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A novel gallium arsenate organically templated by propane-1,3-diyldiammonium with a ULM-3-type open framework: $[Ga_3(AsO_4)_3(OH)F](C_3H_{12}N_2)\cdot H_2O$

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Crystals of the title oxyfluorinated gallium arsenate, *viz.* tris(arsenato)fluorohydroxotrigallium propane-1,3-diyldiammonium monohydrate, were synthesized hydrothermally at 453 K under autogenous pressure, using 1,3-diaminopropane as the structure-directing agent. The solid crystallizes in the orthorhombic system and its structure was determined from single-crystal X-ray diffraction analysis. The structure is similar to that of gallium or aluminium phosphates with the ULM-3 structural type and is built up from a three-dimensional anionic framework composed of corner-linked hexameric $Ga_3(AsO_4)_3(OH)F$ units. The Ga atoms have an octahedral $[GaO_4(OH)F]$ or trigonal-bipyramidal $[GaO_4(OH)$ and $GaO_4F]$ coordination. These units are connected to one another and to the tetrahedral AsO_4 groups *via* OH or F bridges. The three-dimensional framework contains ten-ring channels along [010], crosslinked by eight-ring channels along [110] and $[1\bar{1}0]$. The diprotonated organic species and water molecules reside within the ten-ring channels. The cation is linked to the framework *via* an N—H···F hydrogen bond. A strong N—H···O hydrogen bond links the cation and the water molecule.

Comment

Nanoporous metal phosphates have attracted much attention because of their potential applications in diverse areas, such as catalysis, gas separation and ionic exchangers. During the past two decades, the open-framework phosphate series has been studied extensively (Cheetham *et al.*, 1999), and structural analyses of several aluminium phosphates showed that they possess three-dimensional networks identical to those encountered in the aluminosilicate zeolite family. The replacement of aluminium by gallium in these structures and the use of HF as a mineralizing agent have led to the discovery of novel large-pore open-framework compounds. For example, the gallium phosphates MIL-50 (Beitone *et al.*, 2003), cloverite (Estermann *et al.*, 1991) and $Ga_2(DETA)(PO_4)_2\cdot 2H_2O$ (Lin *et al.*, 2001) are characterized by unique topologies, with pores delimited by 18-, 20- and 24-ring channels, respectively.

One of the structural features of the fluorinated gallium phosphate series (Sassoye *et al.*, 2002) is the occurrence of the hexameric building species Ga_3P_3, comprising three phosphate groups and three gallium polyhedra (one central GaO_4X_2 octahedron connected to two GaO_4X trigonal bipyramids *via* X bridges; X = OH and F). This type of building unit is specifically reported in the aluminium (Natarajan *et al.*, 1996; Renaudin *et al.*, 1996) and gallium phosphates ULM-3 (Loiseau *et al.*, 1994, 1996; Yin & Nazar, 1994; Brouca-Cabarrecq & Mosset, 2000), and the gallium phosphates ULM-4 (Cavellec *et al.*, 1994; Loiseau *et al.*, 1997) and TREN-GaPO (Weigel *et al.*, 1997; Beitone *et al.*, 2002). These observations originated in structure-prediction calculations based on the building-unit concept by means of the AASBU method (Mellot-Draznieks *et al.*, 2002).

A variety of possible three-dimensional frameworks have been investigated using the hexameric M_3P_3 unit (M = Al and Ga), and several new topologies have been generated. In this series, the network of ULM-4 is found to be closely related to that of the gallium arsenate $GaAsO_4$-2 (Chen *et al.*, 1989). As discussed by Loiseau *et al.* (1997), only the orientations of the adjacent hexameric units differ in the two structures, leading to two distinct structure descriptions, although the crystal system remains monoclinic. It seems that the replacement of phosphate by arsenate groups plays a critical role for the formation of such three-dimensional open frameworks. This observation prompted us to study gallium arsenate, in order to compare the crystal chemistry of the gallium arsenates and phosphates.

The synthesis of organically templated aluminium or gallium arsenates has rarely been reported in the literature. Besides the preparation of $GaAsO_4$-2, the structural characterizations of two aluminium and gallium arsenates have been described (Yang *et al.*, 1989; Li *et al.*, 1991; Liao *et al.*, 2000; Feng *et al.*, 2001; Luo *et al.*, 2001). The present paper deals with the synthesis and structural characterization of the novel gallium arsenate $[Ga_3(AsO_4)_3(OH)F](C_3H_{12}N_2)\cdot H_2O$. The structure of this solid is similar to that of the gallium phosphate ULM-3 (Loiseau *et al.*, 1994) obtained with the same diamine, *viz.* 1,3-diaminopropane.

The structure is built up *via* the connection by vertices of AsO_4 tetrahedra to $GaO_4(OH)F$ octahedra, and $GaO_4(OH)$ and GaO_4F trigonal bipyramids. The three crystallographically non-equivalent As atoms are tetrahedrally coordinated to O atoms, with typical As—O distances ranging from 1.677 (3) to 1.698 (3) Å. One of the three Ga atoms, Ga2, is octahedrally connected to four O atoms, atom F1 and one hydroxy group (O13; the OH group and F atom are in *cis* positions). The location of the OH group was confirmed by bond-valence calculations (O'Keeffe & Brese, 1992); the bond-valence sum is 0.983 valence units for atom O13. The position of the F atom

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was deduced from single-crystal X-ray diffraction and chemical analyses. The Ga2—O distances range from 1.962 (3) to 1.970 (3) Å, the Ga2—O13 distance is 1.970 (3) Å and the Ga2—F distance is 1.985 (3) Å. This gallium octahedron is linked to the two other Ga atoms, Ga1 and Ga3, *via* the OH^- and F^- anions. These two Ga atoms are fivefold coordinated to four O atoms [Ga—O = 1.832 (3)–1.977 (3) Å] and one OH group [Ga3—O13 = 2.017 (3) Å] or one F atom [Ga1—F1 = 2.010 (3) Å; Table 1]. The resulting gallium trimer is linked to the three arsenate groups. The $As2O_4$ group shares corners with the three gallium polyhedra, whereas the $As1O_4$ and $As3O_4$ groups share corners with one octahedron and one trigonal bipyramid. This connection mode generates the specific moiety $Ga_3(AsO_4)_3(OH)F$ (Fig. 1), which was previously encountered in the gallium arsenate $GaAsO_4$-2 (Chen *et al.*, 1989) and gallium phosphates ULM-*n* and MIL-*n* (Sassoye *et al.*, 2002).

The arrangement of these hexameric blocks connected to one another *via* all their remaining free O atoms describes a three-dimensional framework, delimiting marquise-shaped ten-ring channels (4.5 × 3 Å, based on the ionic radius of 1.35 Å for oxygen) running along [010] (Fig. 2), and eight-ring channels along [110] and $[1\bar{1}0]$. A strict gallium and arsenic alternation is observed in this structure, except for the occurrence of the Ga1—Ga2—Ga3 linkage present in the hexameric block. The propane-1,3-diyldiammonium species is trapped in the ten-ring tunnels, together with a water molecule (O*W*).

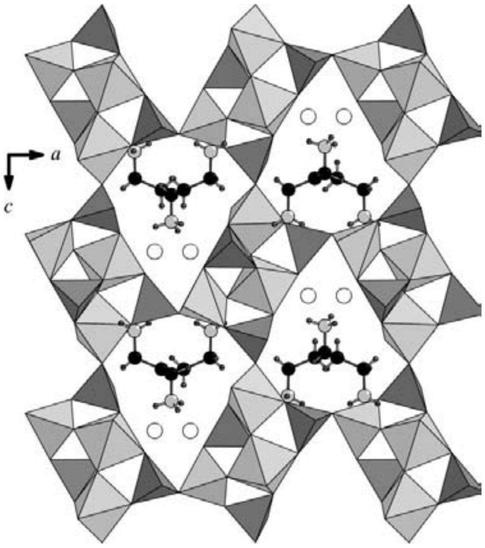

Figure 2
A polyhedral projection of the structure of $[Ga_3(AsO_4)_3(OH)F]$-$(C_3H_{12}N_2)\cdot H_2O$ (ULM-3 type) along [010], showing the ten-ring channels encapsulating propane-1,3-diyldiammonium counter-ions (grey circles: N atoms; black circles: C atoms; small open circles: H atoms) and water molecules (open circles). Pale-grey polyhedra represent Ga polyhedra and dark-grey tetrahedra represent As polyhedra.

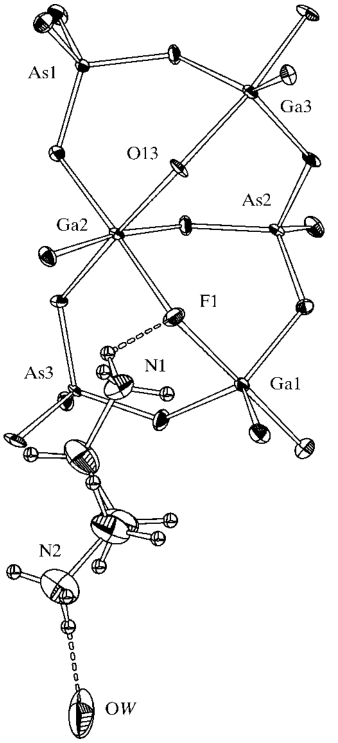

Figure 1
A displacement ellipsoid plot (50% probability level) of the hexameric $Ga_3(AsO_4)_3(OH)F$ building unit, with the propane-1,3-diyldiammonium counter-ions and free water molecule (O*W*). Dotted lines indicate the preferential hydrogen-bond interactions between atoms N1, H1*C* and F1, and between N2, H2*B* and O*W*.

The organic propane-1,3-diyldiammonium ion is diprotonated and its two positive charges balance the negative charges of the $[Ga_3(AsO_4)_3(OH)F]^{2-}$ anionic framework. One of the ammonium head groups is connected to the anions of the framework *via* hydrogen-bond interactions with the anion. There are strong N—H···O and N—H···F hydrogen bonds involving atom N1; the other ammonium group, containing atom N2, interacts with the water molecule *via* a very strong N—H···O hydrogen bond, thus defining a monohydrated propane-1,3-diyldiammonium moiety that seems to play the role of structure-directing agent for the formation of the title gallium arsenate. This compound exhibits a framework topology identical to that of the phosphate-based solids ULM-3, and no structural difference is observed between the gallium arsenate and phosphate series. This situation differs for ULM-4 (Loiseau *et al.*, 1997), for which two three-dimensional networks based on the hexameric Ga_3T_3 unit (T = P and As) have been synthesized.

Experimental

The title compound was prepared hydrothermally from a mixture of gallium oxohydroxide (GaOOH), arsenic acid (H_3AsO_4, 75%), hydrofluoric acid (HF, 40%), 1,3-diaminopropane ($N_2C_3H_{10}$, 98%) and deionized water in the molar ratio 1:1:0.5:1.1:50. This mixture was sealed in a teflon-lined Parr autoclave and then heated for 48 h at 453 K under autogenous pressure. The pH was 4–5 during the synthesis. After being cooled to room temperature, the solid was separated from the liquid phase by filtration, washed with water and then dried in air. A single crystal was selected optically for the diffraction study and glued to a glass fiber. The presence of fluorine was established by chemical analysis; found: F 2.3%; calculated for one F per $Ga_3(As_3O_4)$ unit: 2.5%. The location of this atom, in one of the bridging sites between the Ga atoms, was deduced from consideration of the displacement parameters and confirmed by bond-valence calculations (O'Keeffe & Brese, 1992).

Crystal data

$[Ga_3(AsO_4)_3(OH)F]$-$(C_3H_{12}N_2)\cdot H_2O$
$M_r = 756.09$
Orthorhombic, *Pbca*
$a = 16.1522$ (1) Å
$b = 10.4928$ (1) Å
$c = 18.9161$ (3) Å
$V = 3205.93$ (6) Å^3
$Z = 8$
$D_x = 3.133$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 102 reflections
$\theta = 2.2$–28.5°
$\mu = 11.24$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colourless
0.70 × 0.22 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.035$, $T_{\max} = 0.260$
20 592 measured reflections
4029 independent reflections
3267 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\max} = 28.5°$
$h = -14 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.02$
4029 reflections
239 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2]$
where $P = (F_o^2 + 2F<_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.63$ e Å^{-3}
$\Delta\rho_{\min} = -2.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00183 (10)

H atoms bonded to N and C atoms were included as riding atoms, with C—H distances of 0.97 Å and N—H distances of 0.89 Å; H atoms bonded to O atoms could not be located.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1296). Services for accessing these data are described at the back of the journal.

Table 1
Selected interatomic distances (Å).

As1—O10	1.680 (3)	Ga2—O11	1.962 (3)
As1—O12	1.681 (3)	Ga2—O2	1.963 (3)
As1—O9	1.684 (3)	Ga2—O13	1.970 (3)
As1—O5	1.694 (3)	Ga2—O10	1.970 (3)
As2—O1	1.677 (3)	Ga2—O1	1.970 (3)
As2—O2$^{\rm i}$	1.684 (3)	Ga2—F1$^{\rm iv}$	1.985 (3)
As2—O6	1.689 (3)	Ga3—O7$^{\rm v}$	1.872 (3)
As2—O8	1.695 (3)	Ga3—O5	1.878 (3)
As3—O3$^{\rm ii}$	1.663 (3)	Ga3—O6	1.892 (3)
As3—O4	1.691 (3)	Ga3—O3	1.971 (3)
As3—O11	1.692 (3)	Ga3—O13	2.017 (3)
As3—O7	1.698 (3)	N1—C3	1.490 (8)
Ga1—O12$^{\rm iii}$	1.832 (3)	N2—C1$^{\rm vi}$	1.462 (8)
Ga1—O4	1.840 (3)	C1—N2$^{\rm vii}$	1.462 (8)
Ga1—O8	1.857 (3)	C1—C2	1.521 (9)
Ga1—O9$^{\rm i}$	1.977 (3)	C2—C3	1.525 (10)
Ga1—F1$^{\rm iv}$	2.010 (3)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O5$^{\rm i}$	0.89	2.04	2.927 (5)	173
N1—H1*B*···F1$^{\rm ii}$	0.89	2.36	3.008 (5)	130
N1—H1*B*···O2$^{\rm iii}$	0.89	2.41	3.265 (6)	162
N1—H1*C*···O9	0.89	2.02	2.882 (6)	163
N2—H2*A*···O11$^{\rm iv}$	0.89	2.20	3.053 (7)	160
N2—H2*A*···O10$^{\rm iv}$	0.89	2.53	3.071 (6)	120
N2—H2*B*···O*W*$^{\rm v}$	0.89	1.85	2.738 (8)	176
N2—H2*C*···O6$^{\rm vi}$	0.89	2.54	3.256 (7)	138

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

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