Preparation and Structural Characterization of a Novel Galloarsenate using a Dimethylamine Template

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A dimethylamine-occluding galloarsenate, designated $GaAsO_4$-2, has been prepared hydrothermally and determined structurally by single crystal *X*-ray diffraction.

Open framework aluminophosphates occluding organic amines have proved to be of interest because of their structures and properties, which are similar to those of zeolites.[1—3] Recently, a series of organic amine-occluding gallophosphates have also been prepared.[4—6] Since As and P belong to the same group in the periodic table, it is of significance to focus attention on the preparation of aluminoarsenates and galloarsenates occluding organic amines. Following our report of the synthesis of $GaAsO_4$-1, a galloarsenate occluding tetramethylammonium hydroxide,[7] we present in this Communication the preparation and structural characterization of a novel open framework galloarsenate occluding dimethylamine.

The inclusion compound, $GaAsO_4$-2, was synthesized by a hydrothermal procedure. Dimethylamine (DMA), $Ga(OH)_3$, pyroarsenic acid, and water were mixed in a mole ratio of $3.6DMA : 1.0Ga_2O_3 : 1.2As_2O_5 : 40H_2O$. The mixture was sealed in a Teflon-lined autoclave and heated at 180 °C for 5 days. Hydrofluoric acid ($HF/Ga_2O_3 = 1.2$) was added to the reaction mixture and the autoclave was resealed and heated at 200 °C for 10 days. The product appeared as a thick plate-like structure under an optical microscope. The *X*-ray powder

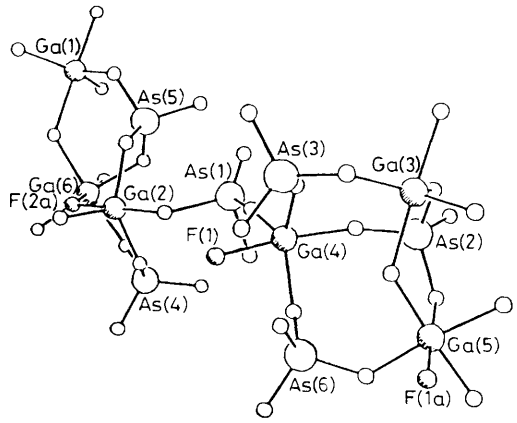

Figure 1. Connections in an asymmetric unit of $GaAsO_4$-2. All the circles except for those labelled represent O atoms. Bond lengths: Ga–O 1.830—2.041, As–O 1.652—1.696, Ga–F 1.984—2.003 Å.

diffraction pattern indicates that $GaAsO_4$-2 has a novel structure.†

Chemical and elemental analyses of $GaAsO_4$-2 gave an empirical formula of $GaAsO_4 \cdot 0.6DMA \cdot 0.3HF \cdot 0.3H_2O$. Structural characterization reveals that the formula of each asymmetric unit (Figure 1) is $Ga_6(AsO_4)_6 \cdot (DMA)_4 \cdot (HF)_2 \cdot (H_2O)_2$, which is consistent with the result above. In each unit cell, there are 24 Ga, 24 As, 104 O, 8 F atoms, and 16 DMA molecules. All the As atoms are tetrahedrally co-ordinated by O atoms. Of the 24 Ga atoms, one third are six-co-ordinated and two thirds five-co-ordinated by O or F atoms. The 104 O atoms can be classified into two types. The first type each connect a Ga and an As atom, with Ga–O bond lengths of 1.83—1.98 Å, whereas the second (only eight) each bridge two Ga atoms with Ga–O bond lengths of 1.97—2.04 Å. In addition, there are F atoms co-ordinating to adjacent Ga atoms in the framework. The Ga–F bond lengths are within 1.97—2.00 Å.

The 3D framework net constructed by Ga, As, O, and F has three kinds of open channels as shown in Figure 2 (O and F atoms are not shown for convenience). One channel is formed by 10-T (T = Ga or As) rings packing along the *b* axis. The other two channels are formed by zigzag packing of 8-T rings along the *a* and *c* axes respectively. The DMA molecules are located in the 10-T channels with their NH groups pointing towards the channel wall. Perhaps[8] they are connected with the framework O and F atoms through weak N···H–O, N···H–F or N–H···O and N–H···F hydrogen bonds.

† *Crystal data*: $Ga_6(AsO_4)_6(C_2H_7N)_4(HF)_2(H_2O)_2$; M = 1508.22, monoclinic, space group $P2_1/n$, a = 18.011(4), b = 10.466(4), c = 19.035(4) Å, β = 113.97(6)°, U = 3278.81 Å^3, D_c = 3.06 g cm^{-3}, $F(000)$ = 2743, Z = 4. The intensity data were collected on a Nicolet XRD R_3 diffractometer within the range $3<2\theta<50°$, graphite monochromator, Mo-K_α (λ = 0.71069 Å), μ = 112.28 cm^{-1}, scan mode ω, variable speed. The structure was solved by direct methods on the basis of 4639 unique reflections [$I \geq 5.0\sigma(I)$] out of 6551 measured. An empirical absorption correction was applied to the data and the R and R_w were refined by using SHELXTL to the values of 0.0795 and 0.0776, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

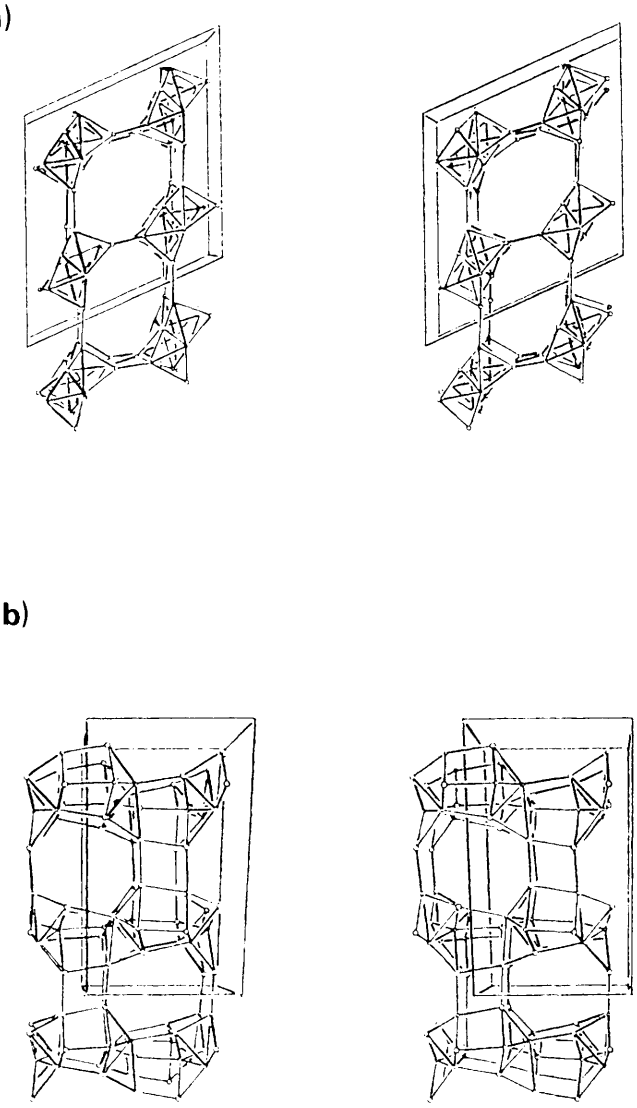

Figure 2. Stereoview of $GaAsO_4$-2 framework composed of Ga and As nodes along (a) the *b* axis and (b) the *a* or *c* axis. All Ga and As atoms are represented by small circles.

The successful preparation of $GaAsO_4$-2 presents an apt illustration of the formation of organic amine-occluding galloarsenates with considerably open frameworks.

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