Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Potassium gadolinium polyphosphate, $KGd(PO_3)_4$

Walid Rekik, Houcine Naïli* and Tahar Mhiri

Laboratoire de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, BP 802, 3018 Sfax, Tunisia
Correspondence e-mail: houcine_naili@yahoo.com

Received 5 January 2004
Accepted 27 February 2004
Online 31 March 2004

Potassium gadolinium polyphosphate, $KGd(PO_3)_4$, was synthesized using the flux method. The atomic arrangement consists of an infinite long-chain polyphosphate organization. Two types of chains, with a period of eight PO_4 tetrahedra, run along the [101] direction. The Gd atoms have an eightfold co-ordination, while the K atoms have nine O-atom neighbours.

Comment

The present structure investigation was performed as part of a research program concerning condensed phosphates with the general formula $M^{I}M^{III}(PO_3)_4$, where M^{I} is a monovalent cation and M^{III} is a trivalent cation. The common chemical features of these polyphosphates indicate that they are stable under normal conditions of temperature and humidity (Hong, 1975*a*,*b*; Koizumi, 1976; Palkina *et al.*, 1977, 1978, 1979; Tarasenkova *et al.*, 1985; Jaouadi *et al.*, 2003). These compounds can be kept for many years in a perfect state of crystallinity, they are not soluble in water, as may be inferred from their estimated molecular weights, and they all produce glasses when heated to their melting points (Durif, 1995). The literature dealing with these compounds was rather confusing for some time, but it is currently well established that the $M^{I}M^{III}(PO_3)_4$ compounds can be classified into seven different types, which are usually denoted by the roman numerals I–VII. This nomenclature, first proposed by Palkina *et al.* (1981), is today generally accepted. In addition, many of these compounds are isotypic and some are polymorphic. Only the cyclic condensed phosphate $KGdP_4O_{12}$ (Ettis *et al.*, 2003) has been elaborated in the ternary K_2O–Gd_2O_3–P_2O_5 system and, up to now, the types of polyphosphates existing in this ternary system have been unknown.

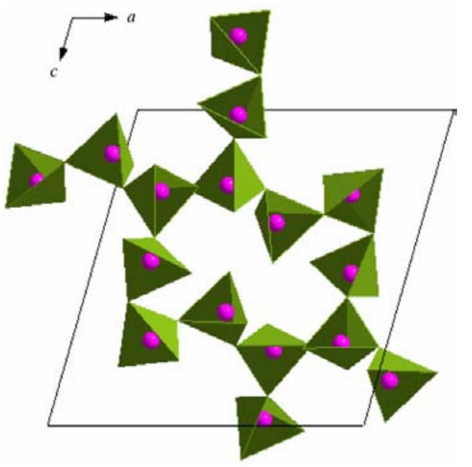

Figure 1
A projection of the structure of $KGd(PO_3)_4$ along the *b* axis. Circles represent P atoms. For clarity, K and Gd atoms have been omitted.

Our attempt to prepare new single crystals from phosphoric acid, gadolinium oxide and potassium dihydrogenphosphate was successful. In fact, this study resulted in a new form of polyphosphate, *viz*. $KGd(PO_3)_4$ (type IV), whose chemical preparation and crystal structure are presented here. The basic structural units are helical ribbons formed by corner-sharing PO_4 tetrahedra. The ribbons (two per unit cell) run along the [101] direction, with a period of eight tetrahedra. Every two chains are symmetrical by a twofold axis (Fig. 1). These chains are joined to one another by GdO_8 dodecahedra, forming a three-dimensional framework structure and delimiting tunnels in which the K^+ cations are located (Fig. 2).

In such a polyphosphate chain, the P—O distances can be divided into linking or bridging P—OL_{ij} and exterior P—OE_{ij} distances [where OL_{ij} denotes the O atom that links atom P_i with atom P_j, and OE_{ij} denotes the *j*th O atom exterior to the chain and bonded to atom P_i (Averbuch-Pouchot *et al.*, 1976)]. The linking distances, P—OL_{ij}, which range from 1.593 (3) to 1.614 (3) Å, are longer than the P—OE_{ij} distances, which range from 1.485 (3) to 1.496 (3) Å. The P—O—P angles range from 124.84 (16) to 133.77 (18)°. Furthermore, three different types of O—P—O angles co-exist in the PO_4 tetrahedra. The O*L*—P—O*L* angles [mean 99.21 (14)°] correspond to the longest P—O bonds, the O*L*—P—O*E* angles have the values expected for a regular tetrahedron and the O*E*—P—O*E* angles correspond to the shortest P—O distances [mean 119.04 (15)°], probably induced by mutual repulsion of the non-bridging O atoms (Table 1). Nevertheless, the calculated mean distortion indices (DI; Baur, 1974) corresponding to the different angles and distances in the independent PO_4 tetra-

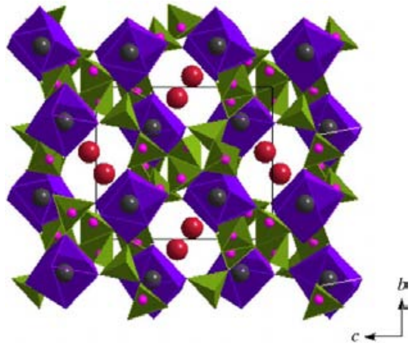

Figure 2
A projection of the structure of $KGd(PO_3)_4$ along the *a* axis. Large and medium-sized circles represent K and Gd atoms, respectively.

DOI: 10.1107/S0108270104004603

hedra [DI(P—O) = 0.0377, DI(O—P—O) = 0.0376 and DI(O···O) = 0.0138] show that the distortion of the P—O distances is greater than that of the O···O distances. The PO_4 tetrahedra therefore have local C_1 symmetry rather than the ideal $\overline{4}3m$ symmetry (Baur, 1974).

All external O atoms of the PO_4 tetrahedra are involved in coordination to the Gd atoms, with Gd—O distances ranging from 2.322 (3) to 2.492 (3) Å (Table 1). These atoms form irregular GdO_8 dodecahedra, which are separated from one another (Fig. 3*a*), the shortest Gd···Gd distance being 6.316 (11) Å. Such a configuration is also common around lanthanide cations, and thus the existence of isotypic $M^{I}Ln(PO_3)_4$ compounds is not surprising. These dodecahedra are regrouped two-by-two along the [001] and [101] directions (Fig. 4). The coordination polyhedra of the K^+ cation are formed by nine O atoms, two of them bridging O atoms (Fig. 3*b*). These polyhedra are very irregular, as seen in other polyphosphates (Palkina *et al.*, 1977); in fact, the K—O distances range from 2.779 (3) to 3.353 (3) Å (Table 1). KO_9 polyhedra are bound to one another, forming chains parallel to the [010] direction (Fig. 5). By comparison with the coordination around the Li^+ and Na^+ ions in the structures of $LiNd(PO_3)_4$ (Hong, 1975*a*) and $NaNd(PO_3)_4$ (Koizumi, 1976), it can be noted that the coordination number decreases from nine for the KO_9 polyhedra in the title structure to six for the NaO_6 octahedra in $NaNd(PO_3)_4$ and four for the LiO_4 tetrahedra in $LiNd(PO_3)_4$. This can be explained on the basis of the radii of the monovalent cation, as $r(K^+) > r(Na^+) > r(Li^+)$; therefore, as the number of O atoms per cation in the chemical formula is constant, it is clear that we pass from an open structure of coordination tetrahedra sharing only vertices in $LiNd(PO_3)_4$ to a compact framework sharing all edges in $KGd(PO_3)_4$ (type IV). If the anionic configuration of $KGd(PO_3)_4$ is compared with that of $NH_4Y(PO_3)_4$ (Bagieu-Beucher *et al.*, 1988), a decrease in the complexity of the chain is seen as the size of the trivalent cation increases; in particular, there is a decrease in the period from 16 to eight tetrahedra. This complication of the chain shape has already

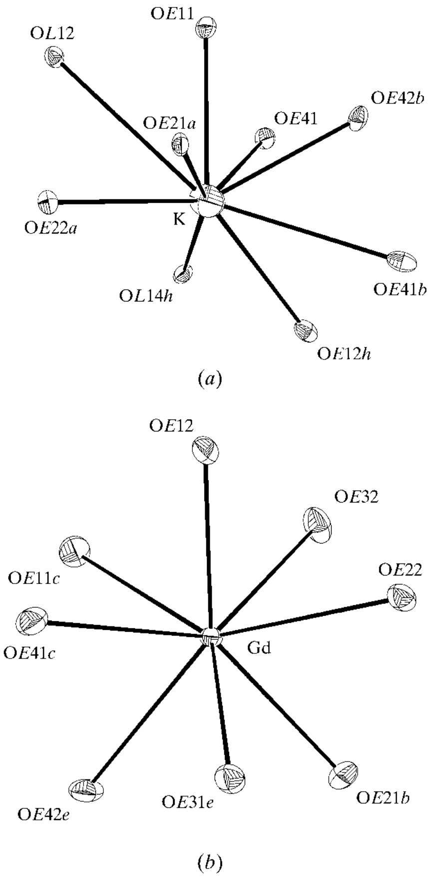

Figure 3
The O-atom coordination around (*a*) the Gd and (*b*) the K atoms (50% probability displacement ellipsoids). [Symmetry codes: (*a*) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (*b*) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{5}{2} - z$; (*c*) $-x, -y, 2 - z$; (*e*) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (*h*) $\frac{1}{2} + x, -y - \frac{1}{2}, \frac{1}{2} + z$.]

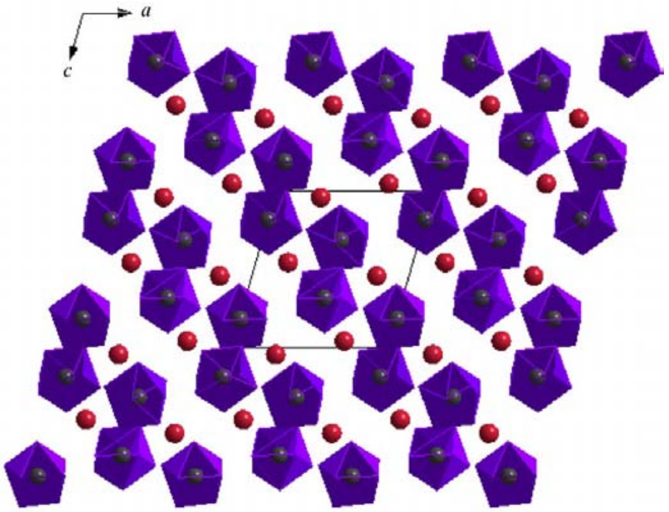

Figure 4
A projection of the structure of $KGd(PO_3)_4$ along the *b* axis. PO_4 tetrahedra have been omitted.

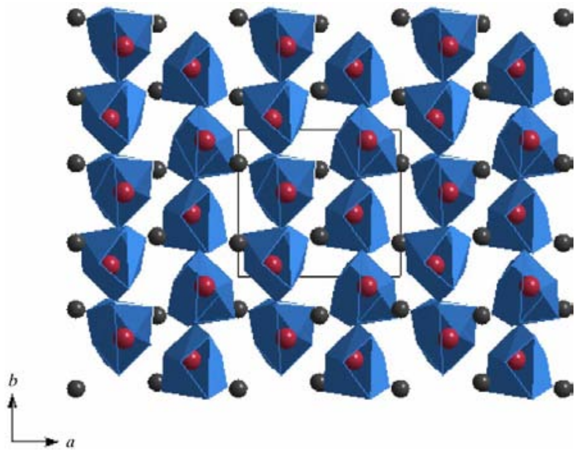

Figure 5
A projection of the structure of $KGd(PO_3)_4$ along the *c* axis. PO_4 tetrahedra have been omitted.

Acta Cryst. (2004). **C60**, i50–i52 Walid Rekik *et al.* • $KGd(PO_3)_4$ **i51**

been observed in other types of polyphosphates, *e.g.* $M^{\rm I}$Ln(PO_3)$_4$ (Palkina, 1982). A future aim is to relate the decrease in period more precisely to the increase in the difference between the sizes of the monovalent and trivalent cations.

Experimental

Crystals of KGd(PO_3)$_4$ were prepared using the flux method. H_3PO_4 (2.8 g), KH_2PO_4 (3.2 g) and Gd_2O_3 (0.4 g) were mixed in a Pt crucible, preheated to 473 K and kept at that temperature for 4 h. The temperature was then inceased to 823 K. Two days later, the temperature was reduced to 323 K at a rate of 40 K d^{-1}. After double washing with boiling water and with nitric acid to eliminate the remaining oxide, Gd_2O_3, colourless hexagonal crystals of KGd(PO_3)$_4$ were formed.

Compound (I)

Crystal data

KGd(PO_3)$_4$
M_r = 512.23
Monoclinic, $P2_1/n$
a = 10.412 (2) Å
b = 8.996 (2) Å
c = 10.836 (2) Å
β = 105.94 (1)°
V = 975.9 (3) Å^3
Z = 4
D_x = 3.486 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11–15°
μ = 7.94 mm^{-1}
T = 293 (2) K
Hexagonal, colourless
0.36 × 0.21 × 0.14 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Gd—O*E*32	2.322 (3)	P1—O*E*11	1.490 (3)
Gd—O*E*12	2.373 (3)	P1—O*E*12	1.491 (3)
Gd—O*E*42$^{\rm i}$	2.389 (3)	P1—O*L*14	1.605 (3)
Gd—O*E*11$^{\rm ii}$	2.400 (3)	P1—O*L*12	1.610 (3)
Gd—O*E*31$^{\rm i}$	2.409 (3)	P2—O*E*21	1.491 (3)
Gd—O*E*41$^{\rm ii}$	2.413 (3)	P2—O*E*22	1.496 (3)
Gd—O*E*21$^{\rm iii}$	2.426 (3)	P2—O*L*23	1.613 (3)
Gd—O*E*22	2.492 (3)	P2—O*L*12	1.614 (3)
K—O*E*42$^{\rm iv}$	2.779 (3)	P3—O*E*32	1.489 (3)
K—O*E*11	2.865 (3)	P3—O*E*31	1.490 (3)
K—O*E*21$^{\rm v}$	2.867 (3)	P3—O*L*23	1.606 (3)
K—O*E*22$^{\rm v}$	2.958 (3)	P3—O*L*34	1.606 (3)
K—O*E*12$^{\rm vi}$	3.081 (3)	P4—O*E*41	1.485 (3)
K—O*L*14$^{\rm vi}$	3.198 (3)	P4—O*E*42	1.489 (3)
K—O*E*41$^{\rm iv}$	3.247 (3)	P4—O*L*34	1.593 (3)
K—O*L*12	3.342 (3)	P4—O*L*14$^{\rm vi}$	1.609 (3)
K—O*E*41	3.353 (3)		
O*E*11—P1—O*E*12	121.70 (15)	O*E*31—P3—O*L*23	109.61 (14)
O*E*11—P1—O*L*14	109.69 (15)	O*E*32—P3—O*L*34	109.08 (15)
O*E*12—P1—O*L*14	107.54 (15)	O*E*31—P3—O*L*34	110.44 (15)
O*E*11—P1—O*L*12	106.00 (15)	O*L*23—P3—O*L*34	98.41 (14)
O*E*12—P1—O*L*12	110.92 (14)	O*E*41—P4—O*E*42	118.09 (16)
O*L*14—P1—O*L*12	98.54 (14)	O*E*41—P4—O*L*34	109.65 (15)
O*E*21—P2—O*E*22	117.25 (15)	O*E*42—P4—O*L*34	110.64 (15)
O*E*21—P2—O*L*23	106.70 (14)	O*E*41—P4—O*L*14$^{\rm vi}$	108.38 (15)
O*E*22—P2—O*L*23	111.23 (14)	O*E*42—P4—O*L*14$^{\rm vi}$	110.65 (15)
O*E*21—P2—O*L*12	108.82 (14)	O*L*34—P4—O*L*14$^{\rm vi}$	97.45 (14)
O*E*22—P2—O*L*12	109.34 (14)	P1—O*L*14—P4$^{\rm vii}$	129.86 (17)
O*L*23—P2—O*L*12	102.44 (13)	P4—O*L*34—P3	133.77 (18)
O*E*32—P3—O*E*31	119.15 (16)	P1—O*L*12—P2	132.11 (17)
O*E*32—P3—O*L*23	108.14 (14)	P3—O*L*23—P2	124.84 (16)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $-x, -y, 2-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{5}{2}-z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{2}+z$; (vii) $x-\frac{1}{2}, -\frac{1}{2}-y, z-\frac{1}{2}$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.149, $T_{\rm max}$ = 0.329
2233 measured reflections
2119 independent reflections
2058 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.017
$\theta_{\rm max}$ = 27.0°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -13 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
S = 1.24
2119 reflections
164 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 2.8091P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.79 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.08 e Å^{-3}

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Larson *et al.*, 1996); software used to prepare material for publication: *SHELXL*97.

Thanks are expressed to Professor A. Driss for the X-ray data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1694). Services for accessing these data are described at the back of the journal.

References

Averbuch-Pouchot, M. T., Durif, A. & Guttel, J. C. (1976). *Acta Cryst.* B**32**, 2440–2448.
Bagieu-Beucher, M. & Guitel, J.-C. (1988). *Z. Anorg. Allg. Chem.* **599**, 123–130.
Baur, W. H. (1974). *Acta Cryst.* B**30**, 1195–1215.
Durif, A. (1995). In *Crystal Chemistry of Condensed Phosphates.* New York: Plenum Press.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Ettis, H., Naïli, H. & Mhiri, T. (2003). *Cryst. Growth Des.* **3**, 599–602.
Fair, C. K. (1990). *MolEN.* Enraf–Nonius, Delft, The Netherlands.
Hong, H. Y.-P. (1975*a*). *Mater. Res. Bull.* **10**, 635–640.
Hong, H. Y.-P. (1975*b*). *Mater. Res. Bull.* **10**, 1105–1110.
Jaouadi, K., Naïli, H., Zouari, N., Mhiri, T. & Daoud, A. (2003). *J. Alloys Compd*, **354**, 104–114.
Koizumi, H. (1976). *Acta Cryst.* B**32**, 2254–2256.
Larson, A. C., Van Dreele, R. B. & Lujan, M. Jr (1996). *DIAMOND.* Neutron Scattering Center, MS-H805, Los Alamos National Laboratory, NM 87545, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Palkina, K. K. (1982). *Izv. Akad. Nauk SSSR Neorg. Mater.* **18**, 1413–1418.
Palkina, K. K., Chudinova, N. N., Litvin, B. N. & Vinogradova, N. V. (1981). *Izv. Akad. Nauk SSSR Neorg. Mater.* **17**, 1501–1503.
Palkina, K. K., Maksimova, S. I., Chudinova, N. N., Vinogradova, N. V. & Chibiskova, N. T. (1979). *Izv. Akad. Nauk SSSR Neorg. Mater.* **17**, 110–117.
Palkina, K. K., Maksimova, S. I. & Kuznetsov, V. G. (1978). *Izv. Akad. Nauk SSSR Neorg. Mater.* **14**, 284–287.
Palkina, K. K., Saiffuddinov, V. Z., Kuznetsov, V. G. & Chudinova, N. N. (1977). *Dokl. Akad. Nauk SSSR*, **237**, 837–839.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Tarasenkova, O. S., Dorokhova, G. I., Chudinova, N. N., Litvin, B. N. & Vinogradova, N. V. (1985). *Izv. Akad. Nauk SSSR Neorg. Mater.* **21**, 452–458.