

were corrected for absorption on the basis of integration. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150678. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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The Hg₃²⁺ Group as a Framework Unit in a Host–Guest Compound: [Hg₁₁As₄](GaBr₄)₄**

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Various inorganic supramolecular compounds with three-dimensional host structures are known.^[1] Among them is a separate group of phases in which the three-dimensional network is formed by tetrahedrally coordinated pnictogen and linearly coordinated mercury atoms.^[2] In some structures, some or all of the pnictogen atoms are joined into dumbbells

while keeping their tetrahedral arrangement.^[3] Here we report on [Hg₁₁As₄](GaBr₄)₄ (**1**), a novel supramolecular complex in which linear Hg₂²⁺ and Hg₃²⁺ fragments as well as Hg₂²⁺ cations take part in the formation of the three-dimensional host network. This is the first example of a linear Hg₃²⁺ group serving as a part of a three-dimensional framework.

The crystal structure^[4] of **1** consists of a three-dimensional [Hg₁₁As₄]⁴⁺ host network and tetrahedral GaBr₄[−] guest anions, which occupy one-dimensional infinite tunnels of the host framework (Figure 1). Large separations between the

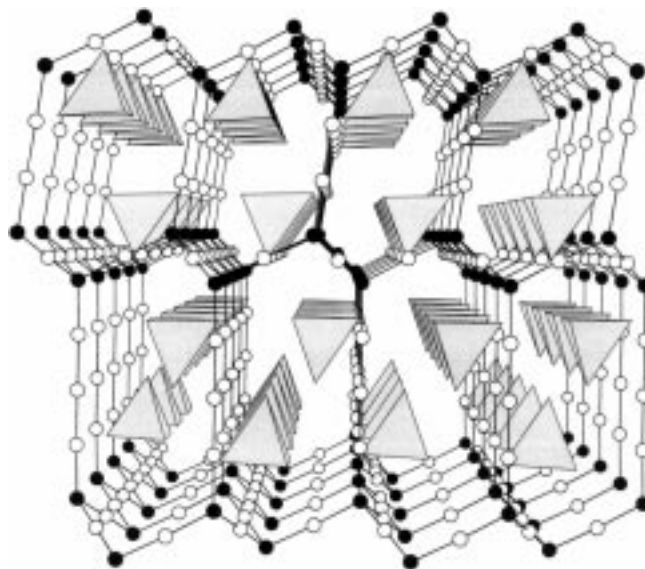


Figure 1. A perspective view of the crystal structure of [Hg₁₁As₄](GaBr₄)₄ (**1**) along the [010] direction of the unit cell. Open circles, mercury; filled circles, arsenic. Polyhedra represent the GaBr₄[−] ions.

bromine atoms of different GaBr₄ tetrahedra (> 3.68 Å), and between the bromine atoms and mercury atoms of the cationic framework (> 3.53 Å) allow the guests to be regarded as almost completely isolated from each other and from the host structure. With such separations, the host–guest interactions between the [Hg₁₁As₄]⁴⁺ framework and the GaBr₄[−] anions are apparently limited to weak electrostatic forces.

All the arsenic atoms in the host framework take part in the formation of corrugated layers, composed of edge-linked six-membered As₆ rings in a chair conformation, in which each edge of a chair is centered by a Hg₂²⁺ cation. These layers are interconnected by linear Hg₂²⁺ and Hg₃²⁺ fragments that alternate along the *c* axis of the unit cell in such a way that tetrahedral coordination of As is achieved. The ordered alternation of the two mercury polycations leads to the formation of two tunnels of different size that extend along the *b* axis of the unit cell (Figure 2). The Hg₂²⁺ and Hg₃²⁺ units serve as boundaries for the smaller and larger tunnels, respectively. The Hg–Hg distances in the Hg₂²⁺ (2.57 Å) dumbbell and in the Hg₃²⁺ group (2.58 Å) are typical of those found in various compounds containing mercury in low oxidation states.^[5] Note that while Hg₂²⁺ dumbbells are quite common in mercury chemistry, only a few compounds containing Hg₃²⁺ are known. In these, such groups are stabilized by AlCl₄[−], AsF₆[−], or (F₅MOSO₂OMF₅)^{2−} (M = Nb,

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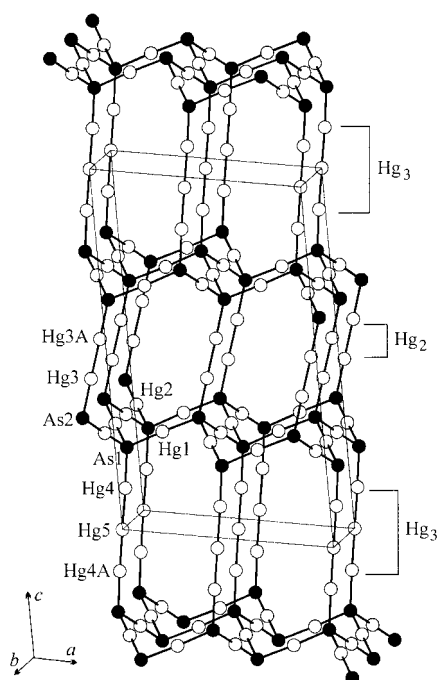


Figure 2. A portion of the ${}^3[\text{Hg}_{11}\text{As}_4]^{4+}$ cationic framework. Alternation of the Hg_2^{2+} and Hg_3^{2+} groups is shown. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Hg3-As2 2.520(4), Hg4-As1 2.545(4), Hg3-Hg3A 2.572(3), Hg4-Hg5 2.580(2); Hg3A-Hg3-As2 179.1(1), Hg5-Hg4-As1 178.4(1), Hg4-Hg5-Hg4A 180.

Ta) anions,^[6] that is, derivatives of very strong Lewis acids. Compound **1** is the first example of an architecture in which both Hg_2^{2+} and Hg_3^{2+} ions are present and take part in the formation of a stiff covalent network. The central mercury atom in the Hg_3^{2+} chain has a high thermal vibration amplitude in the plane perpendicular to the direction of the chain. This atom has only two neighboring mercury atoms to which it is covalently bonded and no other neighbors within a distance of 4.37 $\text{\AA}$.

Both types of tunnels in the framework are large enough to each contain two columns of discrete GaBr_4^- anions (Figure 1). This contrasts with phosphorus analogues of the Millon's base salts, the nearest structural analogues of **1**, in which each tunnel always contains only one column of guest anions.^[7] The orientation of the slightly distorted GaBr_4^- anions (Ga-Br 2.28–2.36 $\text{\AA}$, Br-Ga-Br 105.8–113.4 $^\circ$) is the same in each column, but the mutual orientations of the columns inside the larger and smaller tunnels are different (Figure 1).

The crystal structures of two compounds reported earlier,^[3a] namely, $[\text{Hg}_{23}\text{As}_{12}](\text{ZnBr}_4)_6$ and $[\text{Hg}_{13}\text{As}_8](\text{ZnCl}_4)_4$, provide examples for the adaptation of the three-dimensional mer-

cury–pnictogen frameworks to the size of the guest anions by “stitching” the tunnels with As–As bonds. Compound **1** represents another way of modifying the framework: the Hg–Hg groups expand the tunnels.

Experimental Section

Mercury(I) and mercury(II) bromides, gray arsenic, and gallium were mixed in the ratio 3:5:4:4 (1 g total), vacuum sealed in a quartz ampoule, and annealed for 3 d at 400 $^\circ\text{C}$. The product appeared as a dark red air-stable polycrystalline powder. An X-ray pattern of the sample (STADI-P (STOE), $\text{CuK}\alpha_1$ radiation) was identical to that calculated from the crystal data and did not reveal any impurities.

A single crystal for the structure determination was selected from the sample prepared from mercury(I) bromide, arsenic, and gallium, mixed in a 2:2:1 ratio, vacuum sealed, and heated for 4 d at 400 $^\circ\text{C}$.

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