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Crystal structure of $KNaCuP_2O_7$, a new member of the diphosphate family

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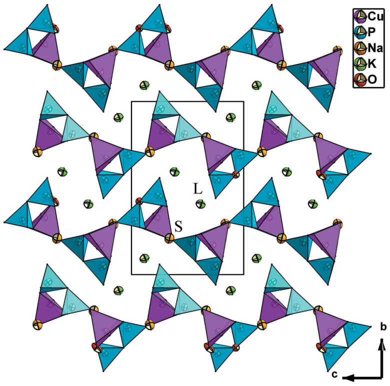
Potassium sodium copper(II) diphosphate(V), $KNaCuP_2O_7$, was synthesized by solid-state reactions. It crystallizes in the α-$Na_2CuP_2O_7$ structure type in space group $P2_1/n$. In the crystal, CuO_5 square-pyramids are linked to nearly eclipsed P_2O_7 groups by sharing corners to build up corrugated layers with composition $[CuP_2O_7]^{2-}$ that extend parallel to (010). The K^+ and Na^+ cations reside in the interlayer space and are connected to nine and seven O atoms, respectively. The structural model was validated by bond-valence-sum (BVS) and charge-distribution (CHARDI) analysis.

1. Chemical context

In order to improve the ionic conductivity in copper diphosphates with general formula $MM'CuP_2O_7$ (M, M' = monovalent cation), we attempted to partially replace the potassium cations in $K_2CuP_2O_7$ by smaller sodium cations. In the $K_2CuP_2O_7$ structure, the alkali cations are located in the interlayer space between corrugated $[CuP_2O_7]^{2-}$ anionic layers. Reducing the size of the cation can increase its mobility, and therefore might improve the material's charge-transport behaviour.



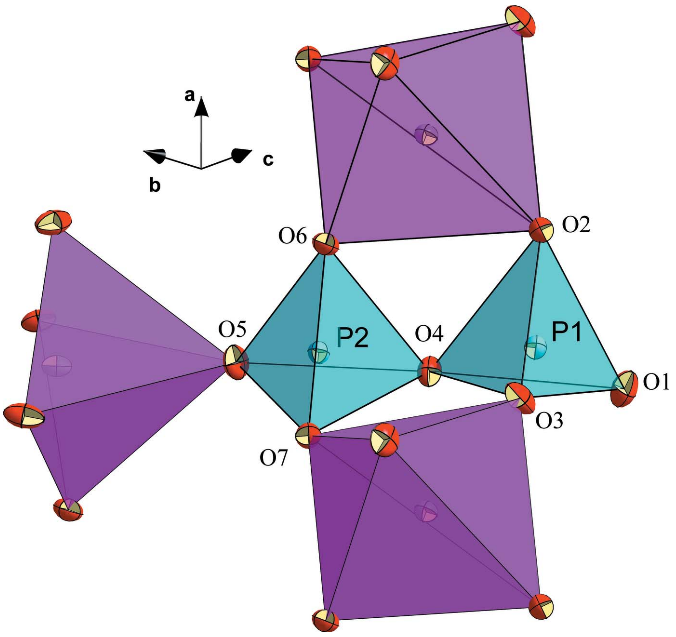


Figure 1
The diphosphate group directly connected to three CuO_5 polyhedra in the structure of $KNaCuP_2O_7$. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond lengths (Å).

Cu—O2	1.9328 (18)	Na—O5	2.398 (2)
Cu—O3^{i}	1.9427 (18)	Na—O7^{i}	2.4442 (19)
Cu—O6	1.9743 (17)	Na—O3^{iv}	2.772 (2)
Cu—O7^{i}	1.9872 (17)	Na—O5^{i}	2.815 (2)
Cu—O5^{ii}	2.3225 (19)	Na—O7^{iv}	2.878 (2)
P1—O1	1.482 (2)	K—O2	2.721 (2)
P1—O2	1.5246 (19)	K—O5^{iii}	2.7245 (18)
P1—O3	1.5313 (19)	K—O1^{i}	2.764 (2)
P1—O4	1.6272 (17)	K—O6^{v}	2.7969 (19)
P2—O5	1.4958 (17)	K—O7^{vi}	2.8450 (19)
P2—O6	1.5252 (17)	K—O3^{vii}	2.8630 (18)
P2—O7	1.5277 (16)	K—O1	3.036 (2)
P2—O4	1.6148 (18)	K—O2^{vii}	3.1973 (19)
Na—O1^{iii}	2.249 (2)	K—O3^{i}	3.257 (2)
Na—O6^{iv}	2.397 (2)		

Symmetry codes: (i) $x+1, y, z$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vii) $-x+1, -y+1, -z+1$.

Table 2
CHARDI and BVS analysis of cation polyhedra in $KNaCuP_2O_7$.

Cation	$qi()\cdot$sof(i)	$Q(i)$	$V(i)\cdot$sof(i)	CN(i)	ECoN(i)	$d_{ar}(i)$	$d_{med}(i)$
Cu	2.000	1.94	1.995	5	4.35	2.031	2.031
P1	5.000	5.07	4.921	4	3.84	1.540	1.541
P2	5.000	5.03	4.938	4	3.88	1.540	1.540
K	1.000	0.98	1.103	9	5.20	2.622	2.564
Na	1.000	0.98	1.106	7	7.80	2.912	2.912

Notes: qi = formal oxydation number; sof(i) = site occupation factor; $d_{ar}(i)$ = average distance; $d_{med}(i)$ = weighted average distance; CN(i) = coordination number; ECoN(i)= effective coordination number; σ_{cat} = dispersion factor on cationic charges measuring the deviation of the computed charges; $\sigma_{cat}=[\Sigma_i(q_i - Q_i)^2/N - 1]^{1/2} = 0.019$.

Several attempts were made to prepare crystals of the hypothetical solid solution $K_{2-x}Na_xCuP_2O_7$, with x in the range 0 to 2. All of the attempts led to a compound with $x = 1$, *i.e.* $KNaCuP_2O_7$, the crystal structure of which is reported in this communication.

2. Structural commentary

The title compound $KNaCuP_2O_7$ crystallizes isotypically with α-$Na_2CuP_2O_7$ (Erragh *et al.*, 1995) and also shows resemblance with one form of $K_2CuP_2O_7$ (ElMaadi *et al.*, 1995). It is built up by corrugated $[CuP_2O_7]^{2-}$ layers with the alkali cations situated in the interlayer space. The anionic layers consist of a nearly eclipsed diphosphate group [O2—P2—P1—O6 torsion angle = 15.90 (1)°] linked to CuO_5 square-pyramids by sharing five of the terminal oxygen atoms (O2, O3, O5, O6, O7). The bridging atom O4 of the diphosphate unit is not involved in metal coordination, and atom O1 coordinates to the alkali cations in the interlayer space (Fig. 1).

The P2—O4—P1 bridging angle [119.01 (11)°] of the diphosphate anion is close to those observed in other similar diarsenate and diphosphate structures, such as $KCr_{1/4}Al_{3/4}As_2O_7$ [118.50 (14)°; Bouhassine & Boughzala, 2017], $CsCrAs_2O_7$ [118.7 (2)°; Bouhassine & Boughzala, 2015], $KAlAs_2O_7$ [118.3 (2)°; Boughzala & Jouini, 1995], α-$Na_2CuP_2O_7$ [118.65 (1)°; Erragh *et al.*, 1995] and $K_2CuP_2O_7$ [120.41 (3)°; ElMaadi *et al.*, 1995]. As expected, the Cu—O bond length to the apical oxygen atom O5 is significantly longer than the Cu—O distances to the basal oxygen atoms of the square-pyramid (Table 1). The calculated bond-valence sum (Brown, 2002; Adams, 2003) of 1.94 valence units for the Cu site is in good agreement with the expected value of 2 for divalent copper. The geometry index of the CuO_5 polyhedron

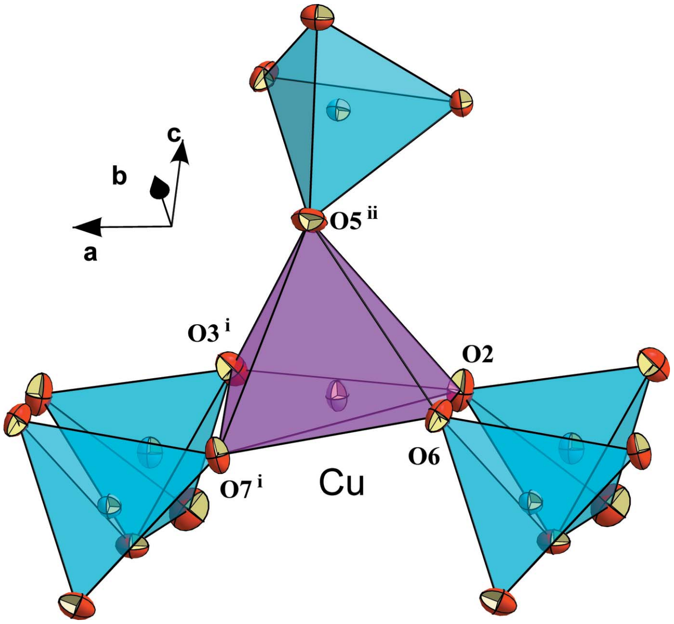


Figure 2
The CuO_5 square-pyramid with neighbouring diphosphate groups in the structure of $KNaCuP_2O_7$. Displacement ellipsoids are drawn at the 50% probability level.

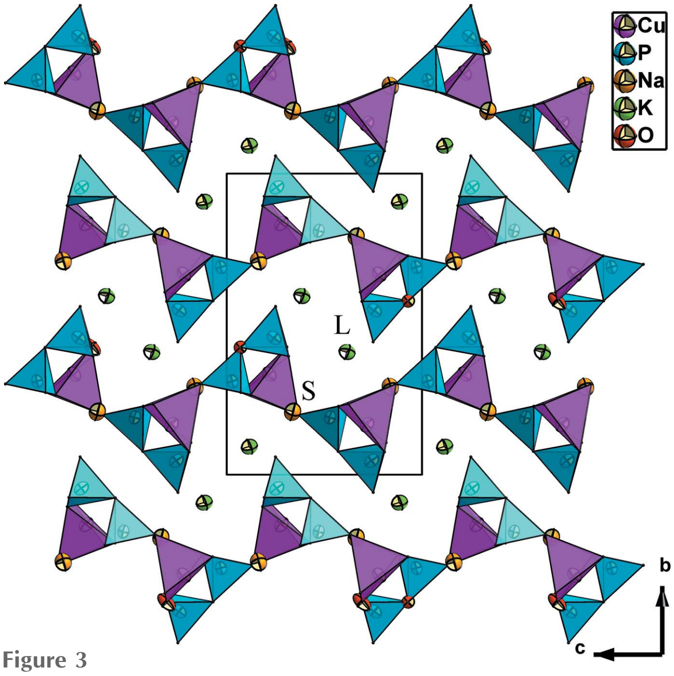


Figure 3
Projection of the $KNaCuP_2O_7$ structure along [100], showing the corrugated interlayer space housing the cations K^+ in the '*L*' sites and Na^+ in the '*S*' sites. Displacement ellipsoids are drawn at the 99% probability level.

Table 3
Structural data (Å, °) for the $M,M'_2CuP_2O_7$ family of compounds.

Compound	Space group	*a*	*b*	*c*	*β*	*Z*	Reference
$Li_2CuP_2O_7$	*I*2/*a*	14.068 (2)	4.8600 (8)	8.604 (1)	98.97 (1)	4	Spirlet *et al.* (1993)
$Li_2CuP_2O_7$	*C*2/*c*	15.3360 (14)	4.8733 (13)	8.6259 (16)	114.795 (10)	4	Gopalakrishna *et al.* (2008)
α-$Na_2CuP_2O_7$	*P*2$_1$/*n*	8.823 (3)	13.494 (3)	5.108 (2)	92.77 (3)	4	Erragh *et al.* (1995)
β-$Na_2CuP_2O_7$	*C*2/*c*	14.715 (1)	5.704 (2)	8.066 (1)	115.14 (1)	4	Etheredge *et al.* (1995)
$K_2CuP_2O_7$	*Pbnm*	9.509 (4)	14.389 (6)	5.276 (2)		4	ElMaadi *et al.* (1995)
$K_2CuP_2O_7$	$P\bar{4}2_1m$	8.056 (2)		5.460 (11)		2	Keates *et al.* (2014)
α-$Rb_2CuP_2O_7$	*Pmcn*	5.183 (1)	10.096 (1)	15.146 (2)		4	Chernyatieva *et al.* (2008)
β-$Rb_2CuP_2O_7$	*Cc*	7,002 (1)	12.751 (3)	9.773 (2)	110.93 (3)	4	Shvanskaya *et al.* (2012)
$Cs_2CuP_2O_7$	*Cc*	7.460 (6)	12.973 (10)	9.980 (8)	111.95	4	Mannasova *et al.* (2016)
$NaCsCuP_2O_7$	*Pmn*2$_1$	5.147 (2)	15.126 (3)	9.717 (5)		4	Chernyatieva *et al.* (2009)
$Na_{1.12}Ag_{0.88}CuP_2O_7$	*C*2/*c*	15.088 (2)	5.641 (1)	8.171 (1)	116.11 (1)	4	Bennazha *et al.* (2002)

τ_5, as defined by Addison *et al.* (1984), has a value of 0.26, indicating a distorted square-pyramidal coordination environment (the value for an ideal square-pyramid is 0 while that of an ideal trigonal bipyramid is 1). Each CuO_5 polyhedron shares its vertices with two $P_2O_7^{4-}$ anions, one of which is chelating and the other belongs to two different P_2O_7 groups (Fig. 2). This linkage leads to layers extending parallel to (010) (Fig. 3).

As in the crystal structures of $K_2CuP_2O_7$ and α-$Na_2CuP_2O_7$, the crystal structure of $KNaCuP_2O_7$ exhibits two independent sites hosting the K^+ and Na^+ cations. The first site is larger (‘*L*’) and is occupied by K^+ cations. It is limited by two neighbouring anionic layers (Fig. 3). The resulting KO_9 coordination polyhedron is considerably distorted (Fig. 4, Table 1). Its bond-valence sum is 0.98 valence units (Table 2). The second site is smaller (‘*S*’) and is occupied by Na^+ cations. It is surrounded by three CuO_5 and five PO_4 polyhedra, delimiting an ellipsoidal cavity as shown in Figs. 3 and 5. The irregular coordination sphere of Na^+ is made up of seven oxygen atoms and shows an effective coordination number (ECoN; Nespolo *et al.*, 2001) of 5.2 (for other ECoN values, see Table 2). The Na—O bonds lengths can be divided in groups of four short [2.249 (2)–2.4442 (19) Å] and three long [2.772 (2)–2.878 (2) Å] bonds (Table 1). Its bond-valence sum is 0.98 valence units (Table 2).

3. Database survey

Table 3 summarizes lattice parameters and the symmetry of related $MM'CuP_2O_7$ (M, M' = monovalent cation) compounds

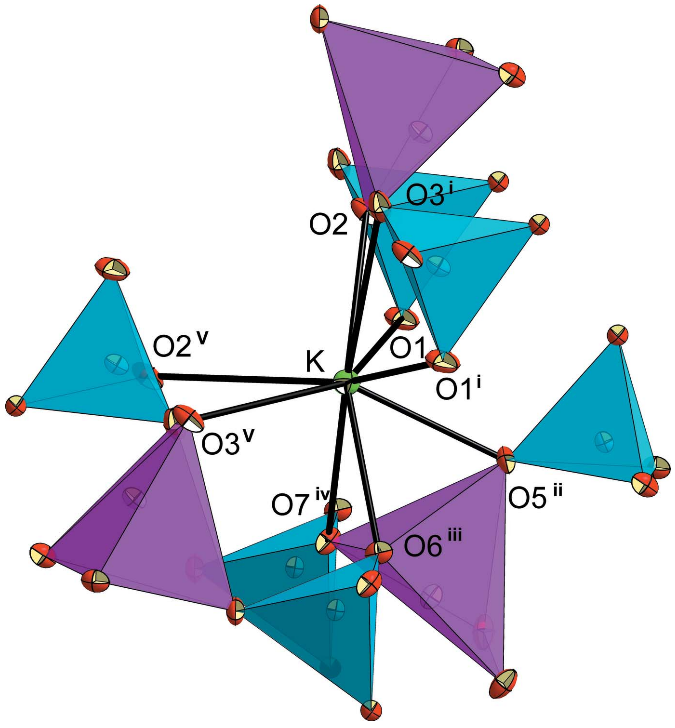


Figure 4
The nine-coordinated K^+ cation in the large ‘*L*’ site within the interlayer space in the structure of $KNaCuP_2O_7$. Displacement ellipsoids are drawn at 50% probability level. [Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$.]

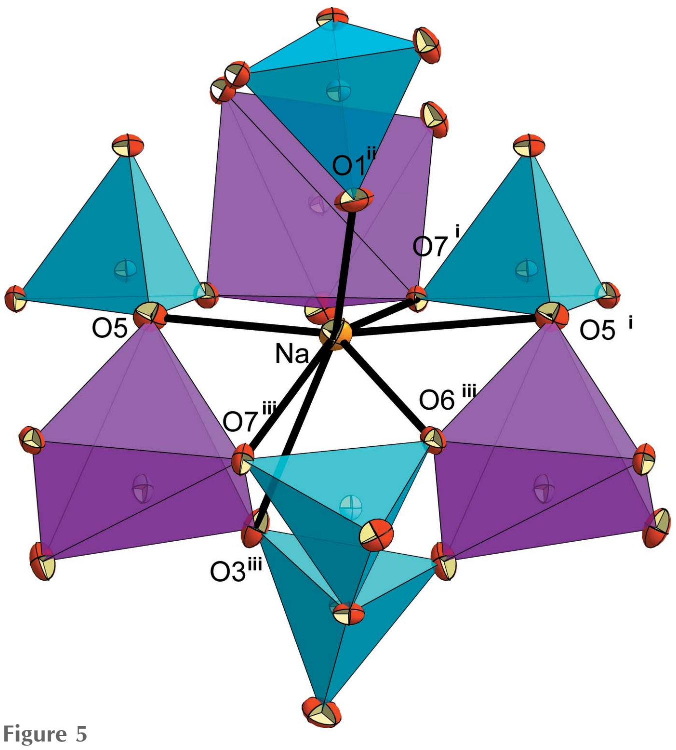


Figure 5
The surrounding of the seven-coordinated Na^+ cation in the ‘*S*’ site in the structure of $KNaCuP_2O_7$. Displacement ellipsoids are drawn at 50% probability level. [Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$].

Table 4
Experimental details.

Crystal data	
Chemical formula	$KNaCuP_2O_7$
M_r	299.57
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, b, c (Å)	5.176 (3), 13.972 (5), 9.067 (3)
β (°)	91.34 (2)
V (Å^3)	655.6 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.51
Crystal size (mm)	0.18 × 0.13 × 0.09
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.868, 0.997
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	3300, 1425, 1291
R_{int}	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.059, 1.01
No. of reflections	1425
No. of parameters	110
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.42

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2008) and *publCIF* (Westrip, 2010).

compiled in the ICSD (ICSD, 2017). It is apparent that the size of the cation(s) defines the structure type.

4. Synthesis and crystallization

Crystals of $KNaCuP_2O_7$ were obtained from a mixture of KH_2PO_4, NaH_2PO_4 and CuO in the molar ratio K:Na:Cu:P = 1:1:2:2. The stoichiometric mixture was finely ground and heated in a porcelain crucible at 623 K for 12 h to eliminate volatile products. The temperature was then increased to 873 K and held for 15 d until fusion was reached. The sample was slowly cooled (5 K d^{-1}) to 500 K and finally allowed to cool radiatively to room temperature. The product was washed with water and rinsed with an aqueous solution of HCl (low concentration). Only one type of regular light-blue prismatic crystals was observed. The obtained crystals were ground and checked by powder X-ray diffraction. Rietveld analysis with the program *TOPAS 4.2* (Coelho, 2009) revealed a single-phase product of $KNaCuP_2O_7$.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The occupancy of the Na^+ and K^+ sites was checked by independent refinement of the site occupation factors. In each case, full occupancy was observed without the contribution of the other cation. The maximum and minimum electron densities remaining in the difference-Fourier map are located 0.67 Å from O7 and 0.48 Å from Cu, respectively.

Acknowledgements

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Crystal structure of $KNaCuP_2O_7$, a new member of the diphosphate family

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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: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Potassium sodium copper(II) diphosphate(V)

Crystal data

$KNaCuP_2O_7$
$M_r = 299.57$
Monoclinic, $P2_1/n$
$a = 5.176$ (3) Å
$b = 13.972$ (5) Å
$c = 9.067$ (3) Å
$\beta = 91.34$ (2)°
$V = 655.6$ (5) Å^3
$Z = 4$
$F(000) = 580$
$D_x = 3.035$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 4.51$ mm^{-1}
$T = 298$ K
Prism, blue
0.18 × 0.13 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.868$, $T_{max} = 0.997$
3300 measured reflections
1425 independent reflections
1291 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.0°$, $\theta_{min} = 2.7°$
$h = -6 \rightarrow 6$
$k = -2 \rightarrow 17$
$l = -11 \rightarrow 11$
2 standard reflections every 120 min
intensity decay: 1.1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.059$
$S = 1.01$
1425 reflections
110 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 0.7316P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: SHELXL-2014/7 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0120 (9)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.76039 (5)	0.66590 (2)	0.21888 (3)	0.01093 (12)
P1	0.26527 (12)	0.54589 (5)	0.24314 (7)	0.01115 (15)
P2	0.25245 (11)	0.68972 (4)	0.02910 (6)	0.00898 (15)
Na	0.7521 (2)	0.70912 (8)	−0.16272 (11)	0.0192 (2)
K	0.75717 (11)	0.40697 (4)	0.38439 (6)	0.01850 (15)
O1	0.2223 (4)	0.44115 (15)	0.2502 (2)	0.0223 (4)
O2	0.5278 (3)	0.57557 (14)	0.3077 (2)	0.0176 (4)
O3	0.0576 (3)	0.60643 (15)	0.31633 (19)	0.0179 (4)
O4	0.2588 (3)	0.57729 (12)	0.07029 (18)	0.0126 (4)
O5	0.2938 (3)	0.69884 (14)	−0.13300 (18)	0.0160 (4)
O6	0.4685 (3)	0.73465 (13)	0.12308 (19)	0.0138 (4)
O7	−0.0125 (3)	0.72712 (13)	0.07246 (19)	0.0139 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.00808 (16)	0.01226 (18)	0.01244 (17)	0.00043 (11)	0.00010 (11)	0.00296 (11)
P1	0.0103 (3)	0.0102 (3)	0.0130 (3)	0.0000 (2)	0.0007 (2)	0.0029 (2)
P2	0.0088 (3)	0.0099 (3)	0.0082 (3)	0.0002 (2)	0.0008 (2)	0.0009 (2)
Na	0.0190 (5)	0.0213 (6)	0.0172 (5)	−0.0021 (4)	−0.0001 (4)	0.0020 (5)
K	0.0220 (3)	0.0153 (3)	0.0182 (3)	0.0022 (2)	−0.0008 (2)	0.0000 (2)
O1	0.0272 (10)	0.0115 (10)	0.0280 (10)	−0.0046 (8)	0.0001 (8)	0.0049 (8)
O2	0.0123 (8)	0.0198 (10)	0.0206 (9)	−0.0026 (8)	−0.0022 (7)	0.0093 (8)
O3	0.0151 (9)	0.0261 (10)	0.0126 (8)	0.0075 (8)	0.0008 (7)	0.0036 (8)
O4	0.0178 (8)	0.0093 (8)	0.0107 (8)	−0.0006 (7)	0.0012 (6)	−0.0003 (7)
O5	0.0213 (9)	0.0179 (9)	0.0088 (8)	0.0015 (8)	0.0025 (7)	0.0013 (7)
O6	0.0115 (8)	0.0115 (8)	0.0181 (8)	−0.0002 (7)	−0.0041 (6)	0.0011 (7)
O7	0.0091 (8)	0.0154 (9)	0.0173 (8)	0.0016 (7)	0.0030 (6)	0.0044 (8)

Geometric parameters (Å, º)

Cu—O2	1.9328 (18)	Na—P2$^{\text{i}}$	3.0977 (12)
Cu—O3$^{\text{i}}$	1.9427 (18)	Na—P2$^{\text{viii}}$	3.1316 (12)
Cu—O6	1.9743 (17)	Na—Cu$^{\text{ix}}$	3.2481 (11)
Cu—O7$^{\text{i}}$	1.9872 (17)	Na—Cu$^{\text{viii}}$	3.3550 (11)
Cu—O5$^{\text{ii}}$	2.3225 (19)	K—O2	2.721 (2)

Cu—Na^{ii}	3.2481 (11)	K—O5^{vii}	2.7245 (18)
Cu—Na^{iii}	3.3550 (11)	K—O1^{i}	2.764 (2)
Cu—K^{iv}	3.4966 (7)	K—O6^{x}	2.7969 (19)
Cu—Na	3.5117 (10)	K—O7^{xi}	2.8450 (19)
Cu—K	3.9169 (7)	K—O3^{v}	2.8630 (18)
P1—O1	1.482 (2)	K—O1	3.036 (2)
P1—O2	1.5246 (19)	K—O2^{v}	3.1973 (19)
P1—O3	1.5313 (19)	K—O3^{i}	3.257 (2)
P1—O4	1.6272 (17)	K—P1^{v}	3.4455 (9)
P1—K	3.4260 (9)	K—Cu^{x}	3.4965 (7)
P1—K^{v}	3.4455 (9)	O1—Na^{vii}	2.249 (2)
P1—K^{vi}	3.5329 (9)	O1—K^{vi}	2.764 (2)
P2—O5	1.4958 (17)	O2—K^{v}	3.1973 (19)
P2—O6	1.5252 (17)	O3—Cu^{vi}	1.9427 (18)
P2—O7	1.5277 (16)	O3—Na^{iii}	2.772 (2)
P2—O4	1.6148 (18)	O3—K^{v}	2.8630 (18)
P2—Na^{vi}	3.0977 (12)	O3—K^{vi}	3.257 (2)
P2—Na^{iii}	3.1316 (12)	O5—Cu^{ix}	2.3225 (19)
P2—Na	3.1617 (12)	O5—K^{vii}	2.7245 (18)
Na—O1^{vii}	2.249 (2)	O5—Na^{vi}	2.815 (2)
Na—O6^{viii}	2.397 (2)	O6—Na^{iii}	2.397 (2)
Na—O5	2.398 (2)	O6—K^{iv}	2.7968 (19)
Na—O7^{i}	2.4442 (19)	O7—Cu^{vi}	1.9872 (17)
Na—O3^{viii}	2.772 (2)	O7—Na^{vi}	2.4441 (19)
Na—O5^{i}	2.815 (2)	O7—K^{xii}	2.8451 (19)
Na—O7^{viii}	2.878 (2)	O7—Na^{iii}	2.878 (2)

O2—Cu—O3^{i}	91.46 (8)	O5—Na—Cu^{ix}	45.56 (5)
O2—Cu—O6	91.34 (7)	O7^{i}—Na—Cu^{ix}	127.14 (6)
O3^{i}—Cu—O6	176.22 (8)	O3^{viii}—Na—Cu^{ix}	36.58 (4)
O2—Cu—O7^{i}	160.62 (8)	O5^{i}—Na—Cu^{ix}	146.13 (6)
O3^{i}—Cu—O7^{i}	90.77 (7)	O7^{viii}—Na—Cu^{ix}	37.24 (4)
O6—Cu—O7^{i}	87.43 (7)	P2^{i}—Na—Cu^{ix}	150.57 (4)
O2—Cu—O5^{ii}	109.22 (7)	P2^{viii}—Na—Cu^{ix}	58.62 (2)
O3^{i}—Cu—O5^{ii}	92.15 (8)	P2—Na—Cu^{ix}	65.37 (2)
O6—Cu—O5^{ii}	84.52 (7)	O1^{vii}—Na—Cu^{viii}	108.65 (6)
O7^{i}—Cu—O5^{ii}	89.93 (7)	O6^{viii}—Na—Cu^{viii}	35.44 (4)
O2—Cu—Na^{ii}	134.76 (6)	O5—Na—Cu^{viii}	148.47 (6)
O3^{i}—Cu—Na^{ii}	58.24 (7)	O7^{i}—Na—Cu^{viii}	81.19 (5)
O6—Cu—Na^{ii}	118.00 (6)	O3^{viii}—Na—Cu^{viii}	77.32 (5)
O7^{i}—Cu—Na^{ii}	61.20 (5)	O5^{i}—Na—Cu^{viii}	43.13 (4)
O5^{ii}—Cu—Na^{ii}	47.48 (5)	O7^{viii}—Na—Cu^{viii}	86.18 (4)
O2—Cu—Na^{iii}	72.89 (6)	P2^{i}—Na—Cu^{viii}	64.76 (2)
O3^{i}—Cu—Na^{iii}	134.08 (6)	P2^{viii}—Na—Cu^{viii}	57.50 (2)
O6—Cu—Na^{iii}	44.76 (5)	P2—Na—Cu^{viii}	151.44 (4)
O7^{i}—Cu—Na^{iii}	118.06 (6)	Cu^{ix}—Na—Cu^{viii}	103.22 (3)
O5^{ii}—Cu—Na^{iii}	55.94 (5)	O2—K—O5^{vii}	102.87 (6)
Na^{ii}—Cu—Na^{iii}	103.22 (3)	O2—K—O1^{i}	96.73 (6)

O2—Cu—K^{iv}	136.72 (6)	O5^{vii}—K—O1^{i}	78.10 (6)
O3^{i}—Cu—K^{iv}	123.31 (6)	O2—K—O6^{x}	163.30 (6)
O6—Cu—K^{iv}	53.04 (5)	O5^{vii}—K—O6^{x}	63.38 (5)
O7^{i}—Cu—K^{iv}	54.45 (5)	O1^{i}—K—O6^{x}	71.95 (6)
O5^{ii}—Cu—K^{iv}	51.11 (5)	O2—K—O7^{xi}	127.36 (6)
Na^{ii}—Cu—K^{iv}	65.54 (2)	O5^{vii}—K—O7^{xi}	66.49 (5)
Na^{iii}—Cu—K^{iv}	64.45 (2)	O1^{i}—K—O7^{xi}	127.46 (6)
O2—Cu—Na	121.97 (6)	O6^{x}—K—O7^{xi}	58.05 (5)
O3^{i}—Cu—Na	120.87 (5)	O2—K—O3^{v}	115.68 (6)
O6—Cu—Na	59.42 (5)	O5^{vii}—K—O3^{v}	141.38 (6)
O7^{i}—Cu—Na	42.40 (5)	O1^{i}—K—O3^{v}	98.78 (6)
O5^{ii}—Cu—Na	115.40 (5)	O6^{x}—K—O3^{v}	78.91 (6)
Na^{ii}—Cu—Na	102.98 (2)	O7^{xi}—K—O3^{v}	87.26 (6)
Na^{iii}—Cu—Na	103.54 (2)	O2—K—O1	51.17 (5)
K^{iv}—Cu—Na	64.59 (2)	O5^{vii}—K—O1	71.36 (6)
O2—Cu—K	39.55 (6)	O1^{i}—K—O1	126.29 (7)
O3^{i}—Cu—K	56.02 (6)	O6^{x}—K—O1	125.76 (6)
O6—Cu—K	127.43 (5)	O7^{xi}—K—O1	77.84 (5)
O7^{i}—Cu—K	131.41 (5)	O3^{v}—K—O1	132.24 (6)
O5^{ii}—Cu—K	122.07 (5)	O2—K—O2^{v}	87.12 (5)
Na^{ii}—Cu—K	112.35 (2)	O5^{vii}—K—O2^{v}	137.25 (6)
Na^{iii}—Cu—K	110.35 (2)	O1^{i}—K—O2^{v}	142.70 (6)
K^{iv}—Cu—K	172.759 (11)	O6^{x}—K—O2^{v}	109.37 (5)
Na—Cu—K	122.43 (2)	O7^{xi}—K—O2^{v}	74.42 (5)
O1—P1—O2	112.67 (12)	O3^{v}—K—O2^{v}	47.81 (5)
O1—P1—O3	114.78 (12)	O1—K—O2^{v}	84.43 (5)
O2—P1—O3	108.17 (11)	O2—K—O3^{i}	54.42 (5)
O1—P1—O4	107.95 (11)	O5^{vii}—K—O3^{i}	110.06 (5)
O2—P1—O4	107.13 (10)	O1^{i}—K—O3^{i}	49.03 (5)
O3—P1—O4	105.64 (10)	O6^{x}—K—O3^{i}	119.15 (5)
O1—P1—K	62.31 (8)	O7^{xi}—K—O3^{i}	176.12 (5)
O2—P1—K	50.40 (8)	O3^{v}—K—O3^{i}	94.86 (5)
O3—P1—K	132.38 (7)	O1—K—O3^{i}	102.97 (5)
O4—P1—K	120.75 (7)	O2^{v}—K—O3^{i}	109.40 (5)
O1—P1—K^{v}	97.92 (9)	O2—K—P1	25.58 (4)
O2—P1—K^{v}	67.78 (7)	O5^{vii}—K—P1	86.44 (4)
O3—P1—K^{v}	55.22 (7)	O1^{i}—K—P1	112.63 (5)
O4—P1—K^{v}	153.15 (7)	O6^{x}—K—P1	148.42 (4)
K—P1—K^{v}	77.51 (2)	O7^{xi}—K—P1	102.86 (4)
O1—P1—K^{vi}	47.78 (8)	O3^{v}—K—P1	128.38 (4)
O2—P1—K^{vi}	132.43 (7)	O1—K—P1	25.61 (4)
O3—P1—K^{vi}	67.06 (8)	O2^{v}—K—P1	85.94 (4)
O4—P1—K^{vi}	119.91 (7)	O3^{i}—K—P1	78.37 (3)
K—P1—K^{vi}	96.10 (2)	O2—K—P1^{v}	93.47 (4)
K^{v}—P1—K^{vi}	72.974 (19)	O5^{vii}—K—P1^{v}	156.78 (4)
O5—P2—O6	113.20 (10)	O1^{i}—K—P1^{v}	116.62 (5)
O5—P2—O7	111.96 (10)	O6^{x}—K—P1^{v}	102.54 (4)
O6—P2—O7	111.49 (10)	O7^{xi}—K—P1^{v}	90.50 (4)

O5—P2—O4	107.91 (10)	O3^{v}—K—P1^{v}	26.06 (4)
O6—P2—O4	105.10 (10)	O1—K—P1^{v}	108.15 (4)
O7—P2—O4	106.66 (10)	O2^{v}—K—P1^{v}	26.19 (3)
O5—P2—Na^{vi}	65.03 (7)	O3^{i}—K—P1^{v}	92.83 (4)
O6—P2—Na^{vi}	150.48 (8)	P1—K—P1^{v}	102.49 (2)
O7—P2—Na^{vi}	51.00 (7)	O2—K—Cu^{x}	139.21 (4)
O4—P2—Na^{vi}	103.13 (7)	O5^{vii}—K—Cu^{x}	41.57 (4)
O5—P2—Na^{iii}	147.30 (9)	O1^{i}—K—Cu^{x}	93.78 (5)
O6—P2—Na^{iii}	48.05 (7)	O6^{x}—K—Cu^{x}	34.34 (3)
O7—P2—Na^{iii}	66.21 (7)	O7^{xi}—K—Cu^{x}	34.63 (3)
O4—P2—Na^{iii}	103.48 (7)	O3^{v}—K—Cu^{x}	101.36 (5)
Na^{vi}—P2—Na^{iii}	116.33 (3)	O1—K—Cu^{x}	91.51 (4)
O5—P2—Na	46.71 (7)	O2^{v}—K—Cu^{x}	107.32 (4)
O6—P2—Na	70.95 (7)	O3^{i}—K—Cu^{x}	141.53 (4)
O7—P2—Na	149.66 (7)	P1—K—Cu^{x}	115.54 (2)
O4—P2—Na	101.43 (7)	P1^{v}—K—Cu^{x}	116.45 (2)
Na^{vi}—P2—Na	111.56 (3)	P1—O1—Na^{vii}	153.68 (14)
Na^{iii}—P2—Na	118.02 (3)	P1—O1—K^{vi}	108.83 (11)
O1^{vii}—Na—O6^{viii}	89.29 (8)	Na^{vii}—O1—K^{vi}	93.05 (7)
O1^{vii}—Na—O5	92.89 (8)	P1—O1—K	92.08 (9)
O6^{viii}—Na—O5	126.37 (7)	Na^{vii}—O1—K	86.20 (7)
O1^{vii}—Na—O7^{i}	111.80 (8)	K^{vi}—O1—K	126.29 (7)
O6^{viii}—Na—O7^{i}	116.12 (7)	P1—O2—Cu	125.16 (11)
O5—Na—O7^{i}	112.48 (7)	P1—O2—K	104.02 (10)
O1^{vii}—Na—O3^{viii}	150.23 (8)	Cu—O2—K	113.55 (8)
O6^{viii}—Na—O3^{viii}	79.37 (6)	P1—O2—K^{v}	86.03 (8)
O5—Na—O3^{viii}	72.83 (6)	Cu—O2—K^{v}	128.21 (9)
O7^{i}—Na—O3^{viii}	97.87 (7)	K—O2—K^{v}	92.88 (5)
O1^{vii}—Na—O5^{i}	85.37 (7)	P1—O3—Cu^{vi}	126.56 (11)
O6^{viii}—Na—O5^{i}	67.10 (6)	P1—O3—Na^{iii}	106.61 (10)
O5—Na—O5^{i}	166.46 (9)	Cu^{vi}—O3—Na^{iii}	85.17 (8)
O7^{i}—Na—O5^{i}	56.39 (5)	P1—O3—K^{v}	98.72 (8)
O3^{viii}—Na—O5^{i}	114.42 (7)	Cu^{vi}—O3—K^{v}	134.68 (8)
O1^{vii}—Na—O7^{viii}	91.46 (7)	Na^{iii}—O3—K^{v}	83.27 (6)
O6^{viii}—Na—O7^{viii}	56.27 (5)	P1—O3—K^{vi}	87.28 (9)
O5—Na—O7^{viii}	70.10 (6)	Cu^{vi}—O3—K^{vi}	94.34 (7)
O7^{i}—Na—O7^{viii}	156.06 (5)	Na^{iii}—O3—K^{vi}	163.09 (7)
O3^{viii}—Na—O7^{viii}	59.34 (5)	K^{v}—O3—K^{vi}	85.14 (5)
O5^{i}—Na—O7^{viii}	123.32 (6)	P2—O4—P1	119.01 (11)
O1^{vii}—Na—P2^{i}	93.49 (6)	P2—O5—Cu^{ix}	128.83 (11)
O6^{viii}—Na—P2^{i}	94.77 (5)	P2—O5—Na	106.28 (10)
O5—Na—P2^{i}	138.41 (6)	Cu^{ix}—O5—Na	86.95 (7)
O7^{i}—Na—P2^{i}	29.06 (4)	P2—O5—K^{vii}	139.70 (11)
O3^{viii}—Na—P2^{i}	114.67 (5)	Cu^{ix}—O5—K^{vii}	87.32 (5)
O5^{i}—Na—P2^{i}	28.80 (4)	Na—O5—K^{vii}	90.88 (6)
O7^{viii}—Na—P2^{i}	150.56 (5)	P2—O5—Na^{vi}	86.16 (8)
O1^{vii}—Na—P2^{viii}	96.04 (6)	Cu^{ix}—O5—Na^{vi}	80.94 (6)
O6^{viii}—Na—P2^{viii}	28.24 (4)	Na—O5—Na^{vi}	166.46 (9)

O5—Na—P2$^{\text{viii}}$	98.55 (5)	K$^{\text{vii}}$—O5—Na$^{\text{vi}}$	82.58 (6)
O7$^{\text{i}}$—Na—P2$^{\text{viii}}$	136.17 (6)	P2—O6—Cu	126.10 (11)
O3$^{\text{viii}}$—Na—P2$^{\text{viii}}$	61.77 (4)	P2—O6—Na$^{\text{iii}}$	103.71 (9)
O5$^{\text{i}}$—Na—P2$^{\text{viii}}$	94.99 (5)	Cu—O6—Na$^{\text{iii}}$	99.80 (7)
O7$^{\text{viii}}$—Na—P2$^{\text{viii}}$	29.06 (3)	P2—O6—K$^{\text{iv}}$	134.97 (10)
P2$^{\text{i}}$—Na—P2$^{\text{viii}}$	121.50 (4)	Cu—O6—K$^{\text{iv}}$	92.63 (6)
O1$^{\text{vii}}$—Na—P2	99.77 (6)	Na$^{\text{iii}}$—O6—K$^{\text{iv}}$	89.12 (6)
O6$^{\text{viii}}$—Na—P2	151.35 (6)	P2—O7—Cu$^{\text{vi}}$	124.98 (11)
O5—Na—P2	27.01 (4)	P2—O7—Na$^{\text{vi}}$	99.93 (9)
O7$^{\text{i}}$—Na—P2	85.78 (5)	Cu$^{\text{vi}}$—O7—Na$^{\text{vi}}$	104.36 (7)
O3$^{\text{viii}}$—Na—P2	79.46 (5)	P2—O7—K$^{\text{xii}}$	137.96 (10)
O5$^{\text{i}}$—Na—P2	140.25 (5)	Cu$^{\text{vi}}$—O7—K$^{\text{xii}}$	90.92 (6)
O7$^{\text{viii}}$—Na—P2	96.10 (4)	Na$^{\text{vi}}$—O7—K$^{\text{xii}}$	89.80 (6)
P2$^{\text{i}}$—Na—P2	111.56 (3)	P2—O7—Na$^{\text{iii}}$	84.73 (7)
P2$^{\text{viii}}$—Na—P2	123.17 (4)	Cu$^{\text{vi}}$—O7—Na$^{\text{iii}}$	81.55 (6)
O1$^{\text{vii}}$—Na—Cu$^{\text{ix}}$	115.94 (6)	Na$^{\text{vi}}$—O7—Na$^{\text{iii}}$	167.87 (8)
O6$^{\text{viii}}$—Na—Cu$^{\text{ix}}$	86.18 (5)	K$^{\text{xii}}$—O7—Na$^{\text{iii}}$	79.43 (5)

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