Structural features of the oxidonitridophosphates $K_3M^{III}(PO_3)_3N$ ($M^{III} = \text{Al, Ga}$)

Igor V. Zatovsky,a* Ivan V. Ogorodnyk,b Vyacheslav N. Baumer,c Ivan D. Zhilyak,d Ruslana V. Hordaa and Nataliya Yu. Strutynskae

*aF.D. Ovcharenko Institute of Bicolloidal Chemistry, NAS Ukraine, 42 Acad. Vernadskoho blv., 03142 Kyiv, Ukraine, bShumUkraine LLC, 18 Chigorina Str., office 429, 01042 Kyiv, Ukraine, cSTC “Institute for Single Crystals”, NAS of Ukraine, 60 Lenin ave., 61001 Kharkiv, Ukraine, dFaculty of Horticulture, Ecology and Plants Protection, Ukrainian National University of Horticulture, 1 Instytutska str., 20305 Uman, Cherkesky region, Ukraine, and eDepartment of Inorganic Chemistry, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska str., 01601, Kyiv, Ukraine.

*Correspondence e-mail: zvigo@ukr.net

Cubic crystals of tripotassium aluminium (or gallium) nitridotriphosphate, $K_3M^{III}(PO_3)_3N$ ($M^{III} = \text{Al, Ga}$), were grown by application of the self-flux method. In their isostructural crystal structures, all metal cations and the N atom occupy special positions with site symmetry 3, while the P and O atoms are situated in general positions. The three-dimensional framework of these oxidonitridophosphates is built up from $[M^{III}O_6]$ octahedra linked together via $(PO_3)_3N$ groups. The latter are formed from three PO$_3$N tetrahedra sharing a common N atom. The coordination environments of the three potassium cations are represented by two types of polyhedra, viz. KO$_9$ for one and KO$_9$N for the other two cations. An unusual tetradentate type of coordination for the latter potassium cations by the $(PO_3)_3N^6-$ anion is observed. These $K_3M^{III}(PO_3)_3N$ ($M^{III} = \text{Al, Ga}$) compounds are isostructural with the $Na_3M^{III}(PO_3)_3N$ ($M^{III} = \text{Al, V, Ti}$) compounds.

1. Chemical context

Oxidonitridophosphates with general compositions $M'_2M^{III}(PO_3)_3N$ and $M'_2M^{II}(PO_3)_2N$ ($M' = \text{Li, Na, K}$; $M^{III} = \text{Al, Cr, Ga, V and Ti}$; $M^{II} = \text{Mg, Fe}$) have been prepared by solid-state synthesis (Feldmann, 1987a,b; Massiot et al., 1996; Conance et al., 1996), high-temperature thermal ammonolysis (Kim & Kim, 2013; Kim et al., 2017; Zhang et al., 2017), flux-growth (Zatovsky et al., 2006) or solid–solid ion-exchange (Liu et al., 2018). In recent years, oxidonitridophosphates containing the $(PO_3)_3N^6-$ anion have been intensively studied as promising cathode materials for Na-ion and Li-ion batteries. In particular, ionic conductivities and redox properties were investigated in detail for $Na_3Ti(PO_3)_3N$ (Liu et al., 2014), $Na_3V(PO_3)_3N$ (Reynaud et al., 2017; Kim et al., 2017; Zhang et al., 2017; Xiao et al., 2021; Wang et al., 2021), $Li_3V(PO_3)_3N$ (Liu et al., 2018), $Na_2Fe_2(PO_3)_3N$ and $Li_2Fe_2(PO_3)_3N$ (Liu et al., 2013), $Na_2Mg_2(PO_3)_3N$ (Cosby et al., 2020), and $Li_2Mg_2(PO_3)_3N$ (Liu et al., 2017). In addition, rare-earth-doped $Na_3Al(PO_3)_3N$ has been studied as a promising phosphor (Bang et al., 2013). However, the structural data for oxidonitridophosphates include only Na- or Li-containing compounds (Massiot et al., 1996; Zatovsky et al., 2006; Kim & Kim, 2013; Liu et al., 2013, 2017, 2018; Zhang et al., 2017).

In this communication, we report the flux-growth synthesis, structural characterization and FTIR spectra for the two
K-containing oxidonitridophosphates $K_3\text{Al(PO}_3\text{)}_3\text{N}$ (I) and $K_3\text{Ga(PO}_3\text{)}_3\text{N}$ (II).

2. Structural commentary

Compounds (I) and (II) (Fig. 1) are isotypic and crystallize in the cubic $Na_3\text{Al(PO}_3\text{)}_3\text{N}$ structure in space-group type $P2_13$. The K, Al (or Ga) and N atoms are localized on threefold rotation axes (Wyckoff position 4 $(a)$). As shown in Fig. 2, the crystal structures of the $K_3\text{M}^{III}\text{(PO}_3\text{)}_3\text{N}$ ($M^{III} = \text{Al, Ga}$) title compounds consist of $[\text{M}^{III}\text{O}_6\text{]}$ octahedra and $(\text{PO}_3\text{)}_3\text{N}^{\text{VI}}$-anions, which are linked via vertices, forming a three-dimensional framework. The $(\text{PO}_3\text{)}_3\text{N}^{\text{VI}}$-anion is built up from three $\text{PO}_3\text{N}$ tetrahedra sharing a common N vertex atom. The $P—O$ bond lengths for both structures range between 1.473 (9) and 1.534 (3) Å (Tables 1 and 2), while the $P—N$ bond lengths are 1.701 (4) Å for (I) and (II), respectively. The lengths of the $P—O$ and $P—N$ bonds are similar to those found in the isotypic oxidonitridophosphates such as $Na_3\text{Al(PO}_3\text{)}_3\text{N}$ (Conanec et al., 1994, 1996), $Na_3\text{Ti(PO}_3\text{)}_3\text{N}$ (Zatovsky et al., 2006), or $Na_3\text{V(PO}_3\text{)}_3\text{N}$ (Kim & Kim, 2013). The octahedral coordination environments around $\text{M}^{III}$ are slightly distorted, as indicated by the different $\text{M}^{III}$—O bond lengths (Tables 1 and 2). The $[\text{M}^{III}\text{O}_6\text{]}$ octahedra are slightly squeezed along the cubic cell diagonal. The average Al—O and Ga—O distances are 1.907 (3) and 1.963 (9) Å, respectively. These values are close to the sums of the ionic radii (Shannon, 1976) of Al$^{3+}$ and O$^{2-}$ (1.92 Å) and Ga$^{3+}$ and O$^{2-}$ (2.00 Å), respectively.

Fig. 3 shows the coordination environments of potassium cations for (I) and (II). K1 has nine O-atom neighbors with

### Table 1

| Bond               | Length (Å) | Symmetry Code |
|--------------------|------------|---------------|
| $K_1—O^{3}$        | 2.623 (3)  | $K_3—N$       |
| $K_1—O^{1}$        | 2.761 (3)  | $K_3—O^{3}$   |
| $K_1—O^{2}$        | 3.261 (3)  | $\text{Al}—O^{1}$ |
| $K_2—O^{3}$        | 2.765 (3)  | $\text{Al}—O^{2}$ |
| $K_2—N$            | 2.904 (6)  | $\text{P}—O^{3}$ |
| $K_2—O^{1}$        | 2.967 (3)  | $\text{P}—O^{1}$ |
| $K_2—O^{2}$        | 3.263 (3)  | $\text{P}—O^{2}$ |
| $K_3—O^{3}$        | 2.679 (3)  | $\text{P}—N$  |
| $K_3—O^{2}$        | 2.803 (3)  |               |

### Table 2

| Bond               | Length (Å) | Symmetry Code |
|--------------------|------------|---------------|
| $O_3—P_1—O^{1}$    | 1.158 (17) | $O_1—P_1—N_1$ |
| $O_3—P_1—O^{2}$    | 1.345 (16) | $O_2—P_1—N_1$ |
| $O_1—P_1—O^{2}$    | 1.095 (16) | $P_1^{III}—N_1—P_1^{III}$ |
| $O_3—P_1—N_1$      | 1.105 (2)  |               |

Symmetry codes: (i) $-x, y, z$; (ii) $-x, -y, z$; (iii) $x, y, z$; (iv) $-x, -y, -z$; (v) $y, -x, z$; (vi) $-y, x, z$; (vii) $x, -y, z$; (viii) $-x, y, z$; (ix) $x, y, -z$; (x) $-x, -y, -z$; (xi) $y, -x, z$; (xii) $-y, x, z$; (xiii) $x, y, -z$; (xiv) $-x, -y, -z$; (xv) $y, -x, z$; (xvi) $-y, x, z$. 

Figure 1: A view of the asymmetric units of $K_3\text{Al(PO}_3\text{)}_3\text{N}$ (I) and $K_3\text{Ga(PO}_3\text{)}_3\text{N}$ (II), with displacement ellipsoids drawn at the 50% probability level.

Figure 2: $[\text{M}^{III}\text{O}_6\text{]}$ octahedra and ‘three-blade propeller’-type anions $(\text{PO}_3\text{)}_3\text{N}^{\text{VI}}$ as principle building units for formation of the three-dimensional framework of (I) and (II).

Figure 3: The coordination environment of potassium cations in (I) and (II).
K—O distances ranging from 2.623 (3) to 3.261 (3) Å, which includes three mono- and three bidentately coordinating (PO₃)₃N₆⁻ anions. K₂O₉N and K₃O₉N polyhedra are formed as a result of one tetra- and three bidentately coordinating oxidonitridophosphate anions. In the latter case, the upper boundary for K—O distances is 3.412 (8) Å; K₂—N distances are 2.904 (6) and 2.977 (18) Å and K₃—N contacts are 3.340 (6) and 3.310 (18) Å for (I) and (II), respectively. The coordination environments around the alkali metal for K-containing oxidonitridophosphates (K₂O₉N and K₃O₉N polyhedra) differ from those of the Na-containing compounds (Na₂O₆N and Na₃O₆N polyhedra). In addition, the (PO₃)₃N₆⁻ polyhedra differ from those of the Na-containing compounds (Na₂O₆N and Na₃O₆N polyhedra). In the latter case, the upper boundary for K—O distances is 3.412 (8) Å; K₂—N distances are 2.904 (6) and 2.977 (18) Å and K₃—N contacts are 3.340 (6) and 3.310 (18) Å for (I) and (II), respectively. The coordination environments around the alkali metal for K-containing oxidonitridophosphates (K₂O₉N and K₃O₉N polyhedra) differ from those of the Na-containing compounds (Na₂O₆N and Na₃O₆N polyhedra). In addition, the (PO₃)₃N₆⁻ anions coordinate the two potassium cations in a tetradentate manner (Fig. 4). As is shown schematically in Fig. 4 and in Table 3 for the isotypic M₃IIIO₆(PO₃)₆N compounds, the M³, M¹I and N atoms are arranged along the [111] direction in the sequence −M¹I−M²I−N−M³I−M¹I−M¹I−M³I−M¹I−M²I−N−M³I−M¹I−M²I−N−M³I−M¹I−M²I−N− whereby the M²I—N—M³I distances change in a different manner (Fig. 4). As is shown schematically in Fig. 4 and in Table 3 for the isotypic M₃IIIO₆(PO₃)₆N compounds, the M³, M¹I and N atoms are arranged along the [111] direction in the sequence −M¹I−M²I−N−M³I−M¹I−M¹I−M³I−M¹I−M²I−N−M³I−M¹I−M²I−N−M³I−M¹I−M²I−N−M³I−M¹I−M²I−N− whereby the M²I—N—M³I distances change in a different manner (Fig. 4).

Table 3

| Central Atom | (I) | (II) |
|--------------|-----|------|
| Al/Ga1       | 3.004 | 3.197 |
| K1           | 1.486 | 1.400 |
| K2           | 1.122 | 1.069 |
| K3           | 1.315 | 1.360 |
| P1           | 3 × 4.903 | 3 × 5.084 |
| Σ            | 21.636 | 22.278 |

Figure 4

Coordination of K2 and K3 cations by the (PO₃)₃N₆⁻ anion for (I) and (II).

Table 4

Distances (Å) between atoms for (I), (II) and isotypic M₃IIIO₆(PO₃)₆N compounds along [111].

| Compound          | Atomic distance between neighboring atoms | Reference   |
|-------------------|-------------------------------------------|-------------|
| Na₃Al(PO₃)₆N      | −Na1–3.438–Na₂–2.875–Na–3.197–Na3–3.068–Al–3.486–Na1– | Massiot et al. (1996) |
| Na₃Ti(PO₃)₆N      | −Na1–3.448–Na₂–2.078–Na–3.188–Na3–3.100–Ti–3.638–Na1– | Zatovsky et al. (2006) |
| Na₃V(PO₃)₆N       | −Na1–3.477–Na₂–2.947–N–3.234–Na3–3.100–V–3.606–Na1– | Kim & Kim (2013) |
| K₃Al(PO₃)₆N       | −K1–3.723–K₂–2.904–N–3.340–K3–3.400–Al–3.429–K1– | This work   |
| K₃Ga(PO₃)₆N       | −K1–3.747–K₂–2.976–N–3.310–K3–3.350–Ga–3.470–K1– | This work   |

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3. Synthesis and crystallization

For the synthesis of (I) and (II), KH₂PO₄, K₃P₂O₇·10H₂O, urea, Al₂O₃ or Ga₂O₃ (all analytically or extra pure grade) were used as initial reagents. The sequence of preparation procedure was as follows: (1) phosphates KPO₃ and K₄P₂O₇ were each prepared by calcining KH₂PO₄ and K₃P₂O₇·10H₂O at 873 K; (2) a mixture of 20.07 g of KPO₃, 13.21 g of K₄P₂O₇ and 30.03 g of urea (molar ratio K:P = 1:1.32, urea:P = 2:1) ground in an agate mortar, was heated to complete degassing at 623 K in a porcelain dish. The resulting solid was reground and heated to become a homogeneous liquid at 1023 K and then quenched by pouring the melt onto a copper sheet to form a glass. The glass was crushed using a mill, and a powder with a particle size of less than 125 μm was separated. According to chemical analysis, the prepared glass had the composition K₁.₃₂PO₂.₄₃N₀.₅₀; (3) a mixture of 10 g of glass K₁.₃₂PO₂.₄₃N₀.₅₀ and 0.3 g of Al₂O₃ or 0.7 g of Ga₂O₃ powders were placed into porcelain crucibles and heated up to 1043 K and then cooled to 923 K at a rate of 25 K h⁻¹. After cooling to room temperature, colorless tetrahedral crystals of (I) or (II) were washed with deionized water. Elemental analysis indicated the presence of K, Al (or Ga), P and N in the atomic ratio 3:1:3:1.

The growing of well-shaped crystals of (I) and (II) suitable for single crystal X-ray diffraction analysis was one of main tasks during the present study. Hence, a similar way for the preparation of the potassium-containing phosphates to that for the previously reported sodium-containing compounds (Zatovsky et al., 2006). Thermal decomposition of urea is a multistage process and leads to the formation of C₃N₄ (Wang et al., 2017). The initial M³⁺–P–O–N (M³⁺ = alkali metal) melt can be obtained by the reaction of urea with alkali metal phosphates, when a mixture of phosphates and C₃N₄ interact. The change of the phosphate:C₃N₄ ratio (or phosphate:urea) and the nature of the alkali metal affects the composition of the resulting melt. In our case, the molar ratio of K:P was chosen to be 1:1.32 because a mixture of KPO₃ and K₄P₂O₇ in this ratio has the lowest melting point close to 886 K, and the urea:P ratio was set to 2:1. As a result, a glass of composition K₁.₃₂PO₂.₄₃N₀.₅₀ was obtained.

The solubilities of Al₂O₃ and Ga₂O₃ in the K₁.₃₂PO₂.₄₃N₀.₅₀ self-fluxes differ significantly. Crystallization of compound (I) occurs as a result of the interaction of self-fluxes and 2–4%wt. Al₂O₃. The formation of a mixture of (I) and Al₂O₃ was observed when the initial amount of aluminum oxide was higher than 5%wt. The solubility of Ga₂O₃ in the self-flux is about 7%wt. at 1043 K, and subsequent cooling of the homogeneous melt led to the crystallization of compound (II). In all cases, the amount of nitrogen in the self-fluxes rapidly decreases above 1063 K. This process occurs due to the thermal instability of P—N bonds at high temperatures, and leads to a redox reaction with the release of nitrogen and phosphorus. The latter vaporizes from the phosphate melts and starts to burn, which can be observed by periodical sparks on the melt surface (Zatovsky et al., 2000). As a result, K–M³⁺–P–O (M³⁺ = Al, Ga) melts prone to vitrifying are formed.

The obtained compounds (I) and (II) were further characterized using FTIR spectroscopy; FTIR spectra were collected at room temperature on KBr discs using a Thermo NICOLET Nexus 470 spectrophotometer. As can be seen in Fig. 5, the spectra of (I) and (II) are similar with respect to intensities and band positions (the difference in the band positions does not exceed 27 cm⁻¹). The characteristic bands are in good agreement with the presence of the N(PO₃)₃⁻ anion with C₃ᵥ symmetry, which provides for a set of vibration modes: 6Al¹ + 5A2 + 11E (3A1 + A2 + 4E belong to stretching vibrations, and 3A1 + A2 + 7E are due to deformation vibrations). As shown in Fig. 5, the following regions can be distinguished in the FTIR spectra: (1) the bands in the region between 980 and 1220 cm⁻¹ are assigned to v₆(P–O), stretching vibrations [four absorption bands in the frequency range between 1070 and 1220 cm⁻¹ belong to v₆(P–O)], and two bands of between 980 and 1060 cm⁻¹ correspond to v₆(P–O)]; (2) ν₅(P–N–P) and ν₅(P–N–P) bands can be observed in the regions between 920 and 950 cm⁻¹ and around 920 cm⁻¹, respectively; (3) the range between 400 and 680 cm⁻¹ includes absorption bands due to δ(P–O) and ν(P=O) vibrations. In summary, in terms of the set of absorption bands, the FTIR spectra of the N(PO₃)₃⁻ anion resemble those of the P₂O₇⁴⁻ anion.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. As a result of the shapes of the obtained crystals, their cell parameters and chemical compo-
tions, we had expected that both structures should be isostructural with the previously reported Na₃Al(PO₃)₃N and Na₃Ti(PO₃)₃N structures. In fact, analysis of the single-crystal data showed that both compounds crystallize in the same space group type (P2₁3) as the Na-containing oxonitridophosphates. Originally, the crystal structures were solved by direct methods but we also performed refinements using the atomic coordinates of Na₃Ti(PO₃)₃N as a starting model. The results were the same, confirming that both structures are isostructural with Na₃Ti(PO₃)₃N (as well as with all previously reported cubic oxonitridophosphates with the same formula type).

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Table 5
Experimental details.

| (I) | (II) |
|-----|-----|
| Crystal data | Chemical formula | K₃Al(NP₃O₉) | K₃Ga(NP₃O₉) |
| Mᵣ | 395.2 | 437.94 |
| Crystal system, space group | Cubic, P2₁3 | Cubic, P2₁3 |
| Temperature (K) | 293 | 293 |
| a (Å) | 9.6970 (4) | 9.7313 (9) |
| V (Å³) | 911.83 (11) | 921.5 (3) |
| Z | 4 | 4 |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 2.16 | 4.90 |
| Crystal size (mm) | 0.15 × 0.12 × 0.1 | 0.12 × 0.07 × 0.04 |
| Data collection | | |
| Diffractometer | Oxford Diffraction Xcalibur-3 | Oxford Diffraction Xcalibur-3 |
| Absorption correction | Multi-scan (Blessing, 1995) | Multi-scan (Blessing, 1995) |
| T_min/T_max | 0.844, 0.869 | 0.738, 0.804 |
| No. of measured, independent and observed | 7172, 745, 667 | 4964, 753, 517 |
| R_factor | 0.078 | 0.155 |
| (sin θ/λ)_{max} (Å⁻¹) | 0.660 | 0.660 |
| Refinement | | |
| R[F² > 2σ(F²)], wR(F²), S | 0.026, 0.052, 1.05 | 0.059, 0.102, 1 |
| No. of reflections | 745 | 753 |
| No. of parameters | 53 | 53 |
| Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.27, –0.27 | 0.67, –0.60 |
| Absolute structure Flack x determined using 269 quotients | Flack x determined using 153 quotients |
| Absolute structure parameter | [I(1)–I(2)]/[I(1)+I(2)] (Parsons et al., 2013) | [I(1)–I(2)]/[I(1)+I(2)] (Parsons et al., 2013) |
| | –0.02 (6) | 0.03 (5) |

Computer programs: CrysAlis CCD (Oxford Diffraction, 2006), CrysAlis RED (Oxford Diffraction, 2006), SHELX (Sheldrick, 2008), SHELXS2018-3 (Sheldrick, 2015), DIAMOND (Brandenburg, 2006), WinGX (Farrugia, 2012), enCIFer (Allen et al., 2004) and publCIF (Westrip, 2010).
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Structural features of the oxidonitridophosphates $K_3M^{III}(PO_3)_3N$ ($M^{III} = Al, Ga$)

Igor V. Zatovsky, Ivan V. Ogorodnyk, Vyacheslav N. Baumer, Ivan D. Zhilyak, Ruslana V. Horda and Nataliya Yu. Strutynska

Computing details
For both structures, data collection: CrysAlis CCD (Oxford Diffraction, 2006); cell refinement: CrysAlis CCD (Oxford Diffraction, 2006); data reduction: CrysAlis RED (Oxford Diffraction, 2006). Program(s) used to solve structure: SHELXS (Sheldrick, 2008) for (I); SHELXS2013/1 (Sheldrick, 2008) for (II). Program(s) used to refine structure: SHELXL (Sheldrick, 2015) for (I); SHELXL2018/3 (Sheldrick, 2015) for (II). For both structures, molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: WinGX (Farrugia, 2012), enCIFer (Allen et al., 2004) and publCIF (Westrip, 2010).

Tripotassium aluminium nitridotriphosphate (I)

Crystal data
$K_3Al(NP_3O_9)$
$M_r = 395.2$
Cubic, $P2_13$
Hall symbol: P 2ac 2ab 3
$a = 9.6970 (4)$ Å
$V = 911.83 (11)$ Å$^3$
$Z = 4$
$F(000) = 776$

$D_x = 2.879$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7172 reflections
$\theta = 3.0–28.0^\circ$
$\mu = 2.16$ mm$^{-1}$
$T = 293$ K
Tetrahedron, colorless
$0.15 \times 0.12 \times 0.1$ mm

Data collection
Oxford Diffraction Xcalibur-3 diffractometer
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.844, T_{max} = 0.869$
7172 measured reflections

745 independent reflections
$R_{int} = 0.078$
$\theta_{max} = 28.0^\circ, \theta_{min} = 3.0^\circ$
$h = -12\rightarrow 12$
$k = -12\rightarrow 10$
$l = -12\rightarrow 12$

Refinement
Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.052$
$S = 1.05$
745 reflections
53 parameters
0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Deltaho_{max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{min} = -0.27$ e Å$^{-3}$
Extinction correction: SHELXL2018/3 (Sheldrick, 2015)
Extinction coefficient: 0.0037 (14)
Absolute structure: Flack $x$ determined using
269 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons et al., 2013)
Absolute structure parameter: −0.02 (6)

**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.

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

|      | x          | y          | z          | $U_{	ext{iso}}^* / U_{	ext{eq}}$ |
|------|------------|------------|------------|----------------------------------|
| K1   | 0.04655 (9) | 0.04655 (9) | 0.04655 (9) | 0.0178 (4)                     |
| K2   | 0.26820 (10)| 0.26820 (10)| 0.26820 (10)| 0.0195 (4)                     |
| K3   | 0.63996 (10)| 0.63996 (10)| 0.63996 (10)| 0.0207 (4)                     |
| Al1  | 0.84238 (12)| 0.84238 (12)| 0.84238 (12)| 0.0095 (5)                     |
| P1   | 0.32280 (11)| 0.56862 (11)| 0.46909 (11)| 0.0088 (3)                     |
| N1   | 0.4411 (3)  | 0.4411 (3)  | 0.4411 (3)  | 0.0073 (11)                    |
| O1   | 0.2129 (3)  | 0.5055 (3)  | 0.5631 (3)  | 0.0107 (6)                     |
| O2   | 0.2606 (3)  | 0.5994 (3)  | 0.3269 (3)  | 0.0120 (6)                     |
| O3   | 0.3898 (3)  | 0.6909 (3)  | 0.5344 (3)  | 0.0161 (7)                     |

**Atomic displacement parameters ($Å^2$)**

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| K1   | 0.0178 (4)| 0.0178 (4)| 0.0178 (4)| −0.0037 (4)| −0.0037 (4)| −0.0037 (4)|
| K2   | 0.0195 (4)| 0.0195 (4)| 0.0195 (4)| −0.0034 (4)| −0.0034 (4)| −0.0034 (4)|
| K3   | 0.0207 (4)| 0.0207 (4)| 0.0207 (4)| −0.0040 (4)| −0.0040 (4)| −0.0040 (4)|
| Al1  | 0.0095 (5)| 0.0095 (5)| 0.0095 (5)| −0.0006 (5)| −0.0006 (5)| −0.0006 (5)|
| P1   | 0.0081 (5)| 0.0087 (6)| 0.0096 (5)| 0.0003 (4)  | 0.0010 (4)  | 0.0003 (4)  |
| N1   | 0.0073 (11)| 0.0073 (11)| 0.0073 (11)| 0.0001 (13)| 0.0001 (13)| 0.0001 (13)|
| O1   | 0.0103 (15)| 0.0108 (14)| 0.0110 (14)| 0.0004 (11)| 0.0043 (12)| 0.0021 (12)|
| O2   | 0.0116 (15)| 0.0147 (15)| 0.0099 (14)| 0.0022 (12)| −0.0019 (12)| 0.0007 (12)|
| O3   | 0.0163 (16)| 0.0116 (16)| 0.0204 (16)| −0.0023 (12)| −0.0019 (14)| −0.0037 (13)|

**Geometric parameters ($Å, ^\circ$)**

|      | K1—O3v | K1—O3vi | K1—O1iv | K1—O1v | K1—O2iv | K1—Al1vii |
|------|--------|---------|---------|--------|---------|-----------|
| K2   | 2.623 (3)| 2.623 (3)| 2.761 (3)| 2.761 (3)| 3.429 (3)| 3.379 (3)  |
| K3   | 2.623 (3)| 2.623 (3)| 2.761 (3)| 2.761 (3)| 3.429 (3)| 3.379 (3)  |
| Al1  | 2.623 (3)| 2.623 (3)| 2.761 (3)| 2.761 (3)| 3.429 (3)| 3.379 (3)  |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| K1—P1^iv             | 3.5911 (13)  | K3—O3^xii            | 3.379 (3)    |
| K1—P1^vi             | 3.5911 (13)  | K3—Al1               | 3.400 (3)    |
| K2—O3^ii             | 2.765 (3)    | K3—P1^xii            | 3.4997 (14)  |
| K2—O3^i              | 2.765 (3)    | Al1—O1^xiii          | 1.905 (3)    |
| K2—N1                | 2.904 (6)    | Al1—O1^xiv           | 1.905 (3)    |
| K2—O1^iii            | 2.967 (3)    | Al1—O2^i             | 1.909 (3)    |
| K2—O1^i              | 2.967 (3)    | Al1—O2^ii            | 1.909 (3)    |
| K2—O1^a              | 2.967 (3)    | Al1—O2^iii           | 1.909 (3)    |
| K2—O2                | 3.263 (3)    | P1—O3                | 1.493 (3)    |
| K2—O2^iii            | 3.263 (3)    | P1—O1                | 1.530 (3)    |
| K2—O2^x              | 3.263 (3)    | P1—O2                | 1.534 (3)    |
| K2—P1^iii            | 3.4199 (12)  | P1—N1                | 1.7084 (12)  |
| O3^i—K1—O3^ii        | 79.95 (10)   | O2^x—K3—O3^xi       | 60.45 (8)    |
| O3^i—K1—O3^iii       | 79.95 (10)   | O2^xi—K3—O3^vi      | 47.20 (7)    |
| O3^i—K1—O1^iv        | 115.53 (9)   | O2^xii—K3—O3^xi     | 99.58 (8)    |
| O3^ii—K1—O1^iv       | 165.73 (9)   | N1—K3—O3^xi         | 113.91 (5)   |
| O3^ii—K1—O1^iv       | 109.72 (8)   | O3^x—K3—O3^xi       | 104.69 (6)   |
| O3^ii—K1—O1^v        | 109.72 (8)   | O3^xiii—K3—O3^xxii  | 143.68 (7)   |
| O3^ii—K1—O1^v        | 111.53 (9)   | O3^xiii—K3—O3^xii   | 66.44 (10)   |
| O3^ii—K1—O1^v        | 115.73 (9)   | O3^xiii—K3—O3^xii   | 111.63 (2)   |
| O3^ii—K1—O1^v        | 165.73 (9)   | O2^xiii—K3—O3^xii   | 99.58 (8)    |
| O1^vi—K1—O1^v        | 57.44 (9)    | O2^xiv—K3—O3^xii    | 60.45 (8)    |
| O3^i—K1—O1^vi        | 165.73 (9)   | O2^xv—K3—O3^xii     | 47.20 (7)    |
| O3^i—K1—O1^vi        | 109.72 (8)   | N1—K3—O3^xii        | 113.91 (5)   |
| O3^i—K1—O1^vi        | 111.53 (9)   | O3^xv—K3—O3^xii     | 104.69 (6)   |
| O1^vi—K1—O1^vi       | 57.44 (9)    | O3^xvi—K3—O3^xii    | 104.69 (6)   |
| O1^i—K1—O1^vi        | 57.44 (9)    | O3^xvi—K3—Al1       | 129.57 (6)   |
| O3^i—K1—O2^iv        | 63.69 (8)    | O3^xvi—K3—Al1       | 129.57 (6)   |
| O3^i—K1—O2^iv        | 143.60 (8)   | O3^xvi—K3—Al1       | 129.57 (6)   |
| O3^i—K1—O2^iv        | 94.55 (8)    | O2^xvi—K3—Al1       | 34.15 (6)    |
| O1^iv—K1—O2^iv       | 48.34 (7)    | O2^xvi—K3—Al1       | 34.15 (6)    |
| O1^i—K1—O2^iv        | 81.13 (8)    | O2^xvi—K3—Al1       | 34.15 (6)    |
| O1^v—K1—O2^iv        | 105.77 (8)   | N1—K3—Al1           | 180.00 (9)   |
| O3^i—K1—O2^vi        | 143.60 (8)   | O3^xvi—K3—Al1       | 66.09 (5)    |
| O3^i—K1—O2^vi        | 94.55 (8)    | O3^xvi—K3—Al1       | 66.09 (5)    |
| O3^ii—K1—O2^vi       | 63.69 (8)    | O3^xvi—K3—Al1       | 66.09 (5)    |
| O1^iv—K1—O2^vi       | 81.13 (8)    | O3^xvi—K3—P1^xii    | 168.66 (7)   |
| O1^v—K1—O2^vi        | 105.77 (8)   | O3^xvi—K3—P1^xii    | 86.65 (6)    |
| O1^v—K1—O2^vi        | 48.34 (7)    | O3^xvi—K3—P1^xii    | 101.22 (6)   |
| O2^vi—K1—O2^vi       | 115.34 (4)   | O2^xvi—K3—P1^xii    | 82.96 (7)    |
| O3^i—K1—O2^v         | 94.55 (8)    | O2^xvi—K3—P1^xii    | 64.96 (6)    |
| O3^i—K1—O2^v         | 63.69 (8)    | O2^xvi—K3—P1^xii    | 25.22 (6)    |
| O3^ii—K1—O2^v        | 143.60 (8)   | N1—K3—P1^xii        | 125.75 (3)   |
| O1^iv—K1—O2^v        | 105.77 (8)   | O3^xvi—K3—P1^xii    | 79.71 (6)    |
| O1^v—K1—O2^v         | 48.34 (7)    | O3^xvi—K3—P1^xii    | 112.01 (6)   |
| O1^v—K1—O2^v         | 81.13 (8)    | O3^xvi—K3—P1^xii    | 24.99 (5)    |
| Bond                        | Bond Angle (°) | Bond Angle (°) |
|-----------------------------|----------------|----------------|
| O2v—K1—O2v                  | 115.34 (4)     | All—K3—P1i    |
| O2v—K1—O2v                  | 115.34 (4)     | O1xii—All—O1xv| 54.25 (3) |
| O3i—K1—Allvi                | 132.11 (7)     | O1xii—All—O1xv| 88.28 (14) |
| O3ii—K1—Allvi               | 132.11 (7)     | O1xii—All—O1xv| 88.28 (14) |
| O1v—K1—Allvi                | 33.70 (6)      | O1xii—All—O2x | 92.92 (12) |
| O1v—K1—Allvi                | 33.70 (6)      | O1xii—All—O2x | 92.92 (12) |
| O2v—K1—Allvi                | 77.34 (5)      | O1xii—All—O2x | 92.92 (12) |
| O2v—K1—Allvi                | 77.34 (5)      | O1xii—All—O2x | 92.92 (12) |
| O3i—K1—P1i                  | 88.98 (7)      | O1xii—All—O2x | 92.92 (12) |
| O3i—K1—P1i                  | 168.77 (7)     | O1xii—All—O2x | 92.92 (12) |
| O3ii—K1—P1i                 | 100.08 (6)     | O1xii—All—O2x | 92.92 (12) |
| O1v—K1—P1i                 | 23.55 (6)      | O1xii—All—O2x | 92.92 (12) |
| O1v—K1—P1i                 | 70.37 (6)      | O1xii—All—O2x | 92.92 (12) |
| O1v—K1—P1i                 | 80.83 (7)      | O1xii—All—O2x | 92.92 (12) |
| O2v—K1—P1i                 | 25.29 (5)      | O1xii—All—O2x | 92.92 (12) |
| O2v—K1—P1i                 | 95.49 (6)      | O1xii—All—O2x | 92.92 (12) |
| O2v—K1—P1i                 | 115.87 (6)     | O1xii—All—O2x | 92.92 (12) |
| Al1—K1—Pi                  | 55.54 (3)      | O1xii—All—K3  | 55.4 (10) |
| O3i—K1—Pi                  | 168.77 (7)     | O1xii—All—K3  | 55.4 (10) |
| O3ii—K1—Pi                 | 100.08 (6)     | O1xii—All—K3  | 55.4 (10) |
| O3iii—K1—Pi                | 88.98 (7)      | O1xii—All—K1xi| 53.5 (10) |
| O1v—K1—Pi                 | 70.37 (6)      | O1xii—All—K1xi| 53.5 (10) |
| O1v—K1—Pi                 | 80.83 (7)      | O1xii—All—K1xi| 53.5 (10) |
| O1v—K1—Pi                 | 23.55 (6)      | O1xii—All—K1xi| 53.5 (10) |
| O2v—K1—Pi                 | 115.87 (6)     | O1xii—All—K1xi| 53.5 (10) |
| O2v—K1—Pi                 | 25.29 (5)      | O1xii—All—K1xi| 53.5 (10) |
| O2v—K1—Pi                 | 95.49 (6)      | O1xii—All—K1xi| 53.5 (10) |
| Al1—K1—Pi                  | 55.54 (3)      | O1xii—All—K1xi| 53.5 (10) |
| P1i—K1—P1i                 | 91.14 (4)      | O1xii—All—K1xi| 53.5 (10) |
| O3ii—K2—O3i                | 75.10 (9)      | O1xii—All—K2xiv| 54.13 (8) |
| O3ii—K2—O3i                | 75.10 (9)      | O2xiv—All—K2xiv| 54.13 (8) |
| O3i—K2—O3i                | 75.10 (9)      | O2xiv—All—K2xiv| 54.13 (8) |
| O3i—K2—N1                  | 135.27 (6)     | O2xiv—All—K2xiv| 54.13 (8) |
| O3i—K2—N1                  | 135.27 (6)     | O2xiv—All—K2xiv| 54.13 (8) |
| O3i—K2—N1                  | 135.27 (6)     | O2xiv—All—K2xiv| 54.13 (8) |
| O3i—K2—O1iii               | 51.57 (8)      | O1xii—All—K2xiv| 125.19 (12) |
| O3i—K2—O1iii               | 123.82 (8)     | O1xii—All—K2xiv| 125.19 (12) |
| N1—K2—O1ii                 | 85.66 (6)      | O1xii—All—K2xiv| 125.19 (12) |
| O3ii—K2—O1i                | 103.08 (8)     | O1xii—All—K2xiv| 125.19 (12) |
| O3i—K2—O1i                 | 51.57 (8)      | O1xii—All—K2xiv| 125.19 (12) |
| O3i—K2—O1i                 | 123.82 (8)     | O1xii—All—K2xiv| 125.19 (12) |
| N1—K2—O1i                  | 85.66 (6)      | O1xii—All—K2xiv| 125.19 (12) |
| O1iii—K2—O1i               | 119.43 (16)    | O1xii—All—K2xiv| 125.19 (12) |
| O3ii—K2—O1ii               | 123.82 (8)     | O1xii—All—K2xiv| 125.19 (12) |
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O3i—K2—O1ii 103.08 (8) O1iv—Al1—K2xii 45.00 (8)
O3i—K2—O1ii 51.57 (8) O2iv—Al1—K2xii 108.53 (8)
N1—K2—O1ii 85.66 (6) O2vi—Al1—K2xii 139.06 (9)
O1iii—K2—O1ii 119.43 (16) O2—Al1—K2xii 54.13 (8)
O1—K2—O1ii 119.43 (16) K3—Al1—K2xii 106.68 (3)
O3ii—K2—O2 120.12 (8) K1xvi—Al1—K2xii 73.32 (3)
O3i—K2—O2 155.11 (7) K2xv—Al1—K2xii 112.11 (3)
O3ii—K2—O2 89.38 (7) K2xvii—Al1—K2xii 112.11 (3)
O3iii—K2—O1iv 49.01 (5) O3—P1—O1 111.58 (17)
N1—K2—O1iv 78.18 (7) O3—P1—O2 113.45 (16)
O1iii—K2—O1iv 155.11 (7) O1—P1—O2 109.85 (16)
N1—K2—O2 52.43 (7) O3—P1—N1 110.5 (2)
O3ii—K2—O2 89.38 (7) O1—P1—N1 105.82 (13)
O3i—K2—O2 120.12 (8) O2—P1—N1 105.20 (17)
O3ii—K2—O2 155.11 (7) O3—P1—K2xvii 52.04 (12)
N1—K2—O2 49.01 (5) O1—P1—K2xvii 60.00 (11)
O1iii—K2—O2 52.43 (7) O2—P1—K2xvii 124.79 (11)
O1—K2—O2 78.18 (7) N1—P1—K2xvii 130.01 (13)
O1—K2—O2 131.74 (9) O3—P1—K3xix 72.98 (11)
O1—K2—O2 81.64 (8) O1—P1—K3xix 98.65 (11)
O2—K2—O2 155.11 (7) O2—P1—K3xix 51.11 (11)
O2—K2—O2 89.38 (7) N1—P1—K3xix 151.24 (7)
O2—K2—O2 120.12 (8) K2xviii—P1—K3xix 75.63 (3)
O3—K2—O2 49.01 (5) O3—P1—K2 161.98 (12)
O3—K2—O2 131.74 (9) O1—P1—K2 83.96 (11)
O3—K2—O2 52.43 (7) O2—P1—K2 66.87 (11)
O3—K2—O2 78.18 (7) N1—K2—O2 113.28 (8)
O2—K2—O2 81.64 (8) K2—P1—K3 143.90 (4)
O2—K2—O2 152.93 (6) K2—P1—K3 114.96 (3)
O2—K2—O2 89.38 (7) O3—P1—K3 43.33 (11)
O2—K2—O2 120.12 (8) O1—P1—K3 113.68 (11)
N1—K2—O2 86.94 (7) O2—P1—K3 136.05 (12)
O1iii—K2—O1iv 111.81 (3) N1—P1—K3 68.57 (19)
O1—K2—P1xii 111.81 (3) K2—P1—K3xix 119.41 (3)
O1—K2—P1xii 26.52 (6) K2—P1—K3xix 74.83 (3)
O1—K2—P1xii 123.59 (6) K2—P1—K3xix 119.41 (3)
O2—K2—P1xii 98.86 (5) O3—P1—K1xx 46.13 (11)
O2—K2—P1xii 157.93 (6) O2—P1—K1xx 65.25 (11)
O3—K2—P1xii 157.93 (6) N1—P1—K1xx 128.30 (17)
O3—K2—P1xii 86.94 (7) K2xviii—P1—K1xx 78.82 (3)
O3—K2—P1xii 25.20 (6) K3—K1xx—P1—K1xx 61.97 (3)
N1—K2—P1xii 111.81 (3) K2—P1—K1xx 77.22 (3)
O1iii—K2—P1xii 111.81 (3) K3—P1—K1xx 153.19 (4)
O1—K2—P1xii 26.52 (6) P1xi—N1—P1xviii 118.53 (8)
O1—K2—P1xii 71.74 (5) P1vi—N1—P1xviii 118.53 (8)
O2—K2—P1xii 152.93 (6) P1vi—N1—P1 118.54 (8)
O2—K2—P1xii 71.74 (5) P1vii—N1—K2 97.01 (18)
O2v—K2—P1ii 98.86 (5) P1ix—N1—K2 97.01 (18)
O3viii—K3—O3 83.76 (9) P1viii—N1—K3 82.99 (18)
O3viii—K3—O3 83.76 (9) P1—N1—K3 82.99 (18)
O3viii—K3—O2v 104.80 (8) K2—N1—K3 180.0 (3)
O3—K3—O2x 162.69 (9) P1—O1—Al1xxi 144.58 (18)
O3viii—K3—O2x 104.80 (8) K3—O3—K2xviii 102.41 (10)
O3—K3—O2x 58.18 (9) P1—O2—Al1xx 131.82 (18)
O3viii—K3—O3x 162.69 (9) K1xx—O1—K1xx 92.77 (12)
O3—K3—O3x 104.80 (8) P1—O2—K3xx 103.68 (13)
O3viii—K3—N1 50.43 (6) Al1xx—O2—K3xx 138.56 (12)
O3—K3—N1 50.43 (6) P1—O2—K1xx 89.45 (12)
O2—K3—N1 145.85 (6) K3—O3—K3xx 73.60 (7)
O2—K3—N1 145.85 (6) P1—O2—K1xx 86.08 (7)
O2—K3—N1 145.85 (6) P1—O3—K1xx 153.19 (17)
O3viii—K3—O3x 162.69 (9) P1—O3—K3xx 82.03 (12)
O3—K3—O3x 104.80 (8) P1—O3—K3xx 86.76 (7)

Symmetry codes: (i) −y+1, z−1/2, −x+1/2; (ii) −x+1/2, −y+1, z−1/2; (iii) z−1/2, −x+1/2, −y+1; (iv) −z+1/2, −x, y−1/2; (v) y−1/2, −z+1/2, −x; (vi) −x, y−1/2, z+1; (vii) x−1, y+1, z+1; (viii) x, y, z; (ix) y, z, x; (x) −z+1, x+1/2, −y+3/2; (xi) −y+3/2, −z+1, x+1/2; (xii) x+1/2, −y+3/2, −z+1; (xiii) −z+3/2, −x+1, y+1/2; (xiv) y+1/2, −z+3/2, −x+1; (xv) −x+1, y+1/2, −z+3/2; (xvi) x+1, y+1, z+1; (xvii) −x+3/2, −y+1, z+1/2; (xviii) −y+1/2, −z+3/2, −x+1/2; (xix) −z+1/2, −y+1/2, −z+3/2.

Tripotassium gallium nitridotriphosphate (II)

Crystal data
K3Ga(NP3O9)
Mr = 437.94
Cubic, P213
Hall symbol: P 2ac 2ab 3
a = 9.7313 (9) Å
V = 921.5 (3) Å³
Z = 4
F(000) = 848

\[ D_\lambda = 3.157 \text{ Mg m}^{-3} \]
Mo Kα radiation, \( \lambda = 0.71073 \text{ Å} \)
Cell parameters from 4964 reflections
\( \theta = 3.0-28.0^\circ \)
\( \mu = 4.90 \text{ mm}^{-1} \)
\( T = 293 \text{ K} \)
Irregular tetrahedron, colorless
0.12 × 0.07 × 0.04 mm
Data collection

Oxford Diffraction Xcalibur-3 diffractometer
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)

753 independent reflections
517 reflections with I > 2σ(I)

θmax = 28.0°, θmin = 3.0°

Rint = 0.155

Tmin = 0.738, Tmax = 0.804

4964 measured reflections

Refinement

Least-squares matrix: full
R[F^2 > 2σ(F^2)] = 0.059
wR(F^2) = 0.102
S = 1

753 reflections
53 parameters
0 restraints

Absolute structure: Flack x determined using 153 quotients [(I^+)−(I^-)]/[(I^+)+(I^-)] (Parsons et al., 2013)

Absolute structure parameter: 0.03 (5)

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.

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

|     | x      | y      | z      | U^eq |
|-----|--------|--------|--------|------|
| K1  | 0.0456 | 0.0456 | 0.0456 | 0.0326 |
| K2  | 0.2679 | 0.2679 | 0.2679 | 0.0329 |
| K3  | 0.6410 | 0.6410 | 0.6410 | 0.0358 |
| Gal | 0.83974| 0.83974| 0.83974| 0.0235 |
| P1  | 0.3255 | 0.5696 | 0.4719 | 0.0221 |
| N1  | 0.4446 | 0.4446 | 0.4446 | 0.019  |
| O1  | 0.2172 | 0.5088 | 0.5672 | 0.024  |
| O2  | 0.2578 | 0.5989 | 0.3347 | 0.026  |
| O3  | 0.3941 | 0.6899 | 0.5330 | 0.028  |

Atomic displacement parameters (Å^2)

|     | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|-----|-------|-------|-------|-------|-------|-------|
| K1  | 0.0326| 0.0326| 0.0326| −0.0026|−0.0026|−0.0026|
| K2  | 0.0329| 0.0329| 0.0329|−0.0034|−0.0034|−0.0034|
| K3  | 0.0358| 0.0358| 0.0358|−0.0040|−0.0040|−0.0040|
| Gal | 0.0235| 0.0235| 0.0235| 0.0007 | 0.0007 | 0.0007 |
| P1  | 0.0243| 0.0217| 0.0204|−0.0025|−0.0006|−0.0001|
| N1  | 0.019 | 0.019 | 0.019 | 0.003  | 0.003  | 0.003  |
| O1  | 0.022 | 0.029 | 0.021 |−0.002  | 0.007  | 0.010  |
### Geometric parameters (Å, ‹) |

| Bond/Distance | Value (Å) | Value (°) |
|---------------|-----------|-----------|
| O2—K1—O3i    | 2.642 (8) | 80.8 (3)  |
| O2—K1—O3ii   | 2.642 (8) | 111.5 (2) |
| O2—K1—O3iii  | 2.642 (8) | 165.6 (3) |
| O2—K1—O3iv   | 2.807 (9) | 111.5 (2) |
| O2—K1—O3v    | 2.807 (9) | 165.6 (3) |
| O2—K1—O3vi   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3vii  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3viii | 2.807 (9) | 108.0 (3) |
| O2—K1—O3ix   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3x    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xi   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xii  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xiii | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xiv  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xv   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xvi  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xvii | 2.807 (9) | 108.0 (3) |
| O2—K1—O3xviii| 2.807 (9) | 108.0 (3) |
| O2—K1—O3xix  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3x    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3v    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3vi   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3vii  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3viii | 2.807 (9) | 108.0 (3) |
| O2—K1—O3ix   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3x    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3v    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3vi   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3vii  | 2.807 (9) | 108.0 (3) |
| O2—K1—O3viii | 2.807 (9) | 108.0 (3) |
| O2—K1—O3ix   | 2.807 (9) | 108.0 (3) |
| O2—K1—O3x    | 2.807 (9) | 108.0 (3) |
| O2—K1—O3v    | 2.807 (9) | 108.0 (3) |

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**Supplementary Information**

| Atom  | U1  | U2  | U3  | U12 | U13 | U23 |
|-------|-----|-----|-----|-----|-----|-----|
| O2    | 0.022 (4) | 0.031 (5) | 0.026 (5) | −0.005 (4) | −0.001 (4) | −0.003 (4) |
| O3    | 0.039 (6) | 0.023 (5) | 0.023 (5) | −0.005 (4) | −0.002 (4) | −0.006 (4) |

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| Bond             | Value (°)   |
|------------------|------------|
| O1v—K1—O2v      | 47.6 (2)   |
| O1v—K1—O2v      | 80.4 (2)   |
| O3—K1—O2vi     | 145.2 (3)  |
| O3vi—K1—O2vi   | 93.7 (2)   |
| O1iv—K1—O2vi   | 64.5 (2)   |
| O1iv—K1—O2vi   | 80.4 (2)   |
| O1vi—K1—O2vi   | 106.0 (3)  |
| O1vi—K1—O2vi   | 47.6 (2)   |
| O2v—K1—O2vi    | 114.96 (13)|
| O3—K1—O2vi     | 64.5 (2)   |
| O3i—K1—O2vi    | 145.2 (3)  |
| O3ii—K1—O2vi   | 93.7 (2)   |
| O3iiv—K1—O2vi  | 47.6 (2)   |
| O2v—K1—O2iv    | 80.4 (2)   |
| O2v—K1—O2iv    | 106.0 (3)  |
| O2vi—K1—O2iv   | 114.96 (13)|
| O3—K1—Ga1vii   | 131.6 (2)  |
| O3v—K1—Ga1vii  | 131.6 (2)  |
| O3v—K1—Ga1vii  | 131.6 (2)  |
| O1v—K1—Ga1vii  | 34.33 (17) |
| O1v—K1—Ga1vii  | 34.33 (17) |
| O1vi—K1—Ga1vii | 34.33 (17) |
| O2v—K1—Ga1vii  | 76.82 (17) |
| O2v—K1—Ga1vii  | 76.82 (17) |
| O2vi—K1—Ga1vii | 76.82 (17) |
| O3—K1—P1iv     | 89.16 (19) |
| O3vi—K1—P1iv   | 169.8 (2)  |
| O3ii—K1—P1iv   | 98.99 (18) |
| O1iv—K1—P1iv   | 23.26 (16) |
| O1v—K1—P1iv    | 70.29 (19) |
| O1vi—K1—P1iv   | 81.7 (2)   |
| O2v—K1—P1iv    | 115.3 (2)  |
| O2vi—K1—P1iv   | 95.39 (17) |
| Ga1vii—K1—P1iv | 24.71 (16) |
| O3—K1—P1vi     | 55.56 (9)  |
| O3i—K1—P1vi    | 169.8 (2)  |
| O3iii—K1—P1vi  | 98.99 (18) |
| O3ii—K1—P1vi   | 89.16 (19) |
| O1iv—K1—P1vi   | 70.29 (19) |
| O1v—K1—P1vi    | 81.7 (2)   |
| O1vi—K1—P1vi   | 23.26 (17) |
| O2v—K1—P1vi    | 95.39 (17) |
| O2vi—K1—P1vi   | 24.71 (16) |
| Ga1vii—K1—P1vi | 115.3 (2)  |
| P1iv—K1—P1vi   | 55.56 (9)  |
| P1iv—K1—P1vi   | 91.16 (13) |
| O3—K2—O3i      | 75.1 (3)   |

O2u—K3—O3u      | 46.3 (2)   |
O1—K3—O3u       | 114.13 (16)|
Ga1—K3—O3u      | 65.87 (16) |
O3u—K3—O3u      | 104.44 (18)|
O3u—K3—O3u      | 104.44 (18)|
O3—K3—P1u       | 101.2 (2)  |
O3u—K3—P1u      | 86.72 (18) |
O3u—K3—P1u      | 168.3 (2)  |
O2u—K3—P1u      | 85.1 (2)   |
Ga1—K3—P1u      | 66.1 (2)   |
O2u—K3—P1u      | 24.51 (18) |
N1—K3—P1u       | 125.23 (9) |
Ga1—K3—P1u      | 54.77 (9)  |
O3—K3—P1u       | 79.98 (17) |
Ga1—O1iv—Ga1xv  | 88.9 (4)   |
Ga1—O1iv—Ga1xv  | 88.9 (4)   |
Ga1—O1iv—Ga1xv  | 88.9 (4)   |
Ga1—O1iv—Ga1xv  | 91.7 (3)   |
Ga1—O1iv—Ga1xv  | 176.3 (3)  |
Ga1—O1iv—Ga1xv  | 87.5 (3)   |
Ga1—O1iv—Ga1xv  | 176.3 (3)  |
Ga1—O1iv—Ga1xv  | 87.5 (3)   |
Ga1—O1iv—Ga1xv  | 91.7 (3)   |
Ga1—O1iv—Ga1xv  | 176.3 (3)  |
Ga1—O1iv—Ga1xv  | 92.0 (3)   |
Ga1—O1iv—Ga1xv  | 92.0 (3)   |
Ga1—O1iv—Ga1xv  | 126.1 (2)  |
Ga1—O1iv—Ga1xv  | 126.1 (2)  |
Ga1—O1iv—Ga1xv  | 126.1 (2)  |
Ga1—O1iv—Ga1xv  | 56.2 (2)   |
Ga1—O1iv—Ga1xv  | 56.2 (2)   |
Ga1—O1iv—Ga1xv  | 56.2 (2)   |
Ga1—O1iv—Ga1xv  | 53.9 (2)   |
Ga1—O1iv—Ga1xv  | 53.9 (2)   |
Ga1—O1iv—Ga1xv  | 53.9 (2)   |
Ga1—O1iv—Ga1xv  | 123.8 (2)  |
Ga1—O1iv—Ga1xv  | 123.8 (2)  |
Ga1—O1iv—Ga1xv  | 123.8 (2)  |
Ga1—O1iv—Ga1xv  | 124.6 (3)  |
Ga1—O1iv—Ga1xv  | 68.5 (3)   |
Ga1—O1iv—Ga1xv  | 43.4 (3)   |
Ga1—O1iv—Ga1xv  | 108.3 (2)  |
| Bond | Angle (°) | Bond | Angle (°) |
|------|----------|------|----------|
| O3ii—K2—O3iii | 75.1 (3) | O2v—Ga1—K2xiv | 54.3 (2) |
| O3i—K2—O3iii | 75.1 (3) | O2vi—Ga1—K2xiv | 140.0 (2) |
| O3ii—K2—O1i | 123.7 (3) | K3—Ga1—K2xiv | 107.30 (4) |
| O3i—K2—O1i | 51.4 (2) | K1xi—Ga1—K2xiv | 72.70 (4) |
| O3ii—K2—O1ii | 102.9 (2) | O1xiv—Ga1—K2xvii | 43.4 (3) |
| O3i—K2—O1ii | 51.4 (2) | O1xiv—Ga1—K2xvii | 124.6 (3) |
| O3iii—K2—O1ii | 102.9 (2) | O1xiv—Ga1—K2xvii | 68.5 (3) |
| O1i—K2—O1ii | 123.7 (3) | O2xi—Ga1—K2xvii | 54.3 (2) |
| O1i—K2—O1ii | 119.49 (5) | O2x—Ga1—K2xvii | 140.0 (2) |
| O3—K2—O1ii | 102.9 (2) | O2vi—Ga1—K2xvii | 108.3 (2) |
| O3—K2—O1ii | 123.7 (3) | K3—Ga1—K2xvii | 107.30 (4) |
| O3ii—K2—O1ii | 51.4 (2) | K1xi—Ga1—K2xvii | 72.70 (4) |
| O1—K2—O1ii | 119.49 (5) | K2xv—Ga1—K2xvii | 111.55 (3) |
| O1i—K2—O1ii | 119.49 (5) | O1xiv—Ga1—K2xvii | 68.5 (3) |
| O3—K2—N1 | 135.25 (18) | O1xiv—Ga1—K2xvii | 124.6 (3) |
| O3—K2—N1 | 135.25 (18) | O1xiv—Ga1—K2xvii | 140.0 (2) |
| O3iii—K2—N1 | 135.25 (18) | O2xi—Ga1—K2xvii | 108.3 (2) |
| O1—K2—N1 | 85.89 (18) | O2xi—Ga1—K2xvii | 54.3 (2) |
| O1—K2—N1 | 85.89 (18) | K3—Ga1—K2xvii | 107.30 (4) |
| O3—K2—O2viii | 90.1 (2) | K1xi—Ga1—K2xvii | 72.70 (4) |
| O3—K2—O2viii | 156.0 (2) | K2xv—Ga1—K2xvii | 111.55 (3) |
| O3—K2—O2viii | 119.8 (2) | K2xv—Ga1—K2xvii | 111.55 (3) |
| O1—K2—O2viii | 131.8 (3) | O3—P1—O2 | 113.8 (5) |
| O1—K2—O2viii | 53.5 (2) | O3—P1—O1 | 112.1 (5) |
| O1—K2—O2viii | 77.6 (2) | O2—P1—O1 | 107.9 (5) |
| N1—K2—O2viii | 48.52 (15) | O3—P1—N1 | 108.9 (7) |
| O3—K2—O2ix | 119.8 (2) | O2—P1—N1 | 107.0 (5) |
| O3—K2—O2ix | 90.1 (2) | O1—P1—N1 | 106.8 (4) |
| O3—K2—O2ix | 156.0 (2) | O3—P1—K2xvii | 53.9 (4) |
| O1—K2—O2ix | 53.5 (2) | O2—P1—K2xvii | 122.8 (3) |
| O1—K2—O2ix | 77.6 (2) | O1—P1—K2xvii | 58.8 (4) |
| O1—K2—O2ix | 131.8 (3) | N1—P1—K2xvii | 130.2 (4) |
| N1—K2—O2x | 48.52 (15) | O3—P1—K3xix | 73.8 (3) |
| O2—K2—O2x | 80.9 (2) | O2—P1—K3xix | 49.6 (3) |
| O3—K2—O2 | 156.0 (2) | O1—P1—K3xix | 98.5 (3) |
| O3—K2—O2 | 119.8 (2) | N1—P1—K3xix | 150.7 (2) |
| O3—K2—O2 | 90.1 (2) | K2xv—P1—K3xix | 75.90 (10) |
| O1—K2—O2 | 77.6 (2) | O3—P1—K3 | 42.8 (3) |
| O1—K2—O2 | 131.8 (3) | O2—P1—K3 | 138.4 (3) |
| O1—K2—O2 | 53.5 (2) | O1—P1—K3 | 113.1 (3) |
| N1—K2—O2 | 48.52 (15) | N1—P1—K3 | 67.9 (6) |
| O2—K2—O2 | 80.9 (2) | K2xv—P1—K3 | 75.44 (8) |
| O2—K2—O2 | 80.9 (2) | K3x—P1—K3 | 115.45 (9) |
| O3—K2—P1ii | 80.9 (2) | O3—P1—K2 | 160.8 (4) |
| O3—K2—P1ii | 51.0 (2) | O2—P1—K2 | 66.3 (3) |
| O3—K2—P1ii | 123.33 (17) | O1—P1—K2 | 84.9 (4) |
| O1—K2—P1ii | 123.33 (17) | N1—P1—K2 | 55.6 (6) |
O1ii—K2—P1ii 26.44 (17) K2viii—P1—K2 143.62 (12)
O1ii—K2—P1ii 115.25 (16) K3xx—P1—K2 113.74 (10)
N1—K2—P1i 111.98 (9) K3—P1—K2 123.46 (11)
O2viii—K2—P1ii 72.82 (16) O3—P1—K1xx 121.5 (3)
O2viii—K2—P1ii 98.30 (15) O2—P1—K1xx 62.4 (3)
O2—K2—P1i 153.45 (17) O1—P1—K1xx 46.7 (3)
O2—K2—P1i 99.6 (2) N1—P1—K1xx 128.7 (6)
O3—K2—P1i 25.10 (18) K2viii—P1—K1xx 78.68 (8)
O3—K2—P1i 86.7 (2) K3xx—P1—K1xx 61.82 (9)
O1—K2—P1i 26.44 (17) K3—P1—K1xx 153.65 (11)
O1i—K2—P1i 115.25 (16) K2—P1—K1xx 76.43 (8)
O1—K2—P1i 123.33 (17) P1—N1—P1viii 118.8 (2)
N1—K2—P1i 111.98 (9) P1—N1—P1viii 118.8 (2)
O2viii—K2—P1i 153.45 (17) P1viii—N1—P1ix 118.8 (2)
O2viii—K2—P1i 72.82 (16) P1—N1—K2 96.3 (6)
O2—K2—P1i 98.30 (15) P1viii—N1—K2 96.3 (6)
O2—K2—P1i 106.85 (10) P1—N1—K2 96.3 (6)
P1—K3—O3viii 82.9 (3) P1viii—N1—K3 83.7 (6)
O3—K3—O3xx 82.9 (3) P1—N1—K3 83.7 (6)
O3—K3—O3xx 82.9 (3) K2—N1—K3 180.0 (9)
O3—K3—O2x 111.2 (2) P1—O1—Ga1xxx 143.5 (6)
O3viii—K3—O3xx 164.8 (3) P1—O1—K1xx 110.0 (4)
O3—K3—O2x 103.8 (2) Ga1xxx—O1—K1xx 91.7 (3)
O2viii—K3—O3xx 164.8 (3) P1—O1—K2viii 94.8 (4)
O3viii—K3—O2x 103.8 (2) Ga1xxx—O1—K2viii 109.2 (3)
O3viii—K3—O3xx 111.2 (2) K1xx—O1—K2viii 102.2 (3)
o2—K3—O2xxi 61.1 (3) P1—O2—Ga1xxx 129.8 (5)
o2—K3—O2xxi 103.8 (2) P1—O2—K3xxx 105.8 (4)
o2—K3—O2xxi 111.2 (2) Ga1xxx—O2—K3xxx 87.9 (3)
o2—K3—O2xxi 164.8 (3) P1—O2—K1xx 92.9 (4)
O2viii—K3—O2xxi 61.1 (3) Ga1xxx—O2—K1xx 137.2 (4)
o2viii—K3—O2xxi 164.8 (3) K3xxx—O2—K1xx 74.99 (18)
o3—K3—N1 49.85 (19) P1—O2—K2 88.7 (3)
o3—K3—N1 49.85 (19) Ga1xxx—O2—K2 96.6 (3)
o3—K3—N1 49.85 (19) K3xxx—O2—K2 156.9 (3)
o2viii—K3—N1 144.05 (18) K1xx—O2—K2 86.6 (2)
o2viii—K3—N1 144.05 (18) P1—O3—K1viii 153.3 (5)
o2viii—K3—N1 144.05 (18) P1—O3—K3 115.2 (4)
o2viii—K3—N1 144.05 (18) K1viii—O3—K3 87.5 (3)
o2viii—K3—N1 144.05 (18) P1—O3—K2viii 101.0 (4)
o2viii—K3—N1 144.05 (18) K1viii—O3—K2viii 86.8 (3)
o3—K3—Ga1 130.15 (19) K3—O3—K2viii 102.2 (3)
o3viii—K3—Ga1 130.15 (19) P1—O3—K3xxx 81.7 (3)
o3viii—K3—Ga1 130.15 (19) K1viii—O3—K3xxx 73.36 (19)
o3—K3—Ga1 35.95 (18) K3—O3—K3xxx 158.9 (3)
| Bond | Distance (Å) | Bond Angle (°) |
|------|--------------|---------------|
| O3^viii—K3—O3^v | 143.91 (19) | 111.65 (7) |
| K2^viii—O3—K3^ix | 85.9 (2) |

Symmetry codes: (i) z−1/2, −x+1/2, −y+1; (ii) −y+1, z−1/2, −x+1/2; (iii) −x+1/2, −y+1, z−1/2; (iv) −x, y−1/2, −z+1/2; (v) −z+1/2, −x, y−1/2; (vi) y−1/2, −z+1/2; (vii) x+1, y−1, z; (viii) y, z, x; (ix) z, x, y; (x) −z+1, x+1/2, −y+3/2; (xi) −y+3/2, −z+1, x+1/2; (xii) x+1/2, −y+3/2, −z+1; (xiii) y+1/2, −z+3/2, −x+1; (xiv) −z+1, y+1/2, −x+3/2; (xv) −x+3/2, −z+1, y+1/2; (xvi) x+1, y+1, z+1; (xvii) −x+3/2, −y+1, z+1/2; (xviii) −x+1/2, −y+1, z+1/2; (xix) x−1/2, −y+1/2, −z+3/2; (xx) −x, y+1/2, −z+1/2; (xxi) −x+1, y−1/2, −z+3/2.

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