# The Crystal Structures and Thermal Behaviour of the Mercury Arsenates $Hg_2(H_2AsO_4)_2$, $Hg_2As_2O_6$ and $HgAs_2O_6$

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Crystals of $Hg_2(H_2AsO_4)_2$, which are isotypic with the corresponding dihydrogenphosphate $Hg_2(H_2PO_4)_2$, were obtained from a concentrated arsenic acid solution. The crystal structure ($P2_1/n$, $a$ = 6.1838(4), $b$ = 15.0987(9), $c$ = 4.7989(3) Å, $\beta$ = 91.977(1)°, $Z$ = 2, $R$ = 0.045 for 1318 structure factors, 56 variables) contains a $Hg_2^{2+}$ dumbbell with a distance d(Hg-Hg) = 2.5040(10) Å and a symmetrical coordination of four oxygen atoms for each mercury atom. The oxygen atoms also belong to tetrahedral dihydrogenarsenate groups $H_2AsO_4^-$, which stabilize the structure by hydrogen bonding. On heating $Hg_2(H_2AsO_4)_2$ condenses to give the mercury(I) metaarsenate $Hg_2As_2O_6$. Crystals of that compound were obtained under hydrothermal conditions at 165 °C starting from elemental mercury in 60 wt% aqueous $H_3AsO_4$. The crystal structure ($P\bar{3}1m$, $a$ = 4.8411(2), $c$ = 7.5961(9) Å, $Z$ = 1, $R$ = 0.037 for 376 structure factors, 13 variables) may be represented by sheets of edge sharing [$AsO_6$] octahedra and layers of $Hg_2^{2+}$ dumbbells, which alternate along the $c$ axis. The dumbbells show a distance d(Hg-Hg) = 2.5190(10) Å and are coordinated symmetrically by six oxygen atoms at a distance d(Hg-O) = 2.374(4) Å. They are positioned above and below the vacant sites of adjacent $[As_2O_6]^{2-}$ layers. On further heating $Hg_2As_2O_6$ disproportionates into elemental mercury and mercury(II) metaarsenate, $HgAs_2O_6$. Single crystals of $HgAs_2O_6$ were grown *via* chemical vapor transport from microcrystalline $HgAs_2O_6$ with $HgCl_2$ as transport agent, using a temperature gradient of 650 → 550 °C. $HgAs_2O_6$ ($P\bar{3}1m$, $a$ = 4.8482(2), $c$ = 4.9789(10) Å, $Z$ = 1, $R$ = 0.031 for 367 structure factors, 12 variables) crystallizes in the $PbSb_2O_6$ structure type, where anionic $[Sb_2O_6]^{2-}$ layers have the same arrangement. The divalent mercury atoms have a pseudooctahedral environment of oxygen atoms with a distance d(Hg-O) = 2.353(3) Å.