Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL XP* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The diffraction data were collected by Dr J. Britten (Department of Chemistry, McMaster University) and the microprobe analysis was carried out by Dr C. Cermignani (Department of Earth Sciences, University of Toronto). The work was supported by a research grant to JB from the Canadian Natural Sciences and Engineering Research Council.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1174). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 5–7

Ga_3PO_7

Sophie Boudin and Kwang-Hwa Lii

Institute of Chemistry, Academia Sinica, Taipei, Taiwan.
E-mail: lii@chem.sinica.edu.tw

(*Received 17 March 1997; accepted 30 July 1997*)

Abstract

Trigallium phosphorus heptaoxide was synthesized by high-pressure hydrothermal synthesis. Its structure comprises PO_4 tetrahedra and GaO_5 trigonal bipyramids connected by edges to form Ga_3O_{10} clusters. It is isotypic with Fe_3PO_7 and is the third known compound in the Ga–P–O system.

Comment

Gallium phosphates are rare in the literature. In the Ga–P–O system, only two forms of $GaPO_4$ have been observed previously: the cristobalite (Mooney, 1956) and the α-quartz structure type (Litvin *et al.*, 1987). The structure of the latter has been widely studied under different pressures and temperatures (Sowa, 1994; Nakae *et al.*, 1995) as its compressibility properties are similar to those of the SiO_2 quartz phases. However, no new forms have been observed. By using high-pressure hydrothermal synthesis, we have isolated a third gallium phosphate, Ga_3PO_7, isotypic with the Fe_3PO_7 iron phosphate (Modaressi *et al.*, 1983) and report its structure here.

The Ga_3PO_7 structure (Figs. 1 and 2) contains Ga_3O_{10} clusters of three GaO_5 trigonal bipyramids. Within a cluster, each GaO_5 bipyramid shares two adjacent edges with two others. In this compact structure, each cluster shares six corners with six Ga–O clusters and four corners with four PO_4 tetrahedra. A comparison with the iron analogue shows that the gallium phosphate has smaller cell parameters, in agreement with the smaller size of the Ga^{3+} ion. Moreover, the Ga^{3+}—O distances, ranging from 1.863 (4) to 2.140 (3) Å, are

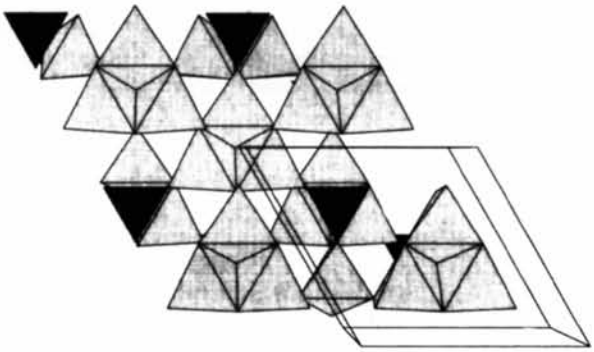

Fig. 1. Perspective view of the Ga_3PO_7 structure projected along the *c* axis with the *a* axis horizontal and the *b* axis close to vertical. The GaO_5 and PO_4 polyhedra are represented as light and medium gray, respectively.

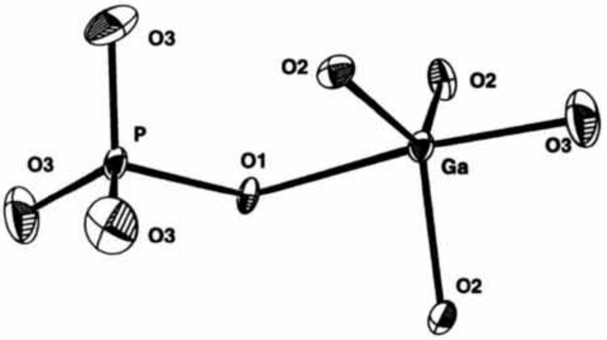

Fig. 2. A view of the GaO_5 and PO_4 units. The displacement ellipsoids are plotted at the 90% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 ©1998

slightly shorter than the Fe^{3+}—O distances, which range from 1.892 (7) to 2.190 (7) Å (Table 2). However, the PO_4 tetrahedra in both structures have a similar size and geometry with three short P—O distances of 1.508 (4) Å in Ga_3PO_7 and 1.502 (8) Å in Fe_3PO_7, and a long P—O distance of 1.574 (6) and 1.57 (1) Å, respectively.

Five-coordinate Ga^{3+} ions are rather rare and have been observed up to now in only a few phosphates, *e.g.* $\{(PrNH_3)[Ga_4(PO_4)_4.OH]\}.H_2O$ (Parise, 1985), $Ga_9P_9O_{36}OH.HNEt_3$ (Yang *et al.*, 1987), $[Ga_3(PO_4)_3F_2](CH_3NH_3)_2.H_2O$ (Cavellec *et al.*, 1994), $Ga_3(PO_4)_2(HPO_4)(H_2O)F_2.(N_4C_6H_{19})$ (Serpaggi *et al.*, 1994), $GaFPO_4$.0.5piperazine (Riou & Ferey, 1994) and $Rb_2[Ga_4(HPO_4)(PO_4)_4].0.5H_2O$ (Lii, 1996). The title compound shows that the Ga–P–O system can be extended with phases in which Ga^{3+} ions adopt a coordination stereochemistry other than tetrahedral.

Experimental

Crystals of Ga_3PO_7 were obtained from a high-pressure hydrothermal synthesis. The starting materials, $(NH_4)H_2PO_4$ (76 mg) and Ga_2O_3 (124 mg) in molar ratio 1:1, and H_2O (50 μl), were sealed in a 1 cm^3 gold tube. The ampoule was placed in a Leco Tem-Pres autoclave in which pressure was applied by water pumped and compressed air. The autoclave was first heated at 773 K for 24 hrs at a pressure of 210×10^6 Pa, then cooled slowly to 543 K at a rate of 4 K hr^{-1}, and finally quenched to room temperature by removing the autoclave from the furnace. The product was filtered, washed with water and methanol, and dried in air.

Crystal data

Ga_3PO_7
$M_r = 352.13$
Trigonal
$R3m$
$a = 7.885$ (1) Å
$c = 6.727$ (1) Å
$V = 362.21$ (8) Å^3
$Z = 3$
$D_x = 4.843$ Mg m$^{-3$}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.75$–17.30°
$\mu = 16.928$ mm^{-1}
$T = 293$ (2) K
Rhomboid
0.100 × 0.088 × 0.075 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.235$, $T_{max} = 0.281$
420 measured reflections
210 independent reflections

414 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0347$
$\theta_{max} = 34.94°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections frequency: 60 min intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.079$
414 reflections
26 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 1.6385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.959$ e Å^{-3}
$\Delta\rho_{min} = -0.869$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0141 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Bernardinelli & Flack (1985)
Flack parameter = 0.55 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ga	0.79674 (3)	$1 - x$	0.7448 (3)	0.00394 (15)
P	0	0	0	0.0041 (3)
O1	0	0	0.2340 (10)	0.0047 (9)
O2	0.5405 (3)	$1 - x$	0.8493 (6)	0.0055 (6)
O3	0.5603 (3)	$1 - x$	0.2729 (6)	0.0117 (6)

Table 2. *Selected geometric parameters (Å, °)*

Ga—O3^{i}	1.863 (4)	P—O3^{vi}	1.508 (4)
Ga—O2^{ii}	1.865 (4)	P—O3^{vii}	1.508 (4)
Ga—O2^{iii}	1.886 (2)	P—O3^{viii}	1.508 (4)
Ga—O2^{iv}	1.886 (2)	P—O1	1.574 (6)
Ga—O1^{v}	2.140 (3)		
O3^{i}—Ga—O2^{ii}	100.3 (2)	O2^{iii}—Ga—O1^{v}	78.78 (14)
O3^{i}—Ga—O2^{iii}	94.74 (12)	O2^{iv}—Ga—O1^{v}	78.78 (14)
O3^{i}—Ga—O2^{iv}	94.74 (12)	O3^{vi}—P—O3^{vii}	113.02 (14)
O3^{i}—Ga—O1^{v}	169.2 (2)	O3^{vi}—P—O3^{viii}	113.02 (14)
O2^{ii}—Ga—O2^{iii}	125.53 (14)	O3^{vi}—P—O1	105.6 (2)
O2^{ii}—Ga—O2^{iv}	125.53 (14)	O3^{vii}—P—O3^{viii}	113.02 (14)
O2^{ii}—Ga—O1^{v}	90.5 (2)	O3^{vii}—P—O1	105.6 (2)
O2^{iii}—Ga—O2^{iv}	104.6 (2)	O3^{viii}—P—O1	105.6 (2)

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

During the last step of the structure determination, the introduction and the refinement of the absolute structure Flack parameter, χ (Bernardinelli & Flack, 1985), clearly reveals the presence of inversion twins in our Ga_3PO_7 crystal with the value $\chi = 0.55$ (3). Significantly lower agreement factors are obtained for the twinned crystal structure model, $R = 0.024$, $wR = 0.061$ and $S = 1.079$, compared with $R = 0.033$, $wR = 0.084$ and $S = 1.114$ for the untwinned model.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *SHELXL*93.

We thank the Institute of Chemistry, Academia Sinica and the National Science Council of ROC for support and Dr K. J. Lin for X-ray data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1167). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 7–9

Un Monophosphate Synthétique de Sodium et de Cobalt: $Na_4Co_7(PO_4)_6$

DILSHAT KOBASHI, SHIZUO KOHARA, JUNJI YAMAKAWA ET AKIRA KAWAHARA

Laboratoire de Minéralogie, Départment des Sciences de la Terre, Faculté des Sciences, Université d'Okayama, Tsushima-Naka 3-1-1, Okayama 700, Japon. E-mail: ofez1011@cc.okayama-u.ac.jp

(Reçu le 6 mai 1997, accepté le 8 septembre 1997)

Abstract

Tetrasodium heptacobalt hexaphosphate, a new monophosphate prepared by hydrothermal methods, comprises CoO_6 and CoO_4 coordination polyhedra connected to each other by corner and edge sharing to form zigzag layers parallel to the *ab* plane. These layers are interconnected by Co–O polyhedra and P–O tetrahedra *via* corner sharing to form a three-dimensional network. The Na^+ ions are located in the tunnels running parallel to the *a* axis. This compound is isostructural with $Na_4Ni_7(PO_4)_6$.

Commentaire

En ce qui concerne les études des monophosphates de sodium et de cobalt, Hammond & Barbier (1996) ont fait la synthèse des deux composés, α-$NaCoPO_4$ et β-, et déterminé les structures cristallines. Moring & Kostiner (1986) ont obtenu $Na_4Ni_7(PO_4)_6$ et déterminé la structure. Nous avons obtenu $Na_4Co_7(PO_4)_6$ par une synthèse hydrothermale, et déterminé la structure.

Ce composé est isomorphe de $Na_4Ni_7(PO_4)_6$ (Moring & Kostiner, 1986), qui appartient aux groupe des monophosphates. Il y a quatre sortes des atomes de cobalt: Co1, Co2, Co3 et Co4 qui ont respectivement six, quatre, six et six voisins d'oxygène.

Le polyèdre de Co1 est lié par des sommets aux deux polyèdres de Co3 et de Co4. Et les polyèdres de Co2 sont liés par des sommets aux deux polyèdres de Co3 et de Co4. Co3 et Co4 sont liés les uns aux autres par des arêtes communes pour former des couches paralleles aux plans *a* et *b*. Ces couches sont liées par les quatre sortes de tétraèdres PO_4.

Trois sortes d'atomes de Na sont situées dans les interstices entre ces couches. La manière de connection des polyèdres des atomes Co et la structure suivant l'axe *a* sont montrés dans Fig. 1. Il y a des pseudo-plans miroir perpendiculaires à l'axe *b*. Ce composé appartient aux monophosphates de cation divalent-monovalent suivant la classification établie par Averbuch-Pouchot & Durif (1996).

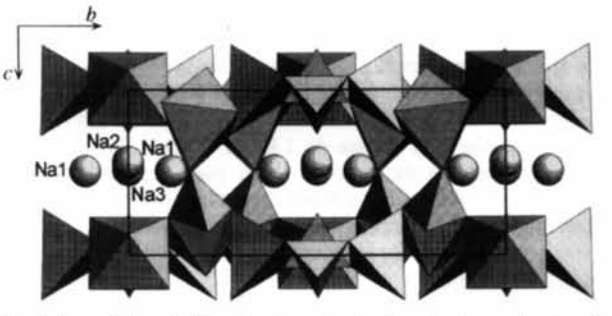

Fig. 1. La maille projetée suivant au plan *bc*. La structure a des tunnels parallèles à l'axe *a*. Chaque tunnel de la maille contient trois atomes de Na (*ATOMS*2.2; Dowty, 1992).

Une vue stéréographique est donnée dans la Fig. 2. Les distances interatomiques moyennes de Co1—O, Co2—O, Co3—O et Co4—O sont respectivement 2,061, 2,013, 2,112 et 2,109 Å [Ni1—O, Ni2—O, Ni3—O et Ni4—O sont respectivement 2,048, 2,139, 2,038 et 2,060 Å dans $Na_4Ni_7(PO_4)_6$; Moring & Kostiner, 1986]. Celles de P1—O, P2—O, P3—O et P4—O sont 1,530, 1,558, 1,552 et 1,530 Å [1,545, 1,534, 1,526 et 1,550 Å dans $Na_4Ni_7(PO_4)_6$; Moring & Kostiner, 1986]. Les distances interatomiques moyennes de Na1—O, Na2—

Acta Crystallographica Section C
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