Synthesis and crystal structure of a novel galloarsenate containing the $As_3O_{10}{}^{5-}$ triarsenate anion: $Cs_2Ga_3As_5O_{18}$

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The synthesis and crystal structure of $Cs_2Ga_3As_5O_{18}$ in which the Ga atoms are octahedrally and square-pyramidally coordinated are described: the three-dimensional structure is unique and contains the very rare triarsenate anion $As_3O_{10}{}^{5-}$.

Microporous aluminophosphates have been extentively studied because of their potential sorption and catalytic properties.[1,2] Numerous gallophosphates have also been synthesized to discover new open-framework materials. The replacement of aluminium by gallium has yielded both novel structures types[3–8] and phases that are analogous to known aluminophosphates and aluminosilicates.[9–11] In contrast, galloarsenates are rare and there were only four structurally characterized galloarsenates in the literature, namely $GaAsO_4$,[12] $Na_7Ga_3(As_2O_7)_4$,[13] $Na_3Ga_2(AsO_4)_3$[14] and $Ga_6(AsO_4)_6(C_2H_7N)_4(HF)_2(H_2O)$.[15] As part of our continuing study on the structural chemistry of phosphates and arsenates containing mixed octahedral–tetrahedral frameworks, we have also examined the A–Ga–As–O (A = alkali metal) system. We report here the synthesis and single-crystal X-ray structure of a novel galloarsenate, $Cs_2Ga_3As_5O_{18}$. Its framework structure is unique and contains five- and six-coordinate Ga-centred polyhedra, AsO_4 tetrahedra and the very rare triarsenate groups As_3O_{10}.

$Cs_2Ga_3As_5O_{18}$ was synthesized from a flux of CsH_2AsO_4 and $NH_4H_2AsO_4$ which were prepared from a solution of arsenic acid with a caesium hydroxide and ammonium hydroxide, respectively. A mixture of CsH_2AsO_4 (0.548 g), $NH_4H_2AsO_4$ (0.476 g) and Ga_2O_3 (0.188 g) (Cs : As mole ratio = 0.4 : 1) was placed in a 15 cm^3 platinum crucible and heated at 100 °C h^{-1} to 500 °C, maintained at 500 °C for 6 h, heated to 750 °C, maintained at 750 °C for 10 h, cooled at 5 °C h^{-1} to 500 °C, and quenched to room temperature by removing the crucible from the furnace. The flux was dissolved with hot water and the solid product was obtained by suction filtration. The product contained colourless plate-shaped crystals of $Cs_2Ga_3As_5O_{18}$. A suitable single crystal was obtained to determine its structure by X-ray diffraction.† Based on powder X-ray diffraction a single phase of $Cs_2Ga_3As_5O_{18}$ was prepared by heating a mixture containing a stoichiometric quantity of the starting materials at 620 °C for two days with an intermediate grinding.

Of the two cystallographically distinct Ga atoms, one is octahedrally coordinated to oxygen [Ga(1)–O_{av} 1.975 Å] and the other square-pyramidally coordinated [Ga(2)–O_{av} = 1.901 Å]. Five-coordinate gallium with square-pyramidal geometry is quite unusual. The four basal oxygen atoms of Ga(2)O_5 are nearly coplanar. The Ga atom is displaced 0.38 Å out of the basal plane towards the apical oxygen O(4). Each arsenic atom in $Cs_2Ga_3As_5O_{18}$ is tetrahedrally coordinated. The structure consists of corner-sharing GaO_6 octahedra, GaO_5 square pyramids, AsO_4 tetrahedra and As_3O_{10} groups. The structural formula is $Cs_2Ga_3(AsO_4)_2(As_3O_{10})$. A projection of the structure along the *b*-axis (Fig. 1) shows that the framework can be described by the stacking of $[GaAs_3O_{10}]_\infty$ mixed layers of GaO_6 octahedra and As_3O_{10} groups with $[Ga_2(AsO_4)_2]_\infty$ mixed layers of GaO_5 square pyramids and AsO_4 tetrahedra. The layers alternate within the structure along the *a*-axis. The framework forms infinite tunnels along the *b*-axis where the the caesium cations are located. Each channel has a seven-sided window formed by the edges of one octahedron, two square pyramids and four tetrahedra. The framework is also characterized by the presence of infinite tunnels along the *c*-axis with six-sided windows defined by the corner-sharing of one octahedron, two square pyramids and three tetrahedra and occupied by Cs^+ cations. Therefore, the compound adopts an intersecting tunnel structure with the Cs^+ cations located at the intersections of these tunnels. Each Ga(1)O_6 octahedron, which sits on an inversion centre, shares its six corners with four different As_3O_{10} groups. Two of the four triarsenates are coordinated to Ga(1) as bidentate ligands. Each As_3O_{10} group is coordinated to four Ga(1) atoms within a $[GaAs_3O_{10}]_\infty$ layer and to two Ga(2) atoms belonging to two adjacent $[Ga_2(AsO_4)_2]_\infty$ layers. Each Ga(2)O_5 square pyramid shares its five corners with four monoarsenates and one triarsenate. Each monoarsenate is coordinated to four different Ga(2)O_5 square pyramids belonging to the same $[Ga_2(AsO_4)_2]_\infty$ layer. The coordination number of Cs^+ in $Cs_2Ga_3As_5O_{18}$ cannot be determined unambiguously. There is no clear-cut gap in the Cs–O distances. If the maximum cation–anion distance for Cs–O, 3.60 Å, as suggested by Donnay and Allmann is considered as interacting, then the number of neighbouring oxygen atoms is much lower than would be predicted for Cs^+. The Cs^+ cation is coordinated by 10 oxygen atoms at distances ranging from 2.988 to 3.695 Å. There are two oxygen atoms at distances of 3.731 and 3.771 Å. The bond-valence sum[17] for the twelve Cs–O bonds is 1.03.

One of the major interests of the structure of $Cs_2Ga_3As_5O_{18}$ rests on the presence of a triarsenate anion $As_3O_{10}{}^{5-}$ (Fig. 2).

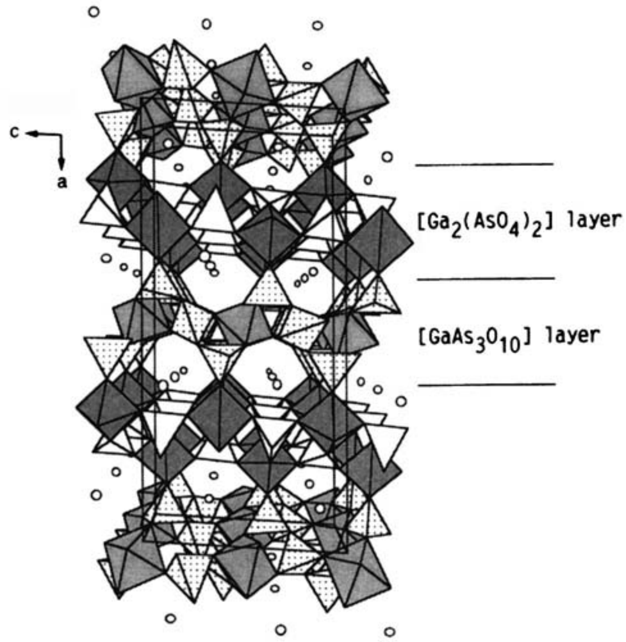

Fig. 1 Polyhedral view of the $Cs_2Ga_3As_5O_{18}$ structure along the *b*-axis. Open circles are Cs atoms.

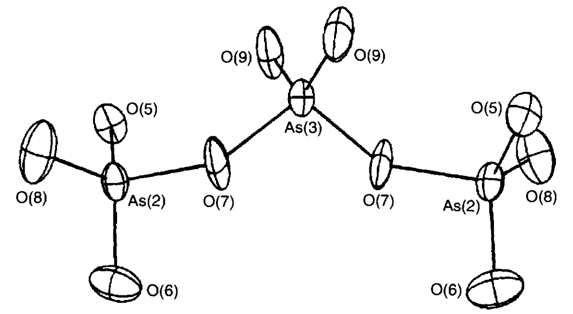

Fig. 2 The $As_3O_{10}^{5-}$ anion in $Cs_2Ga_3As_5O_{18}$. Thermal ellipsoids are shown at 60% probability. Selected bond lengths and angles: As(2)–O(5) 1.664, As(2)–O(6) 1.658, As(2)–O(7) 1.781, As(2)–O(8) 1.657, As(3)–O(7) 1.721, As(3)–O(9) 1.636 Å; As(2)–O(7)–As(3) 129°.

The anion is very rare and up to now few triarsenate(v) structures have been reported, namely, $A_5As_3O_{10}$ (A = K, Rb, Cs)[18] and $Na_3H_2As_3O_{10}$.[19] The $As_3O_{10}^{5-}$ anion in $Cs_2Ga_3As_5O_{18}$ sits on a twofold axis with the As–O_b bond distances 1.781 and 1.721 Å, As–O_t 1.636–1.664 Å and As–O_b–As bond angle 129 °, where O_b and O_t represent bridging and terminal oxygens, respectively. The As atoms are displaced away from the bridging oxygen so that the As–O_b bonds are considerably longer than the As–O_t bonds. The average As–O distances are comparable: As(2)–O 1.690, As(3)–O 1.678 Å. Adjacent AsO_4 tetrahedra are in eclipsed configurations. The distortion in the monoarsenate, $As(1)O_4$, is small in contrast with that in the triarsenate.

In summary, crystals of a novel galloarsenate, $Cs_2Ga_3As_5O_{18}$, were grown from a flux. The framework consists of GaO_6 octahedra, GaO_5 square pyramids, AsO_4 tetrahedra and the very rare triarsenate groups As_3O_{10} which together serve as building units to form an intersecting tunnel structure with the Cs^+ cations located at the intersections of the tunnels.

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Footnote

† *Crystal data* for $As_5Cs_2Ga_3O_{18}$: monoclinic system, space group *C*2/*c*; $a = 27.0360(7)$, $b = 5.1074(2)$, $c = 12.5112(4)$ Å, $\beta = 93.86(1)°$, $U = 1723.7(2)$ Å^3, $Z = 4$, $M_r = 1137.58$, $D_c = 4.384$ g cm^{-3}, μ(Mo-Kα) = 184.4 cm^{-1}, $\lambda = 0.71073$ Å, graphite monochromator, crystal dimensions: 0.25 × 0.12 × 0.03 mm. The crystal was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 1200 frames with increasing ω (width of 0.30 ° per frame). Unit-cell dimensions were determined by a least-squares fit of 3086 reflections having $15 < 2\theta < 40°$. Of the 8523 reflections collected ($2\theta_{max} = 53.5°$), 1486 unique reflections were considered observed [$I > 3.0\sigma(I)$] after Lorentz polarization and empirical absorption corrections. Correction for absorption was based on 3219 symmetry-equivalent reflections using the SHELXTL-PC program package. The transmission factors ranged from 0.262 to 0.983. The structure was solved by direct methods (SHELXTL-PLUS): the Cs, As and Ga atoms were first located and all the oxygen atoms were found in the final difference Fourier map. Refinement (130 variables) was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all atoms. The final Fourier residue of 2.21 e Å^{-3} was near the Cs atom (0.82 Å). The reliability factors converged to $R = 0.035$ and $R_w = 0.042$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/48.

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