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$K_3Ga_2(PO_4)_3$ and $Na_3Ga(PO_4)_2$

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The structures of tripotassium digallium tris(phosphate), $K_3Ga_2(PO_4)_3$, and trisodium gallium bis(phosphate), $Na_3Ga(PO_4)_2$, have different irregular one-dimensional alkali ion-containing channels along the *a* axis of the orthorhombic and triclinic unit cells, respectively. The anionic subsystems consist of vortex-linked PO_4 tetrahedra and GaO_4 tetrahedra or GaO_5 trigonal bipyramids in the first and second structure, respectively.

Comment

Several sodium and potassium phosphates containing gallium are known, such as $K_2Ga_2P_8O_{24}$ (Palkina *et al.*, 1979) and $Na_3GaP_8O_{23}$ (Palkina *et al.*, 1993). A short overview of condensed phosphates of alkaline and trivalent metals was given by Grunze *et al.* (1990). We report here the structures of $K_3Ga_2(PO_4)_3$, (I), and $Na_3Ga(PO_4)_2$, (II). The structure of (I) appears to be isotypic with that of $K_3Al_2(PO_4)_3$ (Nandini Devi & Vidyasagar, 2000). It is noted that these structures are related to the NASICON super ionic conductors, such as $Na_3Sc_2(PO_4)_3$ (Susman *et al.*, 1983) or $Na_3Fe_2(PO_4)_3$ (d'Yvoire *et al.*, 1983).

Fig. 1 shows the constituent polyhedra for the structure of (I). Both trivalent Ga and pentavalent P are in tetrahedral coordination by oxygen, with Ga—O distances ranging between 1.799 (4) and 1.820 (4) Å, and P—O distances ranging between 1.489 (4) and 1.597 (4) Å. The coordination environment of the three independent K atoms is variable and irregular. Atom K6 is approximately at the base of a tetrahedron formed by atoms O11, O13, O19 and O20, whereas atom K4 is sixfold and K5 sevenfold coordinated by oxygen. The Brown criterion that a ligand should contribute at least 4% to the total bond-valence sum in order to be considered being bonded [Brown, 2002; calculations using *VaList* (Wills & Brown, 1999)] gives a maximum bonded distance of about 3.2 Å for K—O. Not including the K4—O13 distance [3.114 (5) Å and a bond-valence contribution (BVC) of 0.070] and the K4—O14 distance [3.210 (5) Å, BVC = 0.054] gives a bond-valence sum (BVS) for atom K4 of 0.991. For atom K5, the bond-valence calculations are less conclusive: in order to arrive at a BVS close to 1.00, the K5—O20 contribution [3.000 (5) Å, BVC = 0.096, thus beyond the Brown criterion of

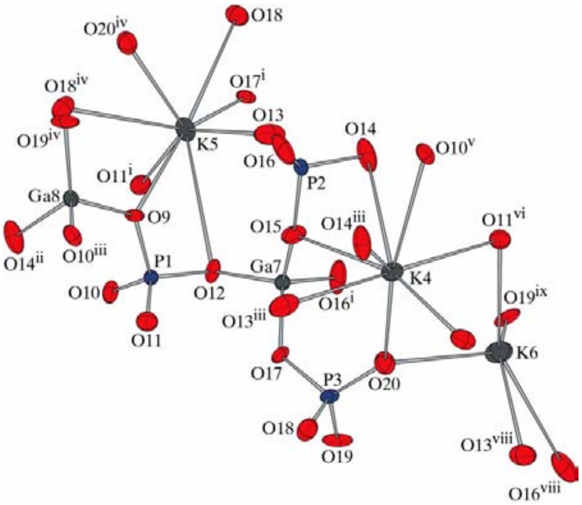

Figure 1
The full coordination environment around each unique metal centre in the asymmetric unit of (I). Symmetry codes are as given in Table 1. Displacement ellipsoids are drawn at the 75% probability level.

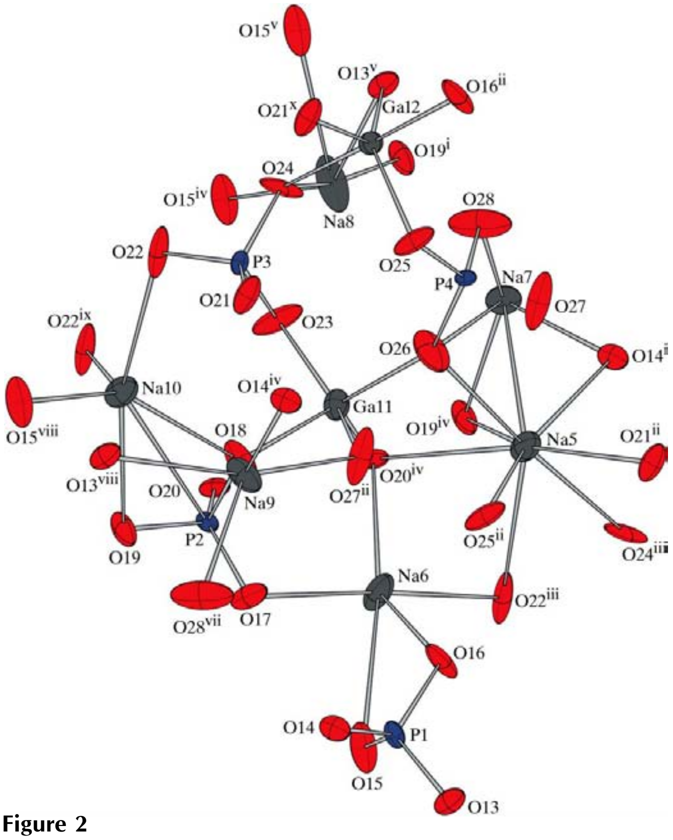

Figure 2
The full coordination environment around each unique metal centre in the asymmetric unit of (II). Symmetry codes are as given in Table 2. Displacement ellipsoids are drawn at the 75% probability level.

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4%] should not be included. Somewhat arbitrarily, however, in Fig. 1 K—O bonds are drawn up to 3.0 Å, thus including the K5—O20 contact.

The constituent polyhedra for the structure of (II) are given in Fig. 2. The P-atom environment is very similar to that in the structure of (I), with P—O distances in the range 1.488 (4)–1.576 (3) Å. The coordination of Ga, however, is not tetrahedral but trigonal bipyrimadal, with Ga—O distances in the range 1.840 (3)–1.968 (4) Å. The Na environment is like the K environment in (I), *viz*. variable and irregular. There are six independent Na atoms, one fourfold coordinated, four fivefold coordinated and one sevenfold coordinated.

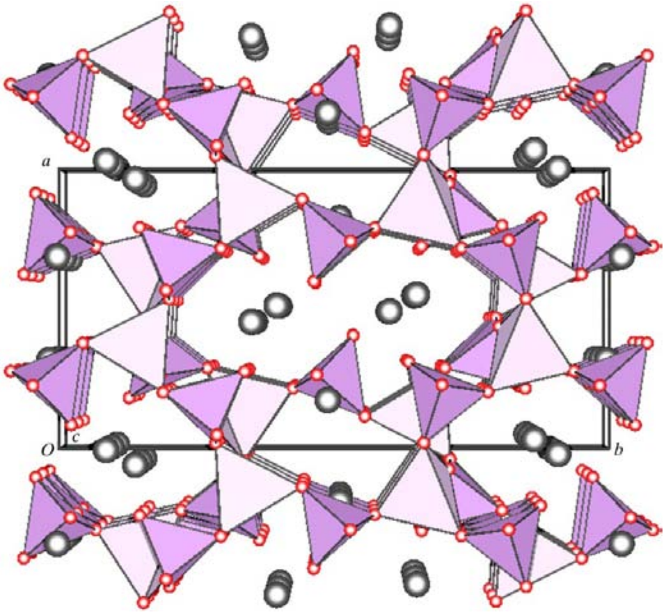

Figure 3
The polyhedral network of (I), viewed along the *c* axis. GaO_4 tetrahedra are depicted with light shading and PO_4 tetrahedra with medium shading.

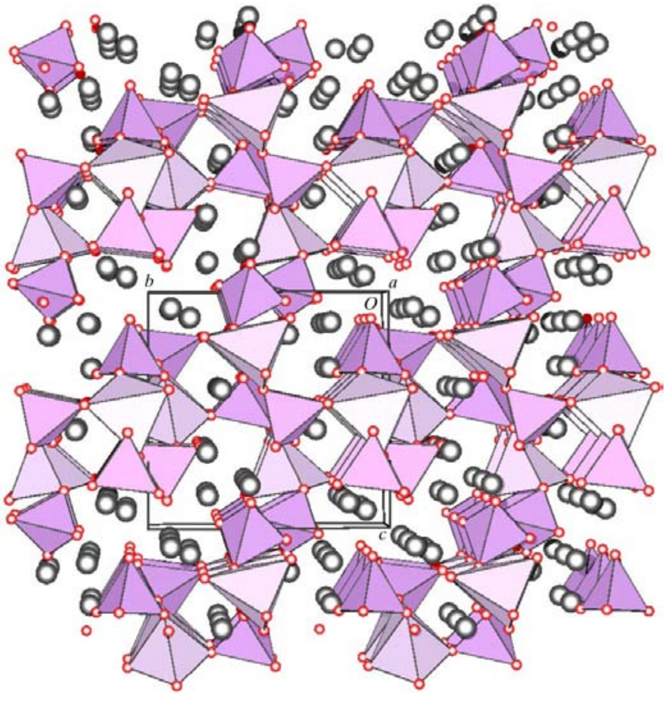

Figure 4
The polyhedral network of (II), viewed along the *a* axis. GaO_4 tetrahedra are depicted with light shading and PO_4 tetrahedra with medium shading.

The crystallographic symmetry of the structures of compounds (I) and (II) is very different, *viz*. $Pna2_1$ and $P\overline{1}$, respectively, but their topology is quite similar. They consist of three-dimensional $[Ga_2P_3O_{12}]^{3-}$ and $[GaP_2O_8]^{2-}$ anionic frameworks for (I) and (II), respectively, with one-dimensional channels occupied by the counter-cations K^+ and Na^+. The anionic subsystem of (I) consists of an interconnected network of corner-sharing tetrahedra, where both types of tetrahedra, *viz*. GaO_4 and PO_4, are only connected to each other. Fig. 3 gives a view down the *c* axis, showing the irregularly shaped K^+ one-dimensional channels of different size. The anionic famework of (II) consists of GaO_4 trigonal bipyramids which share all five corners with PO_4 tetrahedra. Fig. 4 gives a view down the *a* axis, showing different irregularly shaped one-dimensional Na^+ channels. The largest tunnels are delimited by 12 vertex-linked GaO_4 trigonal bipyramids and PO_4 tetrahedra.

Experimental

The $GaPO_4$ compound with the α-quartz structure was obtained in powder form by dissolving 4 *N* Ga metal in nitric acid followed by precipitation with phosphoric acid, as described by Beaurain *et al.* (2006). The K_2MoO_4 and Na_2PO_3F used as starting materials were commercial products (Fluka). The crystal-growth experiments reported were carried out in air in a single temperature zone in an SiC resistance heater furnace and a Eurotherm temperature controller. For compound (I), 85 wt% of K_2MoO_4 was mixed with 15 wt% of α-$GaPO_4$ and homogenized in an agate mortar. For compound (II), 60 wt% of Na_2PO_3F was mixed with 40 wt% of $GaPO_4$. The mixtures were placed in Pt crucibles covered with a lid, heated from room temperature to 1223 K at a ramp rate of 150 K h^{-1} and held at this temperature for 5 h for homogenization. The melted charges were then cooled slowly at a rate of 2 K h^{-1} to 873 K. After 5 h at 873 K, the charges were cooled to room temperature at a rate of 200 K h^{-1}.

Compound (I)

Crystal data

$K_3Ga_2(PO_4)_3$
M_r = 541.65
Orthorhombic, $Pna2_1$
a = 8.67110 (15) Å
b = 17.0109 (3) Å
c = 8.38857 (16) Å
V = 1237.34 (4) Å^3
Z = 4
Mo *Kα* radiation
μ = 5.81 mm^{-1}
T = 293 K
0.25 × 0.16 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
T_{min} = 0.507, T_{max} = 1.000 (expected range = 0.252–0.498)
24311 measured reflections
3885 independent reflections
3024 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 0.98$
3885 reflections
182 parameters
1 restraint
$\Delta\rho_{\max} = 1.32$ e Å^{-3}
$\Delta\rho_{\min} = -1.74$ e Å^{-3}
Absolute structure: Flack (1983), with 1691 Friedel pairs
Flack parameter: 0.014 (15)

Table 1
Selected bond lengths (Å) for (I).

P1—O9	1.540 (4)	K4—O11$^{\rm vi}$	2.833 (4)
P1—O10	1.542 (4)	K4—O13$^{\rm iii}$	3.114 (5)
P1—O11	1.500 (5)	K4—O14	3.210 (5)
P1—O12	1.546 (4)	K4—O14$^{\rm iii}$	2.815 (5)
P2—O13	1.489 (5)	K4—O15	2.956 (5)
P2—O14	1.539 (5)	K4—O18$^{\rm vii}$	2.663 (4)
P2—O15	1.563 (5)	K4—O20	2.690 (5)
P2—O16	1.534 (5)	K5—O9	2.771 (4)
P3—O17	1.564 (4)	K5—O11$^{\rm i}$	2.706 (4)
P3—O18	1.495 (4)	K5—O12	3.348 (4)
P3—O19	1.596 (4)	K5—O13	2.636 (5)
P3—O20	1.498 (4)	K5—O17$^{\rm i}$	2.833 (4)
Ga7—O16$^{\rm i}$	1.815 (4)	K5—O18$^{\rm iv}$	2.879 (5)
Ga7—O12	1.817 (4)	K5—O18$^{\rm i}$	2.960 (4)
Ga7—O15	1.820 (4)	K5—O20$^{\rm iv}$	3.000 (5)
Ga7—O17	1.812 (4)	K6—O11$^{\rm vi}$	2.742 (5)
Ga8—O14$^{\rm ii}$	1.820 (4)	K6—O13$^{\rm viii}$	2.709 (5)
Ga8—O10$^{\rm iii}$	1.815 (4)	K6—O16$^{\rm viii}$	3.239 (5)
Ga8—O19$^{\rm iv}$	1.798 (4)	K6—O19$^{\rm ix}$	2.728 (5)
Ga8—O9	1.827 (4)	K6—O20	2.663 (4)
K4—O10$^{\rm v}$	2.930 (4)		

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

Compound (II)

Crystal data

$Na_3Ga(PO_4)_2$
$M_r = 328.64$
Triclinic, $P\overline{1}$
$a = 8.8595$ (3) Å
$b = 8.8773$ (3) Å
$c = 9.1972$ (3) Å
$\alpha = 88.970$ (3)°
$\beta = 70.982$ (3)°
$\gamma = 87.949$ (3)°
$V = 683.41$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.70$ mm^{-1}
$T = 293$ K
0.16 × 0.16 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{\min} = 0.713$, $T_{\max} = 1.000$ (expected range = 0.564–0.791)
13240 measured reflections
4355 independent reflections
2972 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.138$
$S = 1.00$
4355 reflections
253 parameters
$\Delta\rho_{\max} = 3.29$ e Å^{-3}
$\Delta\rho_{\min} = -1.79$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

P1—O13	1.569 (3)	Na7—O19$^{\rm iv}$	2.358 (4)
P1—O14	1.510 (3)	Na7—O17$^{\rm i}$	2.247 (4)
P1—O15	1.506 (3)	Na7—O28	2.317 (4)
P1—O16	1.543 (4)	Na8—O15$^{\rm iv}$	2.273 (4)
P2—O17	1.507 (3)	Na8—O19$^{\rm i}$	2.395 (4)
P2—O18	1.545 (4)	Na8—O13$^{\rm v}$	2.619 (4)
P2—O19	1.517 (3)	Na8—O15$^{\rm v}$	2.772 (5)
P2—O20	1.575 (3)	Na8—O24	2.575 (5)
P3—O21	1.549 (3)	Na9—O27$^{\rm ii}$	2.336 (4)
P3—O22	1.494 (3)	Na9—O14$^{\rm vi}$	2.340 (4)
P3—O23	1.528 (3)	Na9—O28$^{\rm vii}$	2.256 (4)
P3—O24	1.525 (4)	Na9—O13$^{\rm viii}$	2.543 (4)
P4—O25	1.551 (3)	Na9—O18	2.532 (4)
P4—O26	1.531 (4)	Na10—O15$^{\rm viii}$	2.282 (4)
P4—O27	1.523 (4)	Na10—O22$^{\rm ix}$	2.239 (4)
P4—O28	1.489 (4)	Na10—O18	2.429 (4)
Na5—O14$^{\rm i}$	2.341 (4)	Na10—O19	2.508 (4)
Na5—O25$^{\rm ii}$	2.444 (4)	Na10—O22	2.555 (5)
Na5—O24$^{\rm iii}$	2.481 (4)	Ga11—O27$^{\rm ii}$	1.873 (4)
Na5—O21$^{\rm ii}$	2.703 (4)	Ga11—O20$^{\rm iv}$	1.857 (3)
Na5—O19$^{\rm iv}$	2.726 (4)	Ga11—O18	1.966 (3)
Na5—O20$^{\rm iv}$	2.781 (4)	Ga11—O23	1.841 (3)
Na5—O26	2.503 (4)	Ga11—O26	1.923 (4)
Na6—O22$^{\rm iii}$	2.344 (4)	Ga12—O16$^{\rm ii}$	1.901 (4)
Na6—O20$^{\rm iv}$	2.390 (4)	Ga12—O21$^{\rm x}$	1.889 (3)
Na6—O15	2.783 (5)	Ga12—O13$^{\rm v}$	1.886 (3)
Na6—O16	2.348 (4)	Ga12—O24	1.968 (4)
Na6—O17	2.301 (4)	Ga12—O25	1.905 (3)
Na7—O14$^{\rm i}$	2.314 (4)		

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

Structure (I) was solved in the space group $P1$ in 216 iterations using default values for the charge flipping parameters, followed by five low-density elimination cycles. The systematic reflection extinctions pointed to $P2_1nb$ or $Pmnb$ as possible space-group symmetries. The noncentrosymmetric space group $P2_1nb$ prevaled over the centrosymmetric space group $Pmnb$ since an analysis of the symmetry operations in the resulting electron-density map (Palatinus & Chapuis, 2007), *i.e.* before attribution of the atom types, showed that the m_x mirror plane and the inversion centre were clearly absent with agreement factors of 0.37 and 0.45, respectively (0.10, 0.03, and 0.07 for the 2_1 screw axis, the n-glide and the b-glide, respectively). The coordinates were subsequently transformed to those compatable with the standard setting of $P2_1nb$, *viz.* $Pna2_1$. The refined Flack (1983) parameter of (I) showed that the crystal was single-domain. The structure of (II) was solved in a similar way and the presence of the inversion centre was established on the basis of an analysis of the electron-density map before attribution of the atom types.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *DRAWxtl* (Finger *et al.*, 2007); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3036). Services for accessing these data are described at the back of the journal.

References

Beaurain, M., Armand, P. & Papet, P. (2006). *J. Cryst. Growth*, **294**, 396–400.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model.* Oxford University Press.
Finger, L. W., Kroeker, M. & Toby, B. H. (2007). *J. Appl. Cryst.* **40**, 188–192.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Grunze, H., Chudinova, N. N. & Grunze, I. (1990). *Phosphorus Sulfur Silicon Relat. Elem.* **51–52**, 93–96.

Nandini Devi, R. & Vidyasagar, K. (2000). *Inorg. Chem.* **39**, 2391–2396.

Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.5. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.

Palkina, K. K., Maksimova, S. I., Chubiskova, N. T., Chudinova, N. N. & Karmanovskaya, N. B. (1993). *Izv. Akad. Nauk SSSR Neog. Mater.* **29**, 119–120.

Palkina, K. K., Maksimova, S. I., Kuznetsov, V. G. & Chudinova, N. N. (1979). *Dokl. Akad. Nauk SSSR*, **245**, 1386–1387.

Susman, S., Delbecq, C. J., Brun, T. O. & Prince, E. (1983). *Solid State Ionics*, **9/10**, 839–844.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Wills, A. S. & Brown, I. D. (1999). *VaList*. CEA, France.

Yvoire, F. d′, Pintard-Screpel, M., Bretey, E. & de la Rochere, M. (1983). *Solid State Ionics*, **9/10**, 851–857.