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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{Cr}-\text{O}) = 0.003\text{ \AA}$
Disorder in main residue
 R factor = 0.028
 wR factor = 0.053
Data-to-parameter ratio = 7.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Garnet-type $\text{Li}_{2.44}\text{K}_{0.56}\text{Cr}_2(\text{AsO}_4)_3$

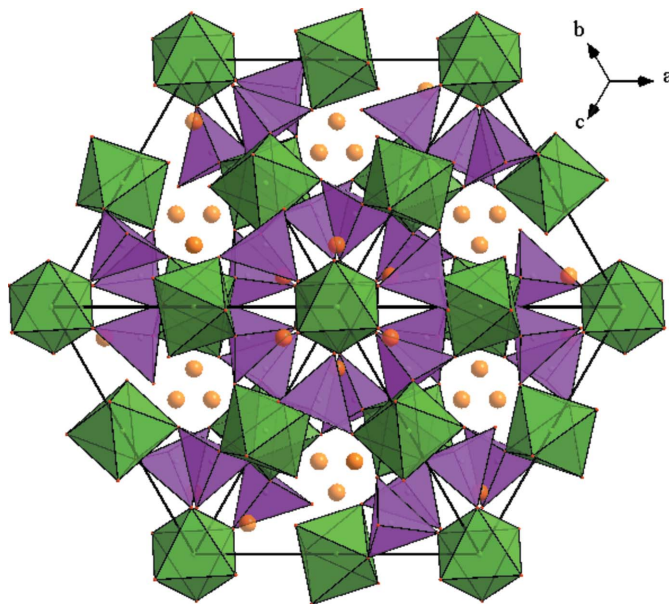
Single crystals of the title compound, lithium potassium dichromium(III) arsenate(V), have been prepared by a solid-state reaction. The compound adopts the garnet structure. The monovalent cations share the same site (Wyckoff position 24c), with 81 (2) and 19 (2)% occupancy for Li and K, respectively, resulting in an eightfold coordination by O atoms.

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Comment

Few ternary compounds in the system $M_2^{\text{I}}\text{O}-M_2^{\text{III}}\text{O}_3-\text{As}_2\text{O}_5$ are known. To our knowledge, for $M^{\text{III}} = \text{Cr}$ only the compound $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$ has been reported (Schwarz & Schmidt, 1972), the structure of which was determined recently (Bouzemi *et al.*, 2002). In attempts to replace Na by other cations, we succeeded in synthesizing crystals of $\text{Li}_{2.44}\text{K}_{0.56}\text{Cr}_2(\text{AsO}_4)_3$, (I), and we report its crystal structure here.

Compound (I) is isostructural with $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$ and $\text{Na}_3\text{Sc}_2(\text{VO}_4)_3$ (Lobanov *et al.*, 1989) and crystallizes in the garnet structure. A general description of this structure type is given by, for example, Resende & Fernandes (2005). In (I), Li and K share the same crystallographic site with 81 (2) and 19 (2)% occupancy, respectively, and the Cr, As and (Li/K) sites substitute for the (Al/Fe), Si and Ca sites in the garnet structure. The CrO_6 octahedra and AsO_4 tetrahedra are slightly distorted and share corners to form a three-dimen-

**Figure 1**

A projection of the structure of (I) along the [111] direction. AsO_4 tetrahedra are shown in purple and CrO_6 octahedra in green, and the (Li,K) cations are indicated as orange spheres.

sional framework (Fig. 1). The monovalent cations are located in the cavities of this arrangement, with a coordination number of 8 and an average $M^I\text{—O}$ distance of 2.388 Å.

The lattice parameter of (I) is smaller than that of the isotypic compound $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$ [$a = 12.164$ (4) Å], which is in agreement with the substitution of Na by K and Li, with $r(X) = r_K \times p_K + r_{\text{Li}} \times p_{\text{Li}} = 1.51 \times 0.19 + 0.92 \times 0.81 = 1.03$ Å, compared with $r_{\text{Na}} = 1.18$ Å, where r is the radius of a cation with coordination number 8 (Shannon, 1976) and p is the occupancy factor. The reduction of the overall monovalent cation size also influences the intrapolyhedral distances of the framework. The As—O and Cr—O distances of 1.685 (3) and 1.965 (3) Å, respectively, are smaller than those in the isotypic compound [1.698 (2) and 1.995 (2) Å, respectively].

The bond-valence sums (Brown & Altermatt, 1985) for each metal atom in (I) are in the expected ranges, with 4.99 v.u. for As, 3.12 v.u. for Cr and 1.07 v.u. for Li/K.

Experimental

Single crystals of (I) were obtained by a solid-state reaction, starting from reagent grade K_2CO_3 , Li_2CO_3 , Cr_2O_3 and H_3AsO_4 mixed in the stoichiometric ratio K:Li:Cr:As = 1:2:2:6. The sample was first heated at 673 K for 6 h and then at 1153 K for 21 d. The reaction product was leached out with water. It contained green crystals of $\text{Li}_{2.44}\text{K}_{0.56}\text{Cr}_2(\text{AsO}_4)_3$. The melting point of the compound at 1354 K was derived from a differential thermal analysis measurement. An IR spectrum was recorded in the range 1000–300 cm^{-1} . The most significant observed bands (in cm^{-1}) are assigned to the following vibrational modes: 875 [$\nu_a(\text{AsO}_3)$]; 840, 800, 780 [$\nu_s(\text{AsO}_3)$]; 650 [$\nu_s(\text{Cr—O—Cr})$]; 580, 500, 398, 355 [$\delta_a + \delta_s[(\text{AsO}_3)_+ (\text{Cr—O—Cr})]$]

Crystal data

$\text{Li}_{2.44}\text{K}_{0.56}\text{Cr}_2(\text{AsO}_4)_3$	Cell parameters from 25 reflections
$M_r = 559.67$	$\theta = 12\text{--}16^\circ$
Cubic, $Ia\bar{3}d$	$\mu = 14.45 \text{ mm}^{-1}$
$a = 11.948$ (1) Å	$T = 293$ (2) K
$V = 1705.6$ (2) Å ³	Fragment, green
$Z = 8$	$0.21 \times 0.18 \times 0.11 \text{ mm}$
$D_x = 4.359 \text{ Mg m}^{-3}$	
Mo $K\alpha$ radiation	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.147$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.9^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -15 \rightarrow 0$
$T_{\text{min}} = 0.062$, $T_{\text{max}} = 0.204$	$k = 0 \rightarrow 15$
842 measured reflections	$l = 0 \rightarrow 15$
159 independent reflections	2 standard reflections
145 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 1.2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
$wR(F^2) = 0.053$	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
$S = 1.15$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
159 reflections	Extinction coefficient: 0.0018 (3)
20 parameters	
$w = 1/[\sigma^2(F_o^2)]$	

Table 1

Selected geometric parameters (Å, °).

Cr—O	1.965 (3)	(K,Li)—O	2.320 (2)
As—O	1.685 (3)	(K,Li)—O ⁱ	2.456 (2)
O ⁱⁱ —As—O	113.67 (8)	As—O—(K,Li)	95.13 (10)
O ⁱⁱⁱ —As—O	101.37 (16)	Cr ^{iv} —O—(K,Li)	102.07 (11)
As—O—Cr ^{iv}	64.62 (7)		

Symmetry codes: (i) $y + \frac{1}{4}, -x + \frac{1}{4}, z - \frac{1}{4}$; (ii) $-z + \frac{1}{4}, -y - \frac{1}{4}, x - \frac{1}{4}$; (iii) $-x + \frac{1}{2}, y, -z$; (iv) $x + \frac{1}{4}, -z - \frac{1}{4}, -y + \frac{1}{4}$.

Li and K were refined with the same xyz and U^{ij} parameters. The sum of their occupancy factors was constrained to be constant (full occupancy). The rather high value of R_{int} is probably a result of the relatively high number of measured reflections.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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