Synthesis and Structure of a Novel Aluminoarsenate with an Open Framework

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An aluminoarsenate, $Al_2As_2O_8$·ethanolamine, denoted as $AlAsO_4$-1, has been synthesized hydrothermally; single crystal *X*-ray diffraction shows that its framework possesses micropores running along the *a*-axis.

Since the first series of microporous aluminophosphates denoted as $AlPO_4$-*n*[1] was prepared in 1982, these materials have been extensively studied.[2—4] Some of them are isostructural with known zeolites, but a majority have novel structures.[5] Recently, the synthesis and structural determination[6,7] of gallophosphates with frameworks as open as those of $AlPO_4$-*n* have been reported. We report the synthesis and structure of a novel aluminoarsenate with an open framework.

To synthesize the title aluminoarsenate, pyroarsenic acid, aluminium isopropoxide, the organic template EAN (EAN =

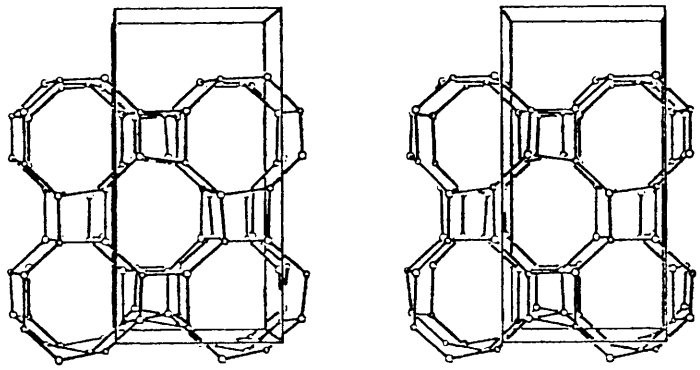

Figure 1. Stereoview of the $AlAsO_4$-1 framework along the *a*-axis, showing connections between alternating Al and As atoms. All Al and As atoms are represented by circles.

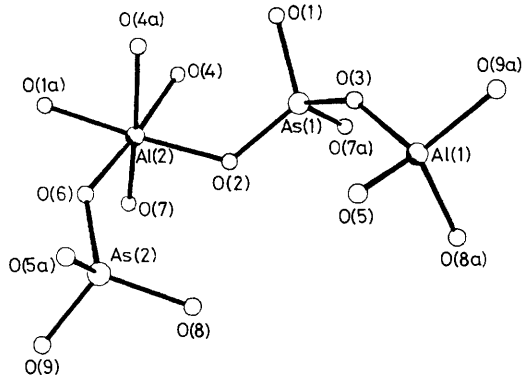

Figure 2. Asymmetric unit of $AlAsO_4$-1. Bond lengths: Al(1)–O(3) 1.728, Al(1)–O(5) 1.733, Al(1)–O(8a) 1.751, Al(1)–O(9a) 1.718, Al(2)–O(1a) 1.913, Al(2)–O(2) 1.883, Al(2)–O(4) 1.949, Al(2)–O(4a) 1.927, Al(2)–O(6) 1.879, Al(2)–O(7) 1.844, As(1)–O(1) 1.682, As(1)–O(2) 1.668, As(1)–O(3) 1.698, As(1)–O(7a) 1.678, As(2)–O(5a) 1.667, As(2)–O(6) 1.649, As(2)–O(8) 1.676, As(2)–O(9) 1.668 Å.

ethanolamine), and distilled water were mixed in the molar ratio of 0.8 EAN : Al_2O_3 : As_2O_5 : 40 H_2O, and stirred until homogeneous. The mixture was sealed in an autoclave lined with polytetrafluoroethylene and heated in an oven at 150—200 °C for 4 days. The product was filtered, washed with distilled water, and dried in air at about 80 °C. Excellent single crystals suitable for structural analysis by *X*-ray diffraction could be selected readily.†

The molar ratio Al/As of $AlAsO_4$-1 was measured by chemical analysis to be unity. The elemental analyses (C, 6.02; H, 1.74; N, 3.43%) indicated that $AlAsO_4$-1 has the empirical formula of $AlAsO_4 \cdot 0.5$ EAN. Structural analysis indicated that in each unit cell there are 16 Al atoms, 16 As atoms, and 8 EAN molecules. Topologically, the three-dimensional framework of $AlAsO_4$-1 is based on up–down linkages from a 4·8·8 two-dimensional net[8] (Figure 1), and the largest one-dimensional open channel of the framework results from packing of 8-membered rings along the *a* axis. There is no channel in any other direction. The formula of the asymmetric unit (as shown in Figure 2) appears to be $Al_2As_2O_8 \cdot$EAN which is concordant with the empirical formula above. Of the 9 oxygen atoms, O(4) or O(4a) is that of EAN molecule. As for the P atom in $AlPO_4$-*n*[5] or $GaPO_4$-*n*,[7] each As atom in $AlAsO_4$-1 is strictly four-co-ordinated by 4 oxygen atoms which are linked with 4 Al atoms. It is of considerable interest that in the asymmetric unit one Al is strictly four-co-ordinated and the other is six-co-ordinated. The former shares 4 oxygen atoms with 4 adjacent As atoms and the latter not only shares 4 oxygen atoms with 4 adjacent As atoms but also is double bridged with another equivalent Al atom by two oxygen atoms of the EAN molecules located in two 8-membered ring channels (Figure 1 does not show the organic template EAN). All the co-ordination polyhedra of the AlO_4 and AsO_4 units are slightly distorted tetrahedra, and all those of the AlO_6 units are strongly distorted octahedra. The length difference between the longest Al–O bond and the shortest one in each AlO_6 unit is 0.105 Å, and the largest difference between two O–Al–O angles is 16.4°.

We conclude that besides Al, P, and O atoms, Al, As, and O atoms are also able to construct a three-dimensional open framework.

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† *Crystal data:* $Al_2As_2O_8 \cdot C_2H_7NO$, M = 392.88, orthorhombic, space group *Pcab*, a = 8.781(2), b, 10.261(5), c = 20.433(2), Å, U = 1841.20 Å^3, Z = 8, D_c = 2.834 g cm^{-3}, $F(000)$ = 1495, μ = 74.70 cm^{-1}, SHELXTL. Mo-K_α 0.71059 Å, graphite monochromator, Nicolet XRD R_3 diffractometer, variable speed, scan mode θ–2θ. The intensity data were collected within $3 < 2\theta < 55°$; the structure was solved by direct methods on the basis of 1730 significant [$I \geq 3.5\,\sigma(I)$] reflections. Refinement by full-matrix least-squares led to final R and R_w values of 0.0401 and 0.0344 respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

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