112.20 (11)	O4—V2—O5^{v}	171.20 (10)
O1^{i}—As2—O8	112.68 (10)	O4—V2—O7	99.06 (11)
O1^{i}—As2—O9	101.71 (11)	O4—V2—O8^{vi}	95.14 (10)
O2—As2—O8	108.44 (10)	O4—V2—O10^{v}	94.17 (10)
O2—As2—O9	114.38 (10)	O5^{v}—V2—O7	84.92 (10)
O8—As2—O9	107.32 (11)	O5^{v}—V2—O8^{vi}	77.00 (9)
O1^{ii}—V1—O3^{iii}	89.52 (10)	O5^{v}—V2—O10^{v}	82.04 (9)
O1^{ii}—V1—O4^{iii}	81.24 (9)	O7—V2—O8^{vi}	89.08 (10)
O1^{ii}—V1—O6	88.06 (9)	O7—V2—O10^{v}	166.76 (10)
O1^{ii}—V1—O9^{iv}	163.57 (9)	O8^{vi}—V2—O10^{v}	90.22 (9)
O1^{ii}—V1—O10	97.49 (10)	As2^{iii}—O1—V1^{vi}	130.63 (13)
O3^{iii}—V1—O4^{iii}	86.39 (9)	As2—O2—V2	132.71 (13)
O3^{iii}—V1—O6	167.57 (9)	V1^{i}—O3—As1	131.00 (10)
O3^{iii}—V1—O9^{iv}	93.90 (10)	V1^{i}—O4—V2	137.25 (13)
O3^{iii}—V1—O10	94.66 (11)	V2^{iv}—O5—As1	131.25 (13)
O4^{iii}—V1—O6	81.19 (9)	V1—O6—As1	123.11 (10)
O4^{iii}—V1—O9^{iv}	82.94 (9)	V2—O7—As1	126.62 (13)
O4^{iii}—V1—O10	178.35 (10)	As2—O8—V2^{ii}	129.37 (13)
O6—V1—O9^{iv}	85.16 (9)	As2—O9—V1^{v}	122.59 (12)
O6—V1—O10	97.74 (10)	V1—O10—V2^{iv}	140.17 (13)
O9^{iv}—V1—O10	98.24 (11)	O3—As1—O5	114.55 (12)
O2—V2—O4	101.33 (10)	O3—As1—O6	107.73 (9)
O2—V2—O5^{v}	86.62 (9)	O3—As1—O7	111.36 (12)
O2—V2—O7	87.53 (10)	O5—As1—O6	112.26 (11)
O2—V2—O8^{vi}	163.51 (9)	O5—As1—O7	105.60 (11)
O2—V2—O10^{v}	89.41 (9)	O6—As1—O7	104.94 (11)

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