Die Kristallstrukturen von Tetraphenylphosphonium-octahalogenodiarsenat(III) und -diantimonat(III) mit Acetonitril, $(PPh_4)_2[E_2X_8]\cdot CH_3CN$ (E = As, Sb; X = Cl, Br)

The Crystal Structures of Tetraphenylphosphonium Octahalogenodiarsenate(III) and Diantimonate(III) with Acetonitrile, $(PPh_4)_2[E_2X_8]\cdot CH_3CN$ (E = As, Sb; X = Cl, Br)

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Octachlorodiarsenate(III), Octachlorodiantimonate(III), Octabromodiarsenate(III), Crystal Structure

$(PPh_4)_2[As_2Cl_8]\cdot CH_3CN$ was obtained from PPh_4Cl and S_2Cl_2 with As or As_4S_4 or $AsCl_3$ in acetonitrile. PPh_4Cl, S_2Cl_2 and Sb_2S_3 yielded $(PPh_4)[Sb_2Cl_8]\cdot CH_3CN$. PPh_4Br and $AsBr_3$ gave $(PPh_4)_2[Sb_2Br_8]\cdot CH_3CN$. $AsCl_2OPh$ (from $AsCl_3$ and NaOPh) reacted with Ph_4Br in acetonitrile in the presence of Na_2Se, selenium, and HCl, affording $(PPh_4)_2[As_2Br_{4,2}Cl_{3,8}]\cdot CH_3CN$. According to their X-ray crystal structure determinations, all products are isotypic (space group $C2/c$, Z=4). The centrosymmetric anions consist of two ψ octahedra sharing an edge. In the $[As_2Br_{4,2}Cl_{3,8}]^{2-}$ ion the bridging positions are taken solely by bromine atoms, whereas Br and Cl atoms occupy the other halogen positions randomly.

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