Synthesis and crystal structure of new double mercury silver phosphide iodide $Hg_{12}Ag_{41}P_{88}I_{41}$

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New double mercury silver phosphide iodide $Hg_{12}Ag_{41}P_{88}I_{41}$ (**1**) was synthesized and its crystal structure was established. Compound **1** crystallizes in the cubic system. The characteristic feature of the crystal structure **1** is the presence of the anionic cage clusters P_{11}^{3-}, which have been previously found in alkali metal compounds only. The well-ordered P_{11}^{3-} clusters form a system of polyhedra, which encapsulate various disordered α-AgI-type fragments.

Key words: double mercury silver phosphide iodide, synthesis, crystal structure, phosphorus cluster, disorder, energy dispersive X-ray analysis.

The tendency of phosphorus to form homonuclear bonds is responsible for the existence of numerous phosphides with various stoichiometries and structures.[1] Both discrete phosphorus clusters and one-, two-, and three-dimensional infinite fragments are known. Finite fragments, for example, such chain anions as P_3^{5-}, P_4^{6-}, and P_5^{7-}, cyclic anions, for example, P_4^{4-} and P_6^{6-}, and the cage anions P_7^{3-}, P_{10}^{6-}, and P_{11}^{3-} belong to discrete clusters. The cage clusters are of interest because they are, in essence, systems of fused rings, but they form cages rather than polymeric fragments, such as layers or frameworks. The adamantane-like cluster P_{10}^{6-} is unique, is not present in binary phosphides, and was found only in mixed phosphides Cu_4SnP_{10} (see Ref. 2) and Au_3SnCuP_{10}.[3] The most abundant are the P_7^{3-} clusters, which were found in phosphides with the compositions M_3P_7 (for alkali metals)[1,4,5] and M_3P_{14} (for Sr and Ba)[6,7] and in the Ba_2P_7Cl compound.[8] Oligomeric and polymeric moieties based on the P_7^{3-} cage clusters were also documented.[1,9,10] The P_{11}^{3-} cage clusters do not form polymeric fragments and were found only in alkali metal compounds, for example, in phosphides with the composition M_3P_{11}.[1,11,12] Compounds, in which the P_{11}^{3-} clusters are stabilized by the coordination of alkali metal atoms to large organic ligands, which prevent the phosphorus atoms from interacting directly with alkali metal atoms and forming simpler structures, were also documented. The $Cs_3(en)_3P_{11}$ compound[13] can be given as an example of such compounds.

In the present study, we report the synthesis and the crystal structure of new double mercury silver phosphide iodide $Hg_{12}Ag_{41}P_{88}I_{41}$ (**1**), which is the first example of the presence of the phosphorus cluster P_{11}^{3-} in compounds containing no alkali metals.

Results and Discussion

Compound **1** is dark-red in color and is stable to atmospheric moisture. It was synthesized by the conventional ampoule techniques. To optimize the conditions of the preparation of a single-phase sample, we varied the annealing temperature (400—650 °C) and the duration of heating (0.5—24 h) and cooling (quenching, the switched-off furnace mode, 5 deg h^{-1}) and used different starting reagents (HgI_2, Hg_2I_2, AgI, Hg, Ag, and P). A single-phase sample was prepared by rapid heating of a mixture with the composition 41AgI : 12Hg : 88P to 500 °C and annealing at this temperature for 5 days followed by cooling in the switched-off furnace. It is conceivable that the rapid achievement of the annealing mode is necessary to prevent the formation of silver phosphides, which are very stable and hinder the formation of compound **1**. The presence of impurities was tested by X-ray powder diffraction, which showed the presence of solely the new compound. Under other annealing conditions, impurities of Ag_3P_{11} and AgI were detected by X-ray powder diffraction, and unconsumed mercury was visually observed.

Earlier,[14] the $Hg_7Ag_2P_8I_6$ compound has been obtained in the Hg—Ag—P—I system. This compound was prepared by annealing a mixture with the composition $3HgI_2$: 4Hg : 8P : 2Ag at 400 °C. However, the synthesis of this compound does not require the rapid achievement

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of the conditions of the synthesis. This difference in the methods for the synthesis of two compounds, *viz.*, **1** and $Hg_7Ag_2P_8I_6$, belonging to the same system, can be attributed to different thermodynamic stability and a substantial difference in the composition and the crystal structure, resulting in the absence of the $Hg_7Ag_2P_8I_6$ phase as an impurity in the case of the synthesis of compound **1**.

Single crystals of **1** suitable for X-ray diffraction analysis were chosen from the annealing products of a mixture with the composition 41AgI : 12Hg : 88P (pre-annealing time was 12 h, annealing at 550 °C for 5 days, and cooling in a switched-off furnace). To determine the crystal structure of **1**, two X-ray diffraction experiments were carried out at low temperature (−100 °C) and one experiment was performed at room temperature (25 °C). The results of these experiments appeared to be virtually identical taking into account the experimental error and the quality of the single crystals used. In the structure of **1**, almost all silver sites are disordered. After the refinement of the occupancies, the number of silver atoms in different X-ray diffraction experiments varies from 160 to 172 per unit cell. This is equal (within experimental error) to 164 silver atoms for the idealized formula, which was derived taking into account the electroneutrality of the compound as a whole (Table 1). The composition of compound **1** was additionally confirmed by the energy dispersive X-ray (EDX) method. The ratio determined from the EDX data (Hg : Ag : P : I — 6.4(2) : 22.5(2) : 46.5(1) : 22.5(2)) is in satisfactory agreement with that calculated for the idealized formula $Hg_{12}Ag_{41}P_{88}I_{41}$ (Hg : Ag : P : I — 6.6 : 22.5 : 48.4 : 22.5) taking into account the systematic error of the EDX method.

The characteristic feature of the crystal structure of the $Hg_{12}Ag_{41}P_{88}I_{41}$ compound is the presence of the anionic cage clusters P_{11}^{3-} (Fig. 1, *a*), which have been previously found only in alkali metal compounds. The P_{11}^{3-} cluster in compound **1**, like that in the compounds described earlier,**[1,11—13]** is built of eight three-bonded phosphorus atoms (3b)P^0 and three two-bonded phosphorus atoms (2b)P^- (in these symbols, the number of homonuclear bonds formed by a particular phosphorus atom is given in parentheses,**[15]** which indicates the formal oxidation state of this atom). The P_{11}^{3-} cluster consists of five independent phosphorus atoms. Nevertheless, the effective symmetry of this cluster can be described by the point group D_3 with the threefold axis passing through the P(3) and P(5) atoms and three twofold axes passing through the P(1) atom and the midpoint of the P(2)—P(4) bond (see Fig. 1, *b*). The P_{11}^{3-} cluster can be considered as a derivative of the previously unknown phosphocubane molecule containing six pentagonal faces instead of the starting square faces due to the involvement of three bridging phosphorus atoms. The P—P distances in compound **1** vary from 2.19 to 2.25 Å (Table 2), which correspond to the single bond length.**[1]**

The overall view of the crystal structure of **1** is presented in Fig. 2. The P_{11}^{3-} anions within 1/8 of the unit cell (octant) are arranged analogously to the sulfur atom in the sphalerite structure. In the structure of **1**, the clusters are linked to each other by mercury and silver atoms. The Ag(1) atom links the phosphorus clusters within the octant, whereas the mercury atoms link the clusters from the adjacent octants. The coordination environment of the Ag(1) atom can be described as a strongly distorted

Table 1. Atomic positional and thermal parameters in the structure of compound **1**

Atom	Site	*x/a*	*y/b*	*z/c*	Occupancy	U_{eq}/Å^2
Hg(1)	48*h*	0.2795(1)	0.0912(1)	0	1	0.022(1)
I(1)	4*a*	0	0	0	1	0.019(1)
I(2)	32*f*	0.0884(1)	0.0884(1)	0.0884(1)	1	0.025(1)
I(3)	48*h*	0.1905(1)	0	0.1843(1)	1	0.020(1)
I(4)	24*e*	0.3561(1)	0	0	1	0.024(1)
I(5)	32*f*	0.1847(1)	0.1847(1)	0.1847(1)	1	0.019(1)
I(6)	24*e*	0.2028(1)	0	0	1	0.031(1)
Ag(1)	48*g*	1/4	0.0666(1)	1/4	1	0.027(1)
Ag(2)	96*i*	0.1871(1)	0.0916(1)	0.1270(1)	0.822(7)	0.031(1)
Ag(3)	96*i*	0.1859(4)	0.0658(9)	0.0980(9)	0.125(8)	0.075(9)
Ag(4)	48*h*	0.0800(7)	0.1456(8)	0	0.092(6)	0.043(7)
Ag(5)	48*h*	0.1023(6)	0	0.0175(9)	0.114(7)	0.030(3)
Ag(6)	48*h*	0.0154(8)	0	0.8989(5)	0.118(7)	0.030(3)
Ag(7)	24*e*	0.4677(4)	0	0	0.236(8)	0.045(3)
Ag(8)	96*i*	0.4471(6)	0.9477(6)	0.0384(3)	0.122(3)	0.038(3)
P(1)	96*i*	0.2703(1)	0.1063(1)	0.0892(1)	1	0.014(1)
P(2)	96*i*	0.3184(1)	0.1018(1)	0.1991(1)	1	0.013(1)
P(3)	32*f*	0.3154(1)	0.1846(1)	0.1846(1)	1	0.012(1)
P(4)	96*i*	0.3295(1)	0.0642(1)	0.1270(1)	1	0.015(1)
P(5)	32*f*	0.4005(1)	0.0995(1)	0.0995(1)	1	0.016(1)

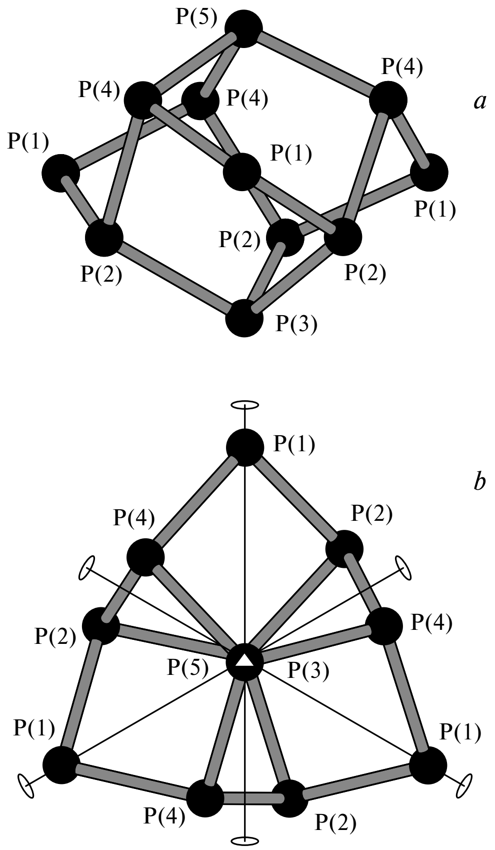

Fig. 1. Structure of the phosphorus cluster P_{11}^{3-}: (*a*) the view perpendicular to the threefold axis; (*b*) the view along the threefold axis (atomic numbering scheme corresponds to that given in Table 1).

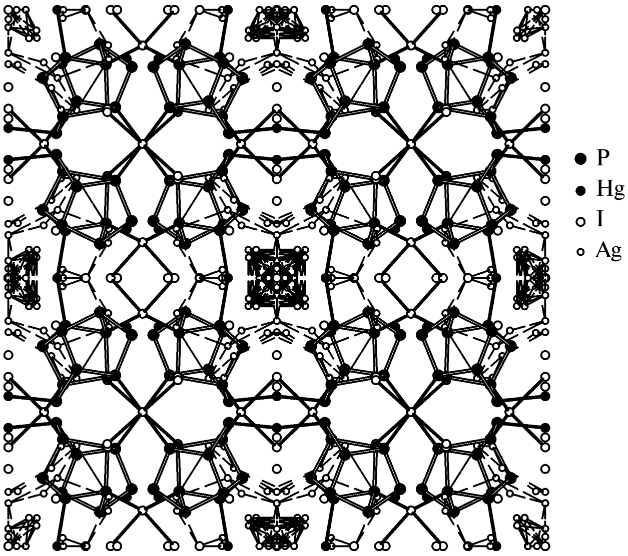

Fig. 2. Overall view of the crystal structure of compound **1**.

tetrahedron formed by two phosphorus atoms and two iodine atoms (d(Ag—P) = 2.46 Å, ω(P—Ag—P) = 135.2°, d(Ag—I) = 2.96 Å, ω(I—Ag—I) = 106.2°). The mercury atom has a distorted linear coordination formed by phosphorus atoms (d(Hg—P) = 2.43 Å, P—Hg—P = 157.6°). The coordination environment of the mercury atom additionally involves two distant iodine atoms (d(Hg—I) = 3.18 Å). The mutual arrangement of the octants is such that the geometric centers of the P_{11}^{3-} clusters form two types of polyhedra, *viz.*, a cube (4^3) and a rhombicuboctahedron (3.4^2) sharing square faces (Fig. 3). From the point of view of the type and arrangement of the polyhedra, the structure of **1** is hierarchical with respect to $BiMn_6PO_{12}$,[16] which contains an analogous combination of polyhedra formed by oxygen atoms. In compound **1**, the iodine and silver atoms form the α-AgI-type fragment (2×2×2) inside the larger rhombicuboctahedron; the iodine atoms are arranged so that they form a body-centered cube, and the silver atoms are randomly distributed between the iodine atoms. The octahedron formed by iodine atoms is located inside the cube formed by the P_{11}^{3-} clusters. There are several disordered silver sites in the center of the latter octahedron, which also can be considered as a fragment of the α-AgI structure (Fig. 4). In the structure of the $Hg_{12}Ag_{41}P_{88}I_{41}$ compound, the silver sites belonging to the α-AgI fragments (Ag(2)—Ag(8)) are partially occupied and strongly disordered. Low occupancies of some silver sites are respon-

Table 2. Selected interatomic distances (d) and bond angles (ω) in the structure of compound **1**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
P(1)–P(2)	2.198(4)	P(4)–P(1)–P(2)	97.5(1)	P(1)–P(4)–P(5)	104.2(1)
P(1)–P(4)	2.188(4)	P(4)–P(1)–Hg(1)	107.1(1)	P(2)–P(4)–P(5)	102.2(1)
P(2)–P(3)	2.246(4)	P(2)–P(1)–Hg(1)	105.3(1)	P(4)–P(5)–P(4)	102.5(1)
P(2)–P(4)	2.191(4)	P(4)–P(2)–P(1)	97.6(1)	P(1)–Hg(1)–P(1)	157.6(1)
P(4)–P(5)	2.241(4)	P(4)–P(2)–P(3)	107.7(1)	P(1)–Hg(1)–I(6)	101.06(7)
Hg(1)–P(1)	2.429(3)	P(1)–P(2)–P(3)	104.3(1)	P(1)–Hg(1)–I(4)	93.53(7)
Ag(1)–P(2)	2.463(3)	P(4)–P(2)–Ag(1)	114.3(1)	I(6)–Hg(1)–I(4)	80.11(4)
Hg(1)-I(6)	3.182(1)	P(1)–P(2)–Ag(1)	114.5(1)	P(2)–Ag(1)–P(2)	135.2(1)
Hg(1)–I(4)	3.183(1)	P(3)–P(2)–Ag(1)	116.4(1)	P(2)–Ag(1)–I(3)	107.43(7)
Ag(1)–I(3)	2.962(1)	P(2)–P(3)–P(2)	98.1(1)	I(3)–Ag(1)–I(3)	106.18(5)
		P(1)–P(4)–P(2)	94.1(1)		

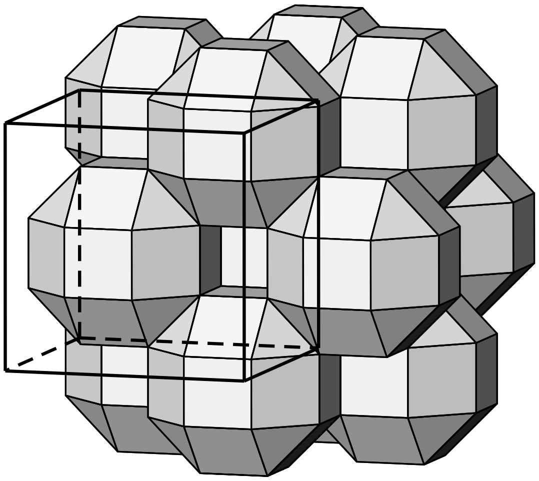

Fig. 3. Polyhedral representation of the structure of compound **1**. The geometric centers of the P_{11}^{3-} clusters are located in the vertices of the polyhedra.

sible for the inaccuracy of the determination of the composition of this compound determined from the X-ray diffraction data.

Earlier,[14,17] it has been demonstrated that different phosphorus clusters, such as P_2^{4-}, P_6^{6-}, and P_8^{8-}, are stabilized in the double mercury silver phosphide halides $Hg_7Ag_2P_8X_6$ (X = Br or I), $Hg_6Ag_4P_8Br_6$, and $Hg_4Ag_5P_8Cl_5$ due to the preferred coordination of phosphorus atoms in different oxidation states by different Ag^+ and Hg^{2+} cations, which have similar coordination but different charges. Phosphorus atoms in the highest negative oxidation state were found to be coordinated mainly by Hg^{2+} cations, whereas the coordination environment of phosphorus in the lowest negative oxidation state additionally involves Ag^+ cations. In compound **1**, only two-bonded P(1) atoms existing in the formal oxidation state 1– are bound to the mercury atoms, whereas the formally uncharged three-bonded atoms are either additionally coordinated by silver atoms or remain three-coordinate. Therefore, a combination of Ag^+ and Hg^{2+} cations leads to stabilization of the P_{11}^{3-} cluster, which has been previously found only in alkali metal phosphides.

Experimental

Compound **1** was synthesized by the conventional ampoule techniques. Red phosphorus (reagent grade), mercury (chemical purity grade), and silver iodide (chemical purity grade) were used as the starting materials. Red phosphorus was additionally purified by successive washing with a 30% KOH solution, water, and ethanol and dried *in vacuo*. The 41AgI : 12Hg : 88P mixture was placed in a quartz ampoule (inner diameter was 8 mm), which was evacuated to the residual pressure of $2 \cdot 10^{-2}$ Torr and then sealed. The annealing was performed at 773 K (temperature was achieved for 30 min) for 5 days followed by cooling in a switched-off furnace. The product was obtained as an air-stable dark-red polycrystalline powder.

The X-ray powder diffraction analysis of the annealing products was carried out on a STADI-P (STOE) powder diffractometer (Cu-Kα1 radiation). A comparison of the X-ray

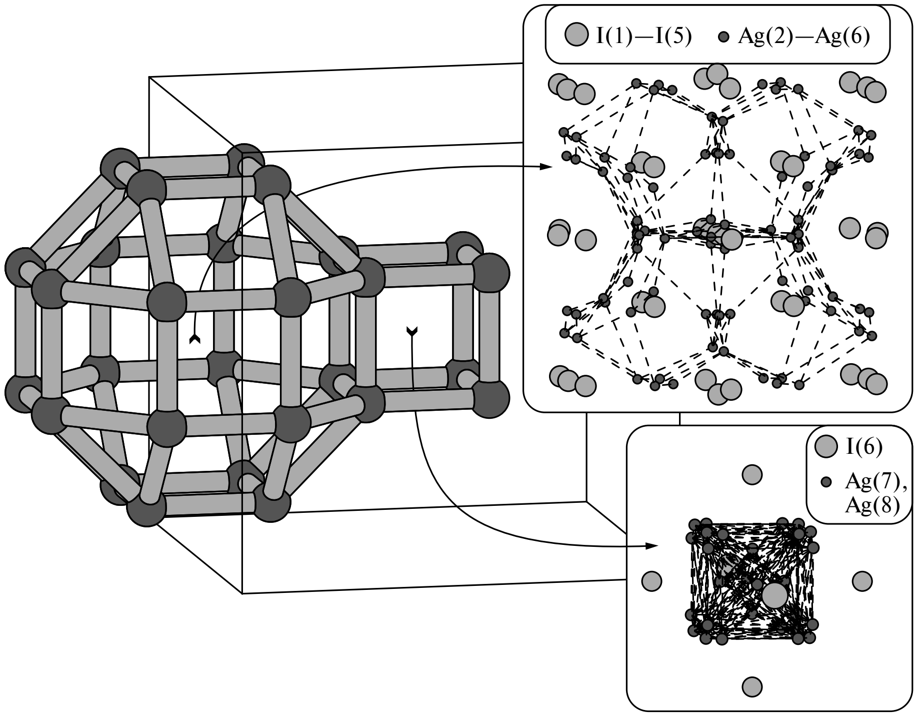

Fig. 4. Distribution of the α-AgI fragments in the polyhedra formed by the P_{11}^{3-} clusters.

Table 3. X-ray data collection and refinement statistics for the crystal structure of **1** at 173 K

Parameter	Characteristics
Molecular formula	$Hg_{12}Ag_{41}P_{88}I_{41}$
Crystal system	Cubic
Space group	$Fm\bar{3}$
a/Å	26.705(1)
V/Å^3	19045(1)
Z	4
d_{calc}/g cm^{-3}	5.147
μ/mm^{-1}	21.14
Scannig range	$1.53 < \theta < 28.27$
Number of measured reflections	40721
Number of independent reflections	2098
Number of parameters in refinement	108
R_1 ($I \geq 2\sigma(I)$)*	0.0422
wR_2** (based on all reflections)	0.0906
Goodness-of-fit on F^2	1.276
Residual electron density (max/min)/e Å^{-3}	1.559/−1.955

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

** $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = \{\sigma^2(F_o)^2 + 2961.8066[(F_o^2 + 2F_c^2)/3]\}^{-1}$.

diffraction pattern with the pattern theoretically calculated from the single-crystal X-ray diffraction data demonstrated that the sample contained solely the new double mercury silver phosphide iodide.

To determine the crystal structure of $Hg_{12}Ag_{41}P_{88}I_{41}$, several single crystals suitable for X-ray diffraction study were chosen from the annealing products. The X-ray diffraction data were collected on a Bruker SMART APEX diffractometer equipped with a CCD detector (Mo-Kα radiation, ω scanning technique with a step of 0.3°; the exposure time was 20 s per frame) at 173 K (Bruker KRYO-FLEX) and on a Nonius CAD 4 diffractometer (Mo-Kα radiation, ω-2θ scanning technique) at room temperature. The crystallographic data and the refinement statistics for the best experiment are given in Table 3. The X-ray data were processed with the use of the Bruker SAINT program package.**[18]** The integration of the frames in the cubic unit cell gave 40721 reflections with the maximum angle $2\theta = 56.54°$, of which 2098 reflections were independent. The empirical absorption correction was applied with the use of the SADABS program**[19]** ($R_{int} = 0.0733$). The structure was solved and refined by the full-matrix least-squares method based on F^2 in the space group $Fm\bar{3}$ (No. 202) with the use of the SHELX-97 program package.**[20,21]** The final anisotropic refinement converged to $R_1 = 0.0422$.*

The energy dispersive X-ray (EDX) analysis was performed on a JEOL JSM-5510 scanning electron microscope (accelerating voltage was 20 kV) equipped with an INCA analytical facility (Oxford Instruments). Crystals of $Hg_{12}Ag_{41}P_{88}I_{41}$ were mounted in the sample holder of the microscope with the use of a double-sided scotch tape.

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