Refinement

Refinement on *F*
$R = 0.040$
$wR = 0.040$
$S = 1.45$
3928 reflections
280 parameters
H atoms not refined
$w = 1/[\sigma^2(F_{obs}) + 0.02F_{obs}]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.17$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Hg—Cl3	2.424 (3)	Hg—Cl4	2.450 (3)
Hg—Cl2	2.430 (3)	Hg—Cl1	2.614 (2)
Cl2—Hg—Cl3	115.39 (9)	Cl1—Hg—Cl3	107.7 (1)
Cl4—Hg—Cl3	115.8 (1)	Cl1—Hg—Cl2	99.18 (8)
Cl4—Hg—Cl2	112.3 (1)	Cl1—Hg—Cl4	104.16 (9)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl4^{i}	0.96	2.70	3.342 (4)	125
N1—H2···Cl4	0.96	2.22	3.159 (6)	166
N2—H19···Cl1	0.96	2.17	3.131 (4)	174
N2—H20···Cl1^{ii}	0.96	2.29	3.207 (4)	159

Symmetry codes: (i) $-x, \frac{1}{2}+y, -z$; (ii) $-x, \frac{1}{2}+y, 1-z$.

The origin was fixed by setting the *y* coordinate of the Hg atom to zero. The absolute structure was determined by anomalous dispersion; the opposite enantiomorph resulted in a weighted *R* value of 0.085. All H-atom positions could be determined from the difference Fourier map. However, the calculated positions at a distance of 0.96 Å were used in the final refinement, with a common isotropic displacement parameter, since the calculated distances were more reasonable than the refined ones. The residual density shows six maxima with values ranging from 1.0 to 1.2 e Å^{-3} close to the Hg atom at distances of 1.1 to 1.2 Å. A similar situation is found for the minima. All refinements were performed using a Levenberg–Marquardt least-squares technique (Spengler, Zimmermann & Burzlaff, 1994; Zimmermann & Spengler, 1995; Spengler & Zimmermann, 1996).

Data collection: local software (Gomm, 1993). Cell refinement: local software. Data reduction: local software. Program(s) used to solve structure: *CRYSTAN* (Burzlaff & Rothammel, 1988). Program(s) used to refine structure: *CRYSTAN* (Spengler & Zimmermann, 1996). Molecular graphics: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTAN* (Burzlaff & Rothammel, 1988).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1221). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1568–1570

A New Gallium Phosphate Templated by Tris(2-aminoethyl)amine: $[Ga(HPO_4)(PO_4)(OH)].[(C_2H_7N)_3N].H_2O$

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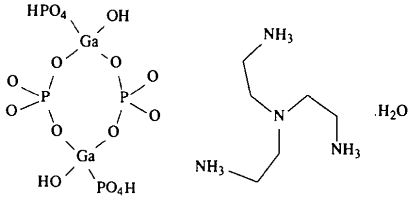
(*Received 20 March 1997; accepted 4 July 1997*)

Abstract

The title compound, bis(μ-phosphato-*O*:*O'*)bis[(hydrogenphosphato-*O*)(hydroxo)gallium] tris(2-aminoethyl)amine hydrate, was hydrothermally synthesized, in the presence of tris(2-aminoethyl)amine (tren), from a non-aqueous mixture in which dimethyl sulfoxide was used as solvent (423 K, 24 h, autogeneous pressure). Its structure consists of isolated hexameric units composed of two GaO_4 and four PO_4 tetrahedra, these units being separated by the tren and water molecules.

Comment

Since the synthesis of a new series of microporous aluminium phosphates (Wilson, Lok, Messing, Cannan & Flanigen, 1982), a large number of novel three-dimensional open-framework compounds has been characterized. Phosphate-based materials are generally prepared from aqueous hydrothermal systems in the presence of an organic amine or a quartenary ammonium as a templating agent. Recent works report the synthesis from organic or mixed solvents in which the water is a minor component (Huo & Xu, 1990). The control of the water content in combination with the use of both a non-aqueous solvent and a mineralizing agent has led to large-crystal materials with dimensions in the size range 0.4–5.0 mm (Kuperman, Nadimi, Oliver, Ozin, Garcés & Olken, 1993). These studies mainly concern the use of alcoholic solvents such as glycols or linear-alkyl alcohols. Our work is focused on the synthesis of phosphates by using dimethyl sulfoxide (DMSO), an aprotic solvent, with hydrofluoric acid (Loiseau, Serpaggi & Férey, 1997). We report here the preparation of a new gallium phosphate, $[Ga(HPO_4)(PO_4)(OH)].[C_2H_7N)_3N].H_2O$, in a DMSO–$H_2O$ mixture in the presence of tris(2-aminoethyl)amine (tren).



(I)

In the purely aqueous system, with the tren molecule, a layered fluorinated gallium phosphate, ULM-8, has already been produced (Serpaggi, Loiseau, Riou, Férey & Hosseini, 1994).

Here, the structure consists of isolated hexameric units composed of two Ga- and four P-centred tetrahedra separated by the tren molecule and water (Fig. 1). Each type of tetrahedron is almost regular with Ga—O and P—O distances in the ranges 1.761 (4)–1.812 (3) and 1.489 (3)–1.578 (3) Å, respectively. The O—Ga—O and O—P—O angles lie in the ranges 105.5 (3)–112.6 (1) and 103.5 (2)–114.6 (2)°, respectively. The Ga1- and P2-containing tetrahedra are corner shared in a strictly alternating manner, giving rise to a square four-membered ring. A second $P1O_4$ tetrahedron is linked to one of the two remaining free vertices of the GaO_4 tetrahedron. For one part, the cohesion of the structure is ensured in the (100) plane through strong hydrogen bonds between the PO_4 tetrahedra and the three terminal ammonium groups of the organic molecule [O1···HN2*C* = 1.85 (1), O1···HN3*B* = 1.96 (1), O1···HN4*C* = 1.99 (2), O2···HN2*A* = 1.94 (2), O2···HN3*A* = 2.12 (2), O2···HN4*A* = 2.02 (1), O3···HN4*B* = 2.12 (2) and O5···HN3*C* = 1.77 (2) Å]. The two terminal non-bonded O atoms, O6 (of the $P1O_4$ unit) and O9 (of the $Ga1O_4$ unit), should correspond to hydroxyl groups in order to balance the three positive charges of the tren molecule (this hypothesis is strengthened by the valence-bond analysis). Hydrogen bonds between the water molecule and both the GaO_4 and $P2O_4$ tetrahedron, *OW*···HO9 and O3···HO*W*, respectively, complete the cohesion of the structure.

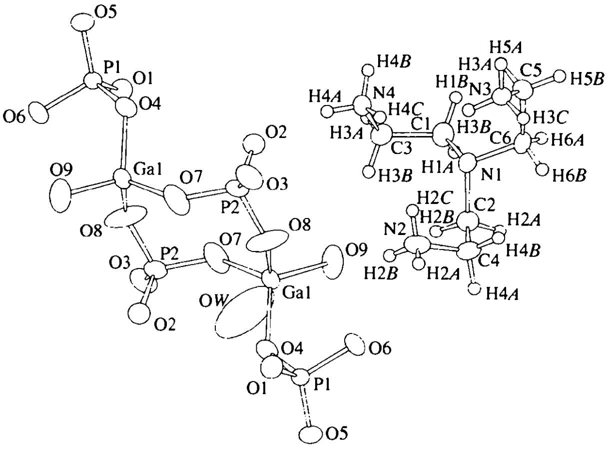


Fig. 1. Projection of the structure along the *a* axis.

Experimental

The title compound was prepared hydrothermally from a mixture of GaO(OH), H_3PO_4, HF, tris(2-aminoethyl)amine, dimethyl sulfoxide and water in the molar ratio 1:1:1:0.9:10:13. The resulting mixture was heated at 423 K for 24 h in an autoclave under autogeneous pressure, then filtered, washed and finally dried at room temperature. Examination under an optical microscope indicated a powder corresponding to GaOOH and colourless large crystalline platelets of the title compound. A suitable single crystal was isolated for X-ray diffraction analysis and its quality was tested on Laue photographs.

Crystal data

$[Ga(HPO_4)(PO_4)(OH)].$-
$C_6H_{21}N_4.H_2O$
$M_r = 444.72$
Monoclinic
$P2_1/c$
$a = 9.4881\ (10)$ Å
$b = 10.3231\ (11)$ Å
$c = 16.3226\ (11)$ Å
$\beta = 90.423\ (6)°$
$V = 1598.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.847$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 32 reflections
$\theta = 30$–$32°$
$\mu = 1.979$ mm^{-1}
$T = 293\ (2)$ K
Prismatic platelet
0.418 × 0.361 × 0.068 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape (Sheldrick, 1993)
$T_{min} = 0.864$, $T_{max} = 0.920$
2998 measured reflections
2891 independent reflections

1971 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 29.95°$
$h = -13 \rightarrow 10$
$k = -8 \rightarrow 13$
$l = -11 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity decay: 5.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.133$
$S = 0.955$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.863$ e Å^{-3}
$\Delta\rho_{min} = -0.501$ e Å^{-3}
Extinction correction: none

2891 reflections
211 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ga1—O9	1.761 (4)	P2—O8	1.555 (4)
Ga1—O8	1.798 (4)	N1—C1	1.469 (5)
Ga1—O7$^{\rm i}$	1.802 (3)	N1—C6	1.473 (5)
Ga1—O4$^{\rm ii}$	1.812 (3)	N1—C2	1.479 (5)
P1—O5	1.489 (3)	N2—C4	1.485 (6)
P1—O1	1.521 (3)	N3—C5	1.476 (6)
P1—O4	1.559 (3)	N4—C3	1.481 (5)
P1—O6	1.578 (3)	C1—C3	1.520 (6)
P2—O2	1.506 (3)	C2—C4	1.508 (6)
P2—O3	1.513 (3)	C6—C5	1.510 (6)
P2—O7	1.543 (4)		
O9—Ga1—O8	105.5 (3)	O2—P2—O8	111.0 (2)
O9—Ga1—O7$^{\rm i}$	109.0 (2)	O3—P2—O8	105.7 (2)
O8—Ga1—O7$^{\rm i}$	108.4 (2)	O7—P2—O8	106.7 (2)
O9—Ga1—O4$^{\rm ii}$	112.1 (2)	P1—O4—Ga1$^{\rm iii}$	123.9 (2)
O8—Ga1—O4$^{\rm ii}$	108.9 (2)	P2—O7—Ga1$^{\rm i}$	136.7 (2)
O7$^{\rm i}$—Ga1—O4$^{\rm ii}$	112.6 (2)	P2—O8—Ga1	131.0 (2)
O5—P1—O1	114.0 (2)	C1—N1—C6	111.0 (3)
O5—P1—O4	111.2 (2)	C1—N1—C2	111.1 (3)
O1—P1—O4	109.1 (2)	C6—N1—C2	110.5 (3)
O5—P1—O6	110.2 (2)	N1—C1—C3	111.8 (3)
O1—P1—O6	108.3 (2)	N1—C2—C4	111.6 (3)
O4—P1—O6	103.5 (2)	N4—C3—C1	111.5 (3)
O2—P2—O3	114.6 (2)	N2—C4—C2	112.5 (4)
O2—P2—O7	110.1 (2)	N3—C5—C6	111.1 (4)
O3—P2—O7	108.4 (2)	N1—C6—C5	112.4 (3)

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

The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990): one Ga and two P atoms were first located and all the remaining atoms, except the H atoms of the HPO$_4$ and HGaO$_4$ groups, were revealed from the difference Fourier map. The Fourier map analysis indicates three residues around the three terminal N atoms corresponding to three ammonium groups. No residue was observed around the central N atom. All H atoms, except those of the water molecule, were refined with restraints applied to maintain C—H and N—H geometry.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996).

The authors thank Professor M. Leblanc (Université du Maine) for the X-ray data collection and Rhône Poulenc for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1179). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1570–1572

Tris(2,2′-bipyridyl-*N*,*N*′)zinc(II) Thiosulfate Heptahydrate

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(*Received 11 February 1997; accepted 10 June 1997*)

Abstract

The structure of the title compound, [Zn(C$_{10}$H$_8$N$_2$)$_3$]S$_2$O$_3$.7H$_2$O, consists of cations, Zn(bipy)$_3^{2+}$ (where bipy is bipyridine), and anions, S$_2$O$_3^{2-}$. There is an unusually short S···S contact of 3.361 (3) Å between the anions and a complex hydrogen-bonding scheme involving the seven molecules of water of crystallization.

Comment

The present work is part of a larger study of the preparation and structures of thiosulfates of Cd and Zn with the organic ligands phen, dmph or bipy (where phen is 1,10-phenanthroline, dmph is 2,9-dimethyl-1,10-phenanthroline and bipy is bipyridine), which have been the subject of our interest in the last few years.

The compounds [Zn$_2$(phen)$_3$(S$_2$O$_3$)$_2$], (1) (Baggio, Baggio, Pardo & Garland, 1996), and [Zn(S$_2$O$_3$)(dmph)]$_2$NaHO.CH$_3$OH.5H$_2$O, (2) (Baggio, Pardo, Baggio & Garland, 1997), show different modes of coordination of the S$_2$O$_3^{2-}$ ion. In (1), the structure consists of [Zn(phen)$_2$]$^{2+}$ cations and [Zn(phen)(S$_2$O$_3$)$_2$]$^{2-}$ anions, with the thiosulfate group bonded to the metal through sulfur. In (2), the thiosulfate acts as a bidentate and bridging ligand with sulfur binding to Zn^{2+} and an oxygen to Na$^+$, thus giving a ten-membered ring structure.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997