New mixed aluminium–chromium diarsenate

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Potassium chromium aluminium diarsenate, $KCr_{1/4}Al_{3/4}As_2O_7$, was prepared by solid-state reaction. The structure consists of $(Cr_{1/4}/Al_{3/4})O_6$ octahedra and As_2O_7 diarsenate groups sharing corners to build up a three-dimensional anionic framework. The potassium cations are located in wide channels running along the c-axis direction. The crystal structure is isostructural with the triclinic $A^IM^{III}X_2O_7$ (A^I = alkali metal; M^{III} = Al, Cr, Fe; X = As, P) compounds. However, the M^{III} octahedrally coordinated site is 25% partially occupied by chromium and 75% by aluminium.

## 1. Chemical context

In recent years, inorganic metal phosphates/arsenates with formula $A^IM^{III}X_2O_7$ (A^I = alkali metal; M^{III} = Al, Cr, Fe; X = As, P) have been part of intensive research activities, with crystals grown either from high-temperature solid-state reactions or under aqueous solution conditions. The crystal chemistry of these compounds with X_2O_7 groups reveals a large structural variety accompanied in some cases by interesting magnetic, electric, optical, or thermal expansion properties. Focusing on compounds with M^{III} = Cr, it is noticeable that the corresponding diphosphates have been studied extensively, in contrast to the scarcely studied chromium diarsenates. The title structure is isostructural with the $A^ICr^{III}As_2O_7$ family; nevertheless, in this crystal structure some of the chromium ions are partly substituted by aluminium in an octahedrally coordinated site. Herein, the preparation and crystal structure of $KCr_{1/4}Al_{3/4}As_2O_7$ is reported. It is one of a series of new potassium chromium–aluminum diarsenate compounds recently isolated by our group.

2. Structural commentary

The structure of $KCr_{1/4}Al_{3/4}As_2O_7$ can be described as a three-dimensional framework of $[(Cr/Al)As_2O_7]^-$ anions built up from corner-sharing $(Cr/Al)O_6$ octahedra and As_2O_7 groups. The $(Cr/Al)O_6$ octahedron shares its six corners with five diarsenate groups while the As_2O_7 anion shares all of its six corners with five octahedra; the interconnection between the polyhedra results in centrosymmetric $(Cr/Al)As_2O_{11}$ units (Fig. 1). The framework can also be described as been formed by polyhedral parallel layers, as in many isoformular compounds, leaving empty channels running along the c axis in which the K^+ cations are located (Fig. 2).

In this structure, the aluminium Al^{III} and the chromium Cr^{III} cations share the same ($2i$) crystallographic site. These cations are surrounded by oxygen atoms in an octahedral
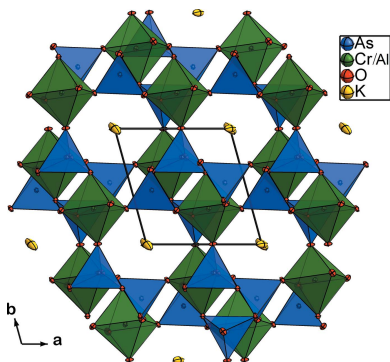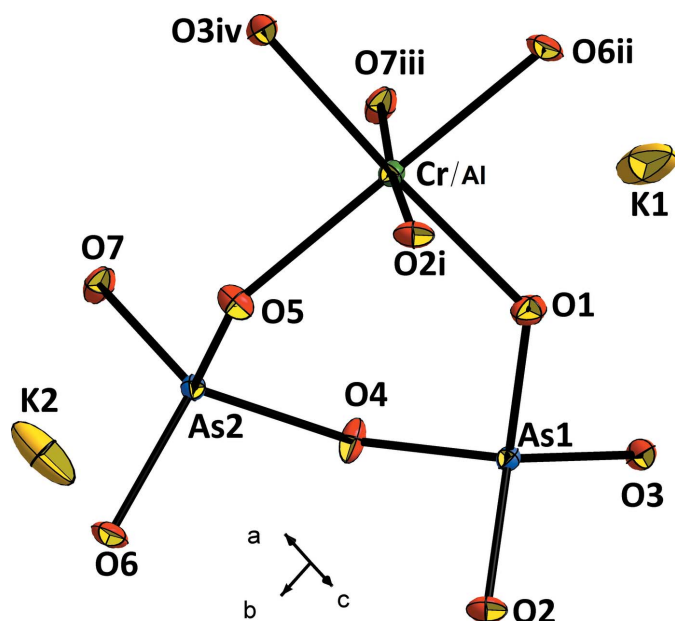
Figure 1
A view of the asymmetric unit of the title compound completed by equivalent atomic positions, showing the principal structural units. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $x + 1, y, z$.]

coordination with an average bond length (Cr/Al)—O of 1.920 (14) Å. The presence of the Cr^{III} cations is proved by the shortening of the Cr—O bond length compared to Al^{III}—O. In fact, according to similar studies (Bouhassine & Boughzala, 2014, 2015) the average Al^{III}—O and Cr^{III}—O bond lengths in octahedral coordination are 1.907 and 1.979 Å, respectively.
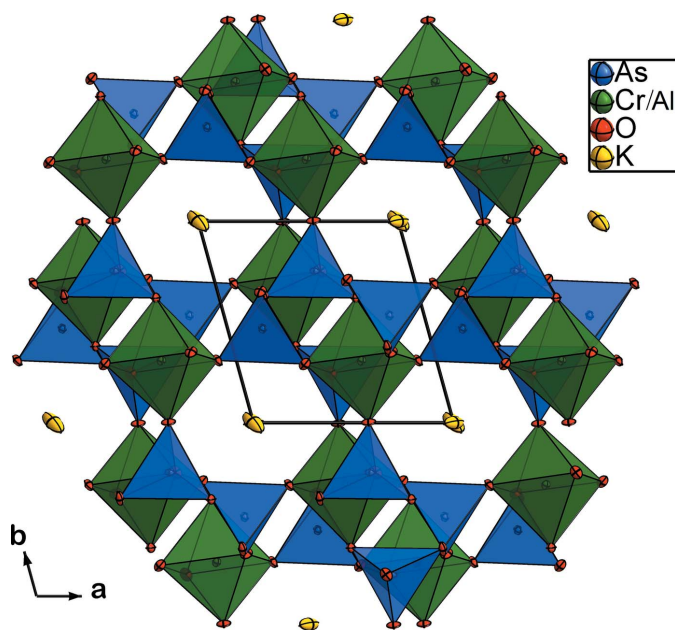
Figure 2
Projection of the $KCr_{1/4}Al_{3/4}As_2O_7$ structure showing the channels parallel to [001] in which the K^+ cations are located.

Table 1
Selected geometric parameters (Å, °).

| As1—O2	1.659 (2)	As2—O4	1.761 (3)
As1—O3^i	1.669 (3)	(Cr/Al)—O6^{ii}	1.898 (3)
As1—O1	1.669 (3)	(Cr/Al)—O3	1.915 (3)
As1—O4	1.776 (2)	(Cr/Al)—O1	1.919 (3)
As2—O6	1.654 (2)	(Cr/Al)—O5	1.925 (3)
As2—O7	1.663 (2)	(Cr/Al)—O2^{iii}	1.925 (3)
As2—O5	1.675 (2)	(Cr/Al)—O7^{iv}	1.940 (3)
As2—O4—As1	118.50 (14)		

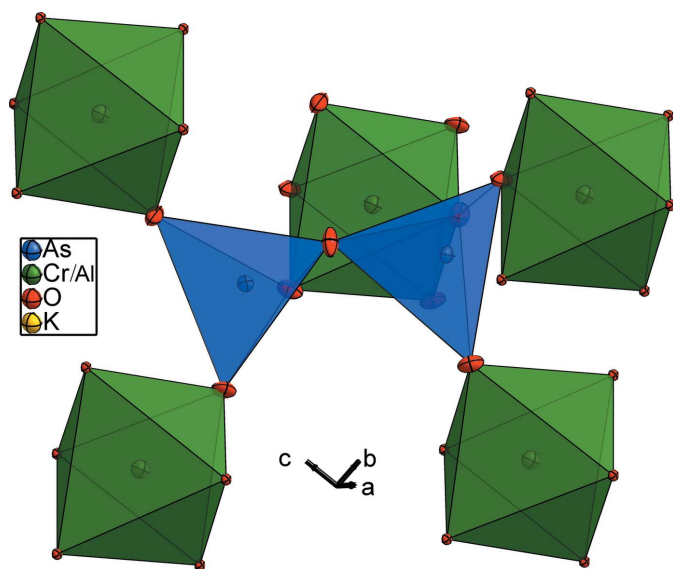Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 1, -z + 2$.

The two arsenic atoms in the unit cell are tetrahedrally coordinated. The AsO_4 polyhedra connected via the bridging O4 atom into a diarsenate As_2O_7 anion. Like in the related triclinic structures of $KAlAs_2O_7$ (Boughzala & Jouini, 1995) and $RbAlAs_2O_7$ (Boughzala et al., 1993), the As—O distances involving the bridging O4 atom are the longest (Table 1). The As1—O4—As2 bridging angle of 118.50 (14)° in the title structure is similar to that in the reported isotypic structures of $CsCrAs_2O_7$ [118.7 (2)°; Bouhassine & Boughzala, 2015] and $KAlAs_2O_7$ [118.3 (2)°; Boughzala & Jouini, 1995]. The O—As—O bond angles for As1 and As2 span the ranges 103.99 (12) to 117.41 (13) and 106.34 (13) to 113.63 (12), respectively, reflecting a slight distortion of each AsO_4 tetrahedron.

The (Cr/Al) cations are in a slightly distorted octahedral oxygen coordination with (Cr/Al)—O distances ranging from 1.898 (3) to 1.940 (3) Å, and with O—(Cr/Al)—O angles ranging from 85.28 (11) to 92.23 (12)° and from 177.25 (11) to 176.41 (11)°. Each $(Cr/Al)O_6$ octahedron is linked by its six vertices to five As_2O_7 anions. Two corners are joined to the same diarsenate group (Fig. 3). On the other hand, each As_2O_7 anion is surrounded by five $(Cr/Al)O_6$ units (Fig. 4).

It is worth mentioning that members of the related aluminium diarsenate family $A^I AlAs_2O_7$ (A^I = K, Rb, Tl, Cs; Boughzala & Jouini, 1992) crystallize in the triclinic space group $P\bar{1}$ and are classified as type II (Durif & Averbuch-
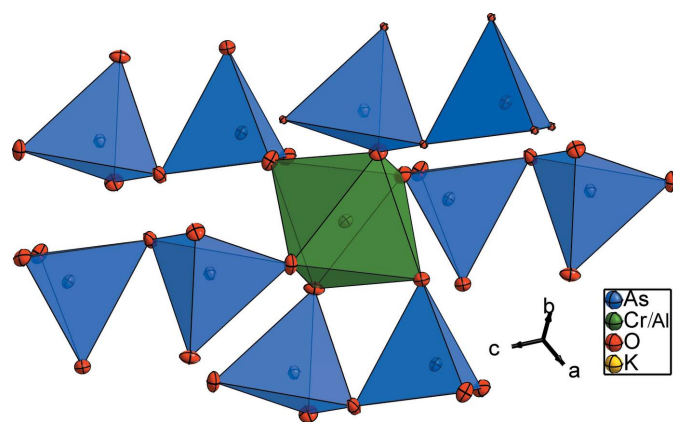
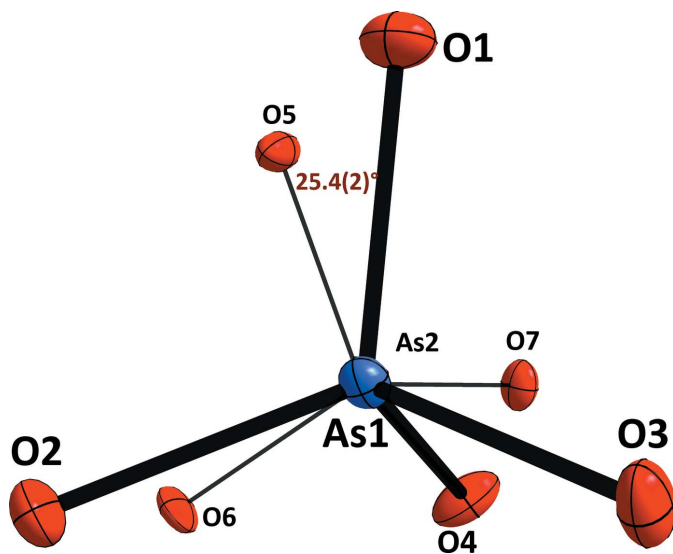**Figure 3**
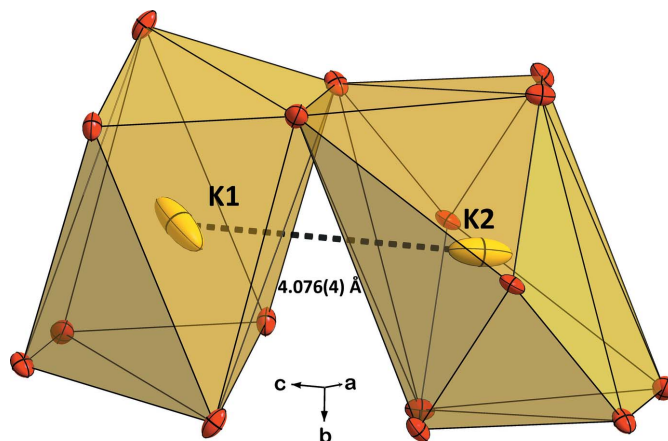The environment of the $(Cr/Al)O_6$ octahedron in the structure of $KCr_{1/4}Al_{3/4}As_2O_7$.

Figure 4
The environment of the diarsenate group As_2O_7 in the title structure.

Figure 6
The eight- and ten-coordinated K1 and K2 atoms (polyhedral plot) in the structure of $KCr_{1/4}Al_{3/4}As_2O_7$.

Pouchot, 1996); the diarsenate groups have a different conformational orientation compared to that of the title structure, which belongs to the type I family of $A^IM^{III}X_2O_7$ diarsenates. In fact, the diarsenate tetrahedra are in a nearly eclipsed conformation with an O1—As1—As2—O5 torsion angle of 25.4 (2)°, as shown in Fig. 5. The corresponding angle is 158.8 (2)° for $KAlAs_2O_7$ (Boughzala & Jouini, 1995).

The potassium cations lodge in two independent special positions in the unit cell, located in wide channels that are delimited by the anionic framework and run along the c-axis direction. The K1 and K2 cations are surrounded by eight and ten oxygen atoms, respectively (Fig. 6), with K—O distances

ranging from 2.769 (3) to 3.246 (3) Å and from 2.806 (3) to 3.205 (3) Å, respectively, forming irregular coordination polyhedra, as often occurs with this cation in homologous structures.

3. Database survey

The structure of $KAlP_2O_7$ (Ng & Calvo, 1973) was the first to be published for the $A^IM^{III}X_2O_7$ family (X = As, P). Afterwards, based on different substitutions and combinations, a large number of different phases were isolated and characterized crystallographically. Replacement of the cations can improve the structural and physical properties, but also affects the coordination numbers, the distortion of the coordination polyhedra and the conformation of the X_2O_7 groups. In addition, the crystal symmetry can be affected. The structures are triclinic, in space group $P\overline{1}$ with two formulas units, for the diarsenate compounds $A^IAlAs_2O_7$ (A^I = K, Rb, Tl, Cs) (Boughzala & Jouini, 1992; Boughzala et al., 1993; Boughzala & Jouini; 1995), whereas the diphosphates are generally monoclinic. The isotypic $A^ICrP_2O_7$ phases crystallize in space group $P2_1/c$ for A^I = Na (Bohatý et al., 1982), K (Gentil et al., 1997), Rb (Zhao & Li, 2011) and Cs (Linde & Gorbunova, 1982). The same applies for the $A^IFeP_2O_7$ phases for A^I = Na (Gabelica-Robert et al., 1982) and K (Riou et al., 1988). However, the two Li-containing phases $LiMP_2O_7$ show a symmetry reduction to space group $P2_1$ (M = Cr, Ivashkevich et al., 2007; M = Fe, Riou et al., 1990). $CsCrAs_2O_7$ (Bouhassine & Boughzala, 2015) is the first phase of the $A^ICrAs_2O_7$ family to crystallize in the $P2_1/c$ space group.

4. Synthesis and crystallization

The crystals of the title compound were obtained from heating a mixture of KNO_3, Cr_2O_3 and $NH_4H_2AsO_4$, with a K:Cr:As molar ratio of 2:1:2. In order to eliminate volatile products, the sample was placed in a porcelain crucible and slowly heated under atmospheric conditions to 673 K and kept for 12 h. In a
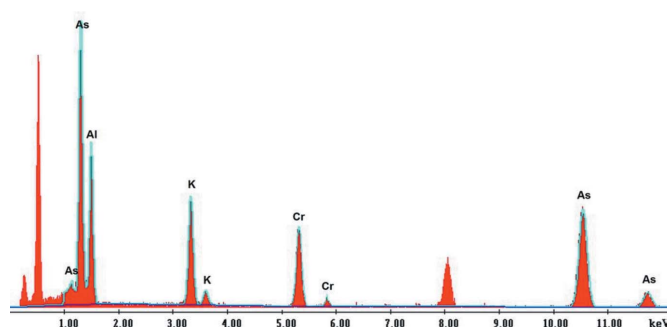

Figure 5
View parallel to the As1—As2 direction, emphasizing the nearly eclipsed conformation of the diarsenate anion.

Table 2
Experimental details.

Crystal data	
Chemical formula	$KCr_{0.25}Al_{0.75}As_2O_7$
M_r	334.17
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	6.243 (3), 6.349 (3), 8.153 (4)
α, β, γ (°)	96.57 (2), 104.45 (3), 103.08 (4)
V (Å^3)	299.8 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	12.37
Crystal size (mm)	$0.40 \times 0.30 \times 0.20$
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.079, 0.182
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1628, 1479, 1306
R_{int}	0.014
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.702
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.059, 1.08
No. of reflections	1479
No. of parameters	104
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.59, −1.09

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2008) and *publCIF* (Westrip, 2010).

second step, the crucible was progressively heated at 1123 K for 10 days and then slowly cooled down at a rate of 5 K/24h to 923 K and finally allowed to cool radiatively to room temperature. A long wash with boiling water liberated green crystals. Manifestly, the aluminium present in the studied composition is coming from the porcelain crucible.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The 2*i* site was initially refined as being entirely occupied by chromium ions with reliability factor $R(F^2) = 0.053$. Trying to improve the convergence factor, the occupation rate of the 2*i* site was refined, leading to $R(F^2) = 0.023$ and a partial occupancy of 67%. Occupied by just Cr^{III}, this occupancy is insufficient to achieve electric neutrality in the empirical formula. To ensure the electro-neutrality, many propositions were considered such as the existence of some vacancies in the positions of the oxygen atoms, or the contribution of more than one oxidation state of chromium in the 2*i* site. The most reasonable idea was to consider a competitive presence of Cr^{III} and Al^{III} in the same crystallographic site endowed with the same U_{ij} parameters. The aluminium has obviously diffused from the porcelain crucible. The last refinement steps lead to the final formula $KCr_{1/4}Al_{3/4}As_2O_7$. The presence of both aluminium and

Figure 7
Qualitative elemental composition determined by TEM (Fei Tecnai G20 STEM microscope). (Low-energy unlabelled peaks are related to oxygen and the one around 8 keV is attributed to the copper sample holder).

chromium in the structure was confirmed by TEM as shown in Fig. 7.

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Riou, D., Nguyen, N., Benloucif, R. & Raveau, B. (1990). *Mater. Res. Bull.* **25**, 1363–1369.
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Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Potassium chromium aluminium diarsenate, $KCr_{1/4}Al_{3/4}As_2O_7$

Crystal data

$KCr_{0.25}Al_{0.75}As_2O_7$	$Z = 2$
$M_r = 334.17$	$F(000) = 314$
Triclinic, $P\bar{1}$	$D_x = 3.702$ Mg m^{-3}
Hall symbol: -p 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.243$ (3) Å	Cell parameters from 25 reflections
$b = 6.349$ (3) Å	$\theta = 3.8–27°$
$c = 8.153$ (4) Å	$\mu = 12.37$ mm^{-1}
$\alpha = 96.57$ (2)°	$T = 293$ K
$\beta = 104.45$ (3)°	Triclinic, green
$\gamma = 103.08$ (4)°	$0.40 \times 0.30 \times 0.20$ mm
$V = 299.8$ (8) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	1479 independent reflections
Radiation source: fine-focus sealed tube	1306 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.014$
$\omega/2\theta$ scans	$\theta_{max} = 30.0°$, $\theta_{min} = 2.6°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 7$
	$k = -8 \rightarrow 8$
$T_{min} = 0.079$, $T_{max} = 0.182$	$l = -11 \rightarrow 11$
1628 measured reflections	2 standard reflections every 120 min
	intensity decay: 1.1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.023$	
$wR(F^2) = 0.059$	
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.5924P]$ where $P = (F_o^2 + 2F_c^2)/3$
1479 reflections	
104 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.59$ e Å^{-3}
	$\Delta\rho_{min} = -1.09$ e Å^{-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. 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 R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
As1	0.82649 (6)	0.53279 (5)	0.68995 (4)	0.00590 (10)	
As2	0.48557 (6)	0.24607 (5)	0.83512 (4)	0.00587 (10)	
Cr	0.37535 (14)	0.69197 (13)	0.72579 (10)	0.0054 (3)	0.255 (6)
Al	0.37535 (14)	0.69197 (13)	0.72579 (10)	0.0054 (3)	0.745 (6)
O1	0.6626 (4)	0.7081 (4)	0.6757 (3)	0.0109 (5)	
O2	0.7856 (4)	0.3500 (4)	0.5149 (3)	0.0105 (5)	
O3	0.0934 (4)	0.6909 (4)	0.7793 (3)	0.0097 (5)	
O4	0.7722 (4)	0.3747 (4)	0.8485 (3)	0.0108 (5)	
O5	0.3164 (4)	0.3800 (4)	0.7206 (3)	0.0100 (5)	
O6	0.4234 (5)	−0.0032 (4)	0.7201 (3)	0.0113 (5)	
O7	0.4552 (4)	0.2466 (4)	1.0321 (3)	0.0106 (5)	
K1	1.0000	1.0000	1.0000	0.0484 (5)	
K2	0.0000	0.0000	0.5000	0.0364 (4)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.00519 (19)	0.00627 (16)	0.00641 (15)	0.00121 (12)	0.00247 (12)	0.00063 (11)
As2	0.00655 (19)	0.00535 (15)	0.00580 (15)	0.00124 (12)	0.00216 (12)	0.00115 (10)
Cr	0.0047 (5)	0.0053 (4)	0.0062 (4)	0.0015 (3)	0.0019 (3)	0.0005 (3)
Al	0.0047 (5)	0.0053 (4)	0.0062 (4)	0.0015 (3)	0.0019 (3)	0.0005 (3)
O1	0.0127 (13)	0.0117 (11)	0.0122 (11)	0.0066 (10)	0.0060 (10)	0.0049 (9)
O2	0.0122 (13)	0.0107 (11)	0.0079 (10)	0.0041 (10)	0.0022 (9)	−0.0015 (8)
O3	0.0070 (12)	0.0095 (11)	0.0097 (10)	−0.0010 (9)	0.0023 (9)	−0.0026 (8)
O4	0.0056 (12)	0.0159 (12)	0.0119 (11)	0.0017 (10)	0.0026 (9)	0.0079 (9)
O5	0.0089 (13)	0.0076 (10)	0.0113 (11)	0.0025 (9)	−0.0010 (9)	0.0011 (8)
O6	0.0163 (14)	0.0064 (11)	0.0109 (11)	0.0033 (10)	0.0045 (10)	−0.0016 (8)
O7	0.0106 (13)	0.0139 (11)	0.0069 (10)	0.0011 (10)	0.0038 (9)	0.0012 (9)
K1	0.0302 (9)	0.0408 (9)	0.0615 (11)	−0.0093 (7)	0.0253 (8)	−0.0310 (8)
K2	0.0354 (9)	0.0148 (6)	0.0393 (8)	0.0055 (6)	−0.0209 (6)	−0.0002 (5)

Geometric parameters (Å, º)

As1—O2	1.659 (2)	O3—K2^v	3.202 (3)
As1—O3^i	1.669 (3)	O4—K1^{iv}	3.246 (3)
As1—O1	1.669 (3)	O5—K2	2.834 (3)

As1—O4	1.776 (2)	O6—Al[iv]	1.898 (3)
As1—K1	3.4388 (16)	O6—Cr[iv]	1.898 (3)
As1—K2[ii]	3.5783 (15)	O6—K2	2.806 (3)
As2—O6	1.654 (2)	O7—Al[vii]	1.940 (3)
As2—O7	1.663 (2)	O7—Cr[vii]	1.940 (3)
As2—O5	1.675 (2)	O7—K1[iii]	2.849 (3)
As2—O4	1.761 (3)	K1—O3[i]	2.769 (3)
As2—K2	3.441 (2)	K1—O3[ix]	2.769 (3)
As2—K1[iii]	3.7159 (17)	K1—O7[vii]	2.849 (3)
As2—K1[iv]	3.8935 (18)	K1—O7[ii]	2.849 (3)
Cr—O6[v]	1.898 (3)	K1—O1[x]	3.032 (3)
Cr—O3	1.915 (3)	K1—O4[xi]	3.246 (3)
Cr—O1	1.919 (3)	K1—O4[v]	3.246 (3)
Cr—O5	1.925 (3)	K1—As1[x]	3.4388 (16)
Cr—O2[vi]	1.925 (3)	K1—As2[ii]	3.7160 (17)
Cr—O7[vii]	1.940 (3)	K1—As2[vii]	3.7160 (17)
Cr—K2[v]	3.6674 (17)	K2—O6[xii]	2.806 (3)
Cr—K1	3.902 (2)	K2—O5[xii]	2.834 (3)
O1—K1	3.032 (3)	K2—O2[xiii]	2.848 (3)
O1—K2[ii]	3.205 (3)	K2—O2[viii]	2.848 (3)
O2—Al[vi]	1.925 (3)	K2—O3[iv]	3.202 (3)
O2—Cr[vi]	1.925 (3)	K2—O3[xiv]	3.202 (3)
O2—K2[i]	2.848 (3)	K2—O1[vi]	3.205 (3)
O3—As1[viii]	1.669 (3)	K2—O1[iii]	3.205 (3)
O3—K1[viii]	2.769 (3)	K2—As2[xii]	3.441 (2)
O2—As1—O3[i]	116.44 (13)	O3[ix]—K1—O4[xi]	119.81 (7)
O2—As1—O1	117.41 (13)	O7[vii]—K1—O4[xi]	93.40 (8)
O3[i]—As1—O1	104.67 (13)	O7[ii]—K1—O4[xi]	86.60 (8)
O2—As1—O4	105.16 (13)	O1[x]—K1—O4[xi]	82.64 (7)
O3[i]—As1—O4	103.99 (12)	O1—K1—O4[xi]	97.36 (7)
O1—As1—O4	108.17 (12)	O3[i]—K1—O4[v]	119.81 (7)
O2—As1—K1	164.68 (9)	O3[ix]—K1—O4[v]	60.19 (7)
O3[i]—As1—K1	52.76 (9)	O7[vii]—K1—O4[v]	86.60 (8)
O1—As1—K1	61.84 (9)	O7[ii]—K1—O4[v]	93.40 (8)
O4—As1—K1	88.94 (9)	O1[x]—K1—O4[v]	97.36 (7)
O2—As1—K2[ii]	94.71 (9)	O1—K1—O4[v]	82.64 (7)
O3[i]—As1—K2[ii]	63.46 (9)	O4[xi]—K1—O4[v]	180.000 (1)
O1—As1—K2[ii]	63.56 (9)	O3[i]—K1—As1[x]	151.32 (5)
O4—As1—K2[ii]	159.92 (8)	O3[ix]—K1—As1[x]	28.68 (6)
K1—As1—K2[ii]	71.00 (4)	O7[vii]—K1—As1[x]	112.10 (6)
O6—As2—O7	113.63 (12)	O7[ii]—K1—As1[x]	67.90 (6)
O6—As2—O5	106.34 (13)	O1[x]—K1—As1[x]	29.03 (5)
O7—As2—O5	111.83 (13)	O1—K1—As1[x]	150.97 (5)
O6—As2—O4	106.77 (13)	O4[xi]—K1—As1[x]	109.51 (6)
O7—As2—O4	109.74 (12)	O4[v]—K1—As1[x]	70.49 (6)
O5—As2—O4	108.26 (12)	O3[i]—K1—As1	28.68 (5)
O6—As2—K2	53.92 (10)	O3[ix]—K1—As1	151.32 (6)

O7—As2—K2	116.01 (10)	O7^{vii}—K1—As1	67.90 (6)
O5—As2—K2	54.99 (9)	O7^{ii}—K1—As1	112.10 (6)
O4—As2—K2	134.24 (8)	O1^{x}—K1—As1	150.97 (5)
O6—As2—K1^{iii}	83.81 (10)	O1—K1—As1	29.03 (5)
O7—As2—K1^{iii}	46.83 (9)	O4^{xi}—K1—As1	70.49 (6)
O5—As2—K1^{iii}	88.35 (10)	O4^{v}—K1—As1	109.51 (6)
O4—As2—K1^{iii}	156.13 (8)	As1^{x}—K1—As1	180.0
K2—As2—K1^{iii}	69.32 (4)	O3^{i}—K1—As2^{ii}	68.09 (6)
O6—As2—K1^{iv}	72.50 (10)	O3^{ix}—K1—As2^{ii}	111.91 (6)
O7—As2—K1^{iv}	85.22 (9)	O7^{vii}—K1—As2^{ii}	154.81 (5)
O5—As2—K1^{iv}	160.88 (9)	O7^{ii}—K1—As2^{ii}	25.19 (5)
O4—As2—K1^{iv}	55.72 (8)	O1^{x}—K1—As2^{ii}	78.58 (6)
K2—As2—K1^{iv}	126.37 (3)	O1—K1—As2^{ii}	101.42 (6)
K1^{iii}—As2—K1^{iv}	110.23 (3)	O4^{xi}—K1—As2^{ii}	94.66 (6)
O6^{v}—Cr—O3	89.05 (12)	O4^{v}—K1—As2^{ii}	85.34 (6)
O6^{v}—Cr—O1	88.35 (12)	As1^{x}—K1—As2^{ii}	87.50 (4)
O3—Cr—O1	177.25 (11)	As1—K1—As2^{ii}	92.50 (4)
O6^{v}—Cr—O5	177.24 (11)	O3^{i}—K1—As2^{vii}	111.91 (6)
O3—Cr—O5	90.41 (12)	O3^{ix}—K1—As2^{vii}	68.09 (6)
O1—Cr—O5	92.23 (12)	O7^{vii}—K1—As2^{vii}	25.19 (5)
O6^{v}—Cr—O2^{vi}	85.28 (11)	O7^{ii}—K1—As2^{vii}	154.81 (5)
O3—Cr—O2^{vi}	88.97 (12)	O1^{x}—K1—As2^{vii}	101.42 (6)
O1—Cr—O2^{vi}	91.72 (12)	O1—K1—As2^{vii}	78.58 (6)
O5—Cr—O2^{vi}	92.00 (11)	O4^{xi}—K1—As2^{vii}	85.34 (6)
O6^{v}—Cr—O7^{vii}	91.24 (11)	O4^{v}—K1—As2^{vii}	94.66 (6)
O3—Cr—O7^{vii}	91.73 (11)	As1^{x}—K1—As2^{vii}	92.50 (4)
O1—Cr—O7^{vii}	87.42 (12)	As1—K1—As2^{vii}	87.50 (4)
O5—Cr—O7^{vii}	91.49 (11)	As2^{ii}—K1—As2^{vii}	180.0
O2^{vi}—Cr—O7^{vii}	176.44 (11)	O6—K2—O6^{xii}	180.0
O6^{v}—Cr—K2^{v}	48.75 (9)	O6—K2—O5	56.38 (8)
O3—Cr—K2^{v}	60.75 (8)	O6^{xii}—K2—O5	123.62 (8)
O1—Cr—K2^{v}	117.88 (8)	O6—K2—O5^{xii}	123.62 (8)
O5—Cr—K2^{v}	128.80 (9)	O6^{xii}—K2—O5^{xii}	56.38 (8)
O2^{vi}—Cr—K2^{v}	50.16 (8)	O5—K2—O5^{xii}	180.0
O7^{vii}—Cr—K2^{v}	127.49 (8)	O6—K2—O2^{xiii}	54.52 (8)
O6^{v}—Cr—K1	71.06 (9)	O6^{xii}—K2—O2^{xiii}	125.48 (8)
O3—Cr—K1	128.54 (8)	O5—K2—O2^{xiii}	109.72 (8)
O1—Cr—K1	49.56 (8)	O5^{xii}—K2—O2^{xiii}	70.28 (8)
O5—Cr—K1	111.31 (9)	O6—K2—O2^{viii}	125.48 (8)
O2^{vi}—Cr—K1	133.48 (9)	O6^{xii}—K2—O2^{viii}	54.52 (8)
O7^{vii}—Cr—K1	44.10 (8)	O5—K2—O2^{viii}	70.28 (8)
K2^{v}—Cr—K1	119.78 (4)	O5^{xii}—K2—O2^{viii}	109.72 (8)
As1—O1—Cr	130.98 (15)	O2^{xiii}—K2—O2^{viii}	180.0
As1—O1—K1	89.13 (11)	O6—K2—O3^{iv}	52.34 (7)
Cr—O1—K1	101.64 (10)	O6^{xii}—K2—O3^{iv}	127.66 (7)
As1—O1—K2^{ii}	88.65 (10)	O5—K2—O3^{iv}	93.39 (7)
Cr—O1—K2^{ii}	139.96 (11)	O5^{xii}—K2—O3^{iv}	86.61 (7)
K1—O1—K2^{ii}	81.57 (8)	O2^{xiii}—K2—O3^{iv}	52.42 (7)

As1—O2—Al^{vi}	136.04 (15)	O2^{viii}—K2—O3^{iv}	127.58 (7)
As1—O2—Cr^{vi}	136.04 (15)	O6—K2—O3^{xiv}	127.66 (7)
Al^{vi}—O2—Cr^{vi}	0.00 (8)	O6^{xii}—K2—O3^{xiv}	52.34 (7)
As1—O2—K2ⁱ	125.20 (12)	O5—K2—O3^{xiv}	86.61 (8)
Al^{vi}—O2—K2ⁱ	98.57 (10)	O5^{xii}—K2—O3^{xiv}	93.39 (7)
Cr^{vi}—O2—K2ⁱ	98.57 (10)	O2^{xiii}—K2—O3^{xiv}	127.58 (7)
As1^{viii}—O3—Cr	131.84 (14)	O2^{viii}—K2—O3^{xiv}	52.42 (7)
As1^{viii}—O3—K1^{viii}	98.56 (11)	O3^{iv}—K2—O3^{xiv}	180.0
Cr—O3—K1^{viii}	129.00 (12)	O6—K2—O1^{vi}	80.54 (8)
As1^{viii}—O3—K2^v	88.74 (10)	O6^{xii}—K2—O1^{vi}	99.46 (8)
Cr—O3—K2^v	87.81 (9)	O5—K2—O1^{vi}	64.92 (8)
K1^{viii}—O3—K2^v	85.79 (7)	O5^{xii}—K2—O1^{vi}	115.08 (8)
As2—O4—As1	118.50 (14)	O2^{xiii}—K2—O1^{vi}	92.66 (7)
As2—O4—K1^{iv}	97.65 (10)	O2^{viii}—K2—O1^{vi}	87.34 (7)
As1—O4—K1^{iv}	131.00 (12)	O3^{iv}—K2—O1^{vi}	131.29 (7)
As2—O5—Cr	127.51 (15)	O3^{xiv}—K2—O1^{vi}	48.71 (7)
As2—O5—K2	96.06 (11)	O6—K2—O1ⁱⁱⁱ	99.46 (8)
Cr—O5—K2	135.48 (11)	O6^{xii}—K2—O1ⁱⁱⁱ	80.54 (8)
As2—O6—Al^{iv}	145.71 (15)	O5—K2—O1ⁱⁱⁱ	115.08 (8)
As2—O6—Cr^{iv}	145.71 (15)	O5^{xii}—K2—O1ⁱⁱⁱ	64.92 (8)
Al^{iv}—O6—Cr^{iv}	0.00 (5)	O2^{xiii}—K2—O1ⁱⁱⁱ	87.34 (7)
As2—O6—K2	97.63 (11)	O2^{viii}—K2—O1ⁱⁱⁱ	92.66 (7)
Al^{iv}—O6—K2	100.69 (11)	O3^{iv}—K2—O1ⁱⁱⁱ	48.71 (7)
Cr^{iv}—O6—K2	100.69 (11)	O3^{xiv}—K2—O1ⁱⁱⁱ	131.29 (7)
As2—O7—Al^{vii}	143.23 (16)	O1^{vi}—K2—O1ⁱⁱⁱ	180.00 (7)
As2—O7—Cr^{vii}	143.23 (16)	O6—K2—As2^{xii}	151.55 (5)
Al^{vii}—O7—Cr^{vii}	0.00 (8)	O6^{xii}—K2—As2^{xii}	28.45 (5)
As2—O7—K1ⁱⁱⁱ	107.98 (11)	O5—K2—As2^{xii}	151.05 (5)
Al^{vii}—O7—K1ⁱⁱⁱ	107.62 (10)	O5^{xii}—K2—As2^{xii}	28.95 (5)
Cr^{vii}—O7—K1ⁱⁱⁱ	107.62 (10)	O2^{xiii}—K2—As2^{xii}	97.04 (6)
O3ⁱ—K1—O3^{ix}	180.000 (1)	O2^{viii}—K2—As2^{xii}	82.96 (6)
O3ⁱ—K1—O7^{vii}	95.75 (8)	O3^{iv}—K2—As2^{xii}	112.12 (6)
O3^{ix}—K1—O7^{vii}	84.25 (8)	O3^{xiv}—K2—As2^{xii}	67.88 (6)
O3ⁱ—K1—O7ⁱⁱ	84.25 (8)	O1^{vi}—K2—As2^{xii}	104.03 (6)
O3^{ix}—K1—O7ⁱⁱ	95.75 (8)	O1ⁱⁱⁱ—K2—As2^{xii}	75.97 (6)
O7^{vii}—K1—O7ⁱⁱ	180.0	O6—K2—As2	28.45 (5)
O3ⁱ—K1—O1^x	126.04 (8)	O6^{xii}—K2—As2	151.55 (5)
O3^{ix}—K1—O1^x	53.96 (8)	O5—K2—As2	28.95 (5)
O7^{vii}—K1—O1^x	126.18 (8)	O5^{xii}—K2—As2	151.05 (5)
O7ⁱⁱ—K1—O1^x	53.82 (8)	O2^{xiii}—K2—As2	82.96 (6)
O3ⁱ—K1—O1	53.96 (8)	O2^{viii}—K2—As2	97.04 (6)
O3^{ix}—K1—O1	126.04 (8)	O3^{iv}—K2—As2	67.88 (6)
O7^{vii}—K1—O1	53.82 (8)	O3^{xiv}—K2—As2	112.12 (6)
O7ⁱⁱ—K1—O1	126.18 (8)	O1^{vi}—K2—As2	75.97 (6)

| O1^x—K1—O1 | 180.0 | O1^{iii}—K2—As2 | 104.03 (6) |
| O3^i—K1—O4^{xi} | 60.19 (7) | As2^{xii}—K2—As2 | 180.0 |

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