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$(Hg_2P)_2HgBr_4$: A phosphorus analogue of the Millon's base salts

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An analogue of the salts of Millon's base, $(Hg_2P)_2HgBr_4$, was prepared by a solid-state synthesis; its crystal structure is based on a three-dimensional net, the tunnels of which are filled by columns of apex-shared, disordered $HgBr_5$ trigonal bipyramids.

A number of mercury complexes with known Hg–N bonding can be classified into four groups by subtracting a dimensionality of Hg–N fragments from their structures.[1] Such compounds have no analogues among the heavier elements of Group 15, even phosphorus, and all known mercury phosphide complexes contain ordinary P–P bonds in the form of dumbbells[2–4] or infinite chains.[5] This article reports the first example of the mercury phosphide $(Hg_2P)_2HgBr_4$ ($Hg_5P_2Br_4$), which contains the $[Hg_2P]^+$ cation having the same geometry as the $[Hg_2N]^+$ cation in Millon's base[6] and its salts.[7–9] The compound of composition $Hg_5P_2Br_4$ was prepared by the reaction of mercury dibromide with phosphine in benzene[10] as early as 1907. Since that time no additional data on this phase has appeared in the literature.

In this work, we prepared $(Hg_2P)_2HgBr_4$ by heating a stoichiometric mixture of mercury dibromide, red phosphorus and mercury in a sealed silica tube at 300 °C for 12 d. The product appeared as a bright yellow polycrystalline powder, which darkens upon exposure to light in the presence of air, but remains unchanged when illuminated under vacuum. Its crystal structure has been determined by X-ray analysis.†

The crystal structure of $Hg_5P_2Br_4$ (Fig. 1) possesses a tridymite-like three-dimensional net comprised of mercury and phosphorus atoms. Within the net, mercury atoms have nearly linear co-ordination with a mean P–Hg–P angle of 171.3°, while the phosphorus atoms possess an almost regular tetrahedral co-ordination of four mercury atoms, the Hg–P separation being very short (2.30–2.43 Å). The tunnels that cross the net are filled with columns of apex-shared $HgBr_5$ trigonal bipyramids. The mercury atom that should ideally lie on an equatorial plane of the bipyramid is split into two half-occupied positions,‡ each of which is characterized by a distorted tetrahedral co-ordination.

As the closest distances between mercury atoms from the three-dimensional net and bromine atoms from the polyhedra are 3.18 Å and greater, we consider $Hg_5P_2Br_4$ to be comprised of $[Hg_2P]^+$ cations and $[HgBr_4]^{2-}$ anions, and formulate the compound as $(Hg_2P)_2HgBr_4$. Such a formula provides an easy comparison with the salts of Millon's base, $(Hg_2N)X$, where X = NO_3, Br or I,[7,8] and $(Hg_2N)_2SO_4$.[9] The composition of the latter is the same as that of $(Hg_2P)_2HgBr_4$ in the sense of the cation to anion ratio, however, the geometry of the three-dimensional nets differs; it is tridymite-like in the case of $Hg_5P_2Br_4$ and quartz-like in the case of the Millon's base sulfate. The crystal structure most similar to that of $Hg_5P_2Br_4$ is that of the Millon's base bromide.[8] This phase exhibits the same, but regular, tridymite-like three-dimensional Hg_2N net and tunnels, which are filled with bromine atoms. The main difference between the two structures is the dimensions of the nets, those of Hg_2P being larger. This allows the incorporation of larger anions, and the full analogue of the Millon's base bromide, $(Hg_2P)Br$, is hardly expected.

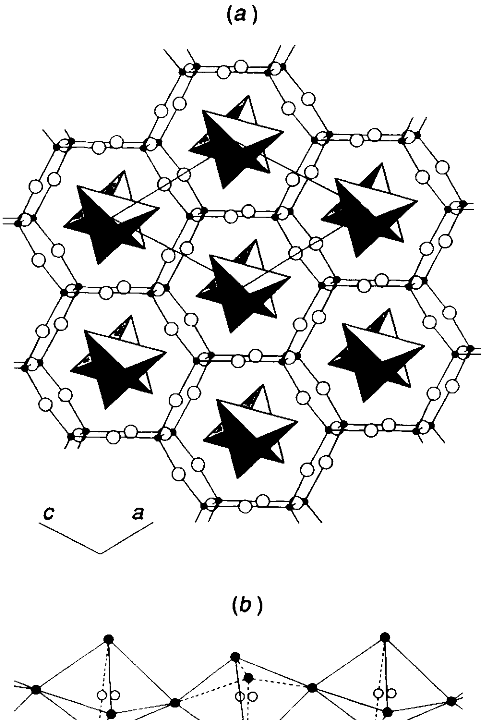

Fig. 1 Crystal structure of $(Hg_2P)_2HgBr_4$. (*a*) Projection onto the *ac* plane; open circles, mercury; filled circles, phosphorus. (*b*) Section of the $HgBr_4$ infinite column; open circles, mercury; filled circles, bromine

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† Crystal data: $Br_4Hg_5P_2$, M = 1384.53, monoclinic, space group $P2_1$, a = 7.776(3), b = 12.226(3), c = 7.930(3) Å, β = 121.340(10)° U = 643.9(4) $Å^3$, Z = 2, D_c = 7.141 g cm^{-3}. Diffraction data were measured on a CAD4F Enraf-Nonius diffractometer (Mo-Kα, λ = 0.710 69 Å, ω–2θ scan technique). The structure was solved by direct methods. The atomic parameters were finally refined anisotropically by full-matrix least-squares procedure on F^2,[11] the twinning of the crystal having been accounted for. The final discrepancy factors obtained were R = 0.0788 for 1103 independent reflections having $I(hkl) > 2\sigma(F)$ and R = 0.1437 for all 1741 data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number which may be obtained from the authors.

‡ During the structure refinement, the occupancies of these positions were refined independently and found to be close to 0.5 each. The occupancies were then kept fixed at 0.5, and atomic parameters of both half-occupied positions were refined isotropically because of their very small separation [0.575(9) Å].

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