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Unprecedented $_{\infty}{}^{1}(P_{10}{}^{3-})$ band anion in the crystal structure of $HgAg_6P_{20}I_2$

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A new phosphorus polyanion $_{\infty}{}^{1}(P_{10}{}^{3-})$ has been determined within the novel double silver mercury phosphide iodide $HgAg_6P_{20}I_2$. It crystallizes in a monoclinic space group $P2_1/m$ with the lattice parameters $a = 6.718(1)$ Å, $b = 27.701(6)$ Å, $c = 7.383(1)$ Å, $\beta = 113.98(3)^{\circ}$, and $Z = 2$. An infinite one-dimensional phosphorus polyanion $_{\infty}{}^{1}(P_{10}{}^{3-})$ is built from short tubular fragments $P_{10}{}^{3-}$ joint through common phosphorus atoms. Mercury and silver atoms having the same coordination but different formal charge are linked to the phosphorus atoms.

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1. Introduction

The crystal chemistry of phosphorus clusters and polyanions is rich and exiting. Anionic polyanions of different dimensionality are known. They range from discrete (or zero dimensional) clusters, like different cycle and cage anions, to assemblies infinite in one or more dimensions [1]. Within this class of compounds, the tubular polyphosphides are of a great interest, because they are related to rare allotrope forms of phosphorus, which are the long-known Hittorf's phosphorus [2] and the recently discovered fibrous phosphorus [3]. The tubular structures of these allotropes are built by a condensation of various cages, in which all phosphorus atoms are three-bonded (i.e. form three P–P bonds). Other compounds, in which a part of phosphorus atoms in a tubular structure are two-bonded are known. These two-bonded phosphorus atoms possess a formal charge −1 making the whole tubular structure a polyphosphide anion. Such polyphosphides form only with groups 1 and 11 metals, barium, and thallium [1,4]. Despite the variety of their structures, all tubular fragments display a similar feature: the coordination of phosphorus atoms noticeably deviates from regular tetrahedral, mainly due to strains in the tubular fragments. It is worth noting that no other element exhibits any tubular structures [5].

Here we report on a new double silver mercury phosphide iodide $HgAg_2P_{20}I_2$ containing a unique band phosphorus polyanion $_{\infty}{}^{1}(P_{10}{}^{3-})$, where the one-dimensional (1D) polyanion is built from short tubular fragments. We describe its crystal structure and discuss the role of the transition metals, Ag and Hg, in stabilizing the 1D $(P_{10}{}^{3-})$ band polyanion.

2. Results and discussion

A new double silver mercury phosphide iodide $HgAg_6P_{20}I_2$ was synthesized by a high-temperature ampoule method (650 K, 5 days) in a quite moderate yield of approximately 30%. Ranging the annealing conditions and/or using different starting materials did not provide better yields of $HgAg_6P_{20}I_2$. In all cases, silver phosphide Ag_3P_{11} is found as a main product in spite of existence of at least two more quaternary compounds in the Hg–P–Ag–I system [6]. The low yields can be explained by the close composition and similar synthesis conditions of the title compound and Ag_3P_{11}. The composition of the title compound was confirmed by the EDX analysis and turned out to be in excellent agreement with the formula $HgAg_2P_{20}I_2$ and with the structural data (see below).

The crystal structure of $HgAg_2P_{20}I_2$ is shown in Fig. 1. Its main feature is the hitherto unknown one-dimensional polyanionic phosphorus band constructed from short $P_{10}{}^{3-}$ tubular fragments (Fig. 2, top). Each $P_{10}{}^{3-}$ fragment can be viewed as a product of

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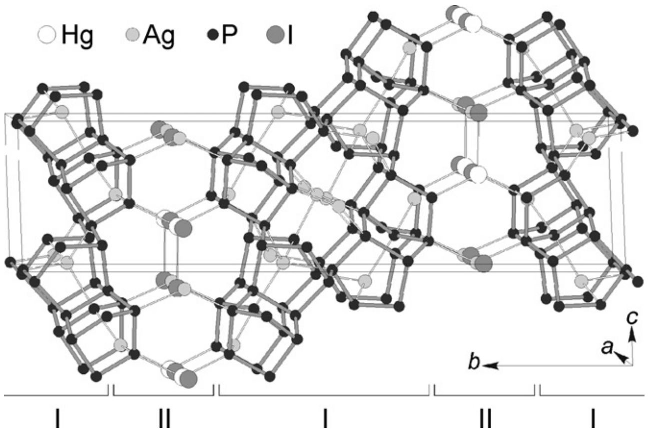

Fig. 1. A view of the crystal structure of $HgAg_6P_{20}I_2$. Alternation of the silver–phosphorus (I) and metal–halide blocks (II) along the *b* axis is shown.

a condensation of three 5-member rings in such a way that the central ring has a common edge with one neighboring ring and shares three phosphorus atoms with the other neighbor. Phosphorus atoms that form the $_\infty^1(P_{10}^{3-})$ polyanion (or 1D (P_{10}^{3-}) polyanion) have different number of homonuclear bonds and thus bear different formal oxidation states. Two types of phosphorus atoms can be distinguished. The atoms of the first type have two homonuclear bonds, hence, they possess a formal oxidation state of −1; they are further connected to two metal atoms. The phosphorus atoms of the second type form three homonuclear bonds and thus formally uncharged. Such atoms are linked to one silver atom. The P–P distances range from 2.16 to 2.26 Å that is in good agreement with the typical value for the single bond [1]. The valence angles vary in a quite large range from 91.8 to 111.6°. Such a strong deviation from ideal tetrahedral values is probably caused by strains typical for tubular phosphorus structures [1].

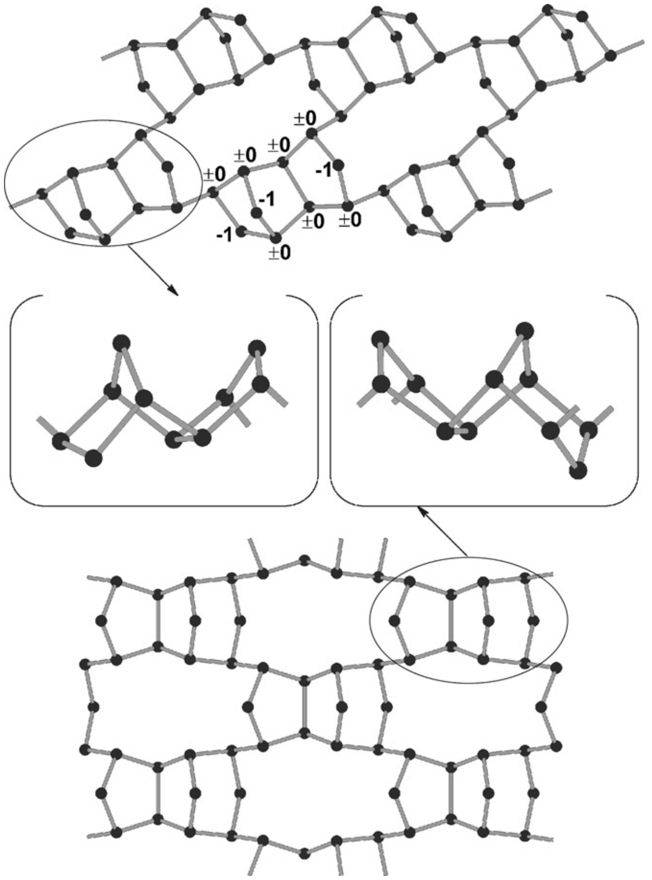

Fig. 2. Phosphorus substructure of the crystal structures of $HgAg_6P_{20}I_2$ and Ag_3P_{11}. Top, a view of the 1D (P_{10}^{3-}) polyanion; middle, P_{10}^{3-} fragment (left) and P_{11}^{3-} fragment (right); bottom, a view of the 2D (P_{11}^{3-}) polyanion. Figures in the upper part represent formal oxidation states of phosphorus atoms.

The 1D (P_{10}^{3-}) polyanions in the crystal structure of $HgAg_6P_{20}I_2$ are linked to each other in two different ways. First, they are connected by silver atoms along the "*a*" axis thus forming a silver–phosphorus block (Fig. 1). Within this part of the crystal structure, the Ag(1), Ag(3), and Ag(4) atoms possess slightly distorted tetrahedral coordination composed either of four phosphorus atoms (Ag(1) and Ag(4)) or of three phosphorus and one iodine atoms (Ag(3)). The Ag–P distances fall in the range of 2.44–2.57 Å, being comparable to those in Ag_3P_{11}. Along the "*b*" axis of the unit cell, such blocks alternate with blocks of the second type. The latter blocks are composed of mercury, iodine, and the remaining silver atom, Ag(2). In this part of the structure, the mercury and Ag(2) atoms display similar 2 + 2 coordination of two phosphorus and two iodine atoms, where the mercury–nonmetal and silver–nonmetal separations are similar (d(Ag(2)–P) = 2.50 Å, d(Hg–P) = 2.50 Å, d(Ag(2)–I) = 2.86–2.92 Å and d(Hg–I) = 2.83–2.95 Å) and point to the strong covalent metal–phosphorus bonding and weaker metal–iodine interactions.

$HgAg_6P_{20}I_2$ is the first example of polyphosphides where short tubular fragments form a one-dimensional band-like structure. Earlier known [1] infinite tubular structures were straight or zigzag 1D tubes found in several alkali metal polyphosphides or 2D layers build either from short tubular fragments as in copper or silver derivatives or by linking tubes through additional phosphorus atoms as, for instance, in BaP_{10}. The building unit of the 1D (P_{10}^{3-}) anion is closely related to that observed in the polyphosphide layer of Ag_3P_{11} (Fig. 2, bottom) [7]. In the latter, the tubular fragment is constructed by a condensation of two 5-member rings and one 6-member ring. Thus, there is one atom more in the building unit of Ag_3P_{11} compared to $HgAg_6P_{20}I_2$. Moreover, in Ag_3P_{11} the linkage of these units occurs in two dimensions leading to the 2D (P_{11}^{3-}) polyanion.

In the crystal structure of $HgAg_6P_{20}I_2$, the $_\infty^1(P_{10}^{3-})$ polyanions are linked by silver and mercury cations in such a way that the three-bonded phosphorus atoms turn out to be linked only to silver atoms while the two-bonded phosphorus atoms are connected to both cations. Hence, the title compound provides one more example of the stabilization of rare and unique phosphorus polyanions by preferable linkage of differently bonded phosphorus atoms to differently charged cations having the same coordination. The similar situation was described for some other silver mercury phosphide halides, $Hg_4Ag_5P_8Cl_5$, $Hg_{12}Ag_{41}P_{88}I_{41}$, and $Hg_7Ag_2P_8I_6(Br_6)$ [6,8,9]. It should be noted that in all earlier known silver and mercury pnictide halides the coordination of silver and mercury atoms is linear, made of two phosphorus atoms, with halide atoms providing the second coordination sphere. In $HgAg_6P_{20}I_2$, the coordination sphere of metal atoms is best described as a 2 + 2 distorted tertrahedron built of two phosphorus and two iodide atoms. Another interesting example of the stabilization of a unique adamantine-like P_{10}^{6-} cage anion is provided by the structures of Cu_4SnP_{10} and $AuCu_3SnP_{10}$ where tin and the group 11 metal atoms displaying similar pyramidal coordination are connected to phosphorus atoms [10,11]. In general, a combination of two different cations having similar coordination but different charge seems to provide a powerful tool for stabilization of rare and/or yet unknown phosphorus polyanions.

Table 1
Atomic coordinates and atomic displacement parameters for $Ag_6HgI_2P_{20}$.

Atom	Wyckoff symbol	x/a	x/b	z/c	U_{eq} (Å^2)[a]
Hg	2*e*	0.5214(1)	1/4	0.1733(1)	0.0302(2)
I(1)	2*e*	0.0790(2)	1/4	0.1640(2)	0.0290(3)
I(2)	2*e*	0.7265(2)	1/4	0.5923(2)	0.0259(3)
Ag(1)	4*f*	0.8412(1)	0.0708(1)	0.4306(1)	0.0180(2)
Ag(2)	2*e*	0.1499(3)	1/4	0.5698(2)	0.0293(3)
Ag(3)	4*f*	0.9020(2)	0.1562(1)	0.9805(2)	0.0249(2)
Ag(4)	4*f*	0.8535(4)	0.0106(1)	0.9796(3)	0.0320(5)
P(1)	4*f*	0.5013(5)	0.1060(1)	0.1676(4)	0.0117(5)
P(2)	4*f*	0.2784(5)	0.1690(1)	0.7206(4)	0.0120(5)
P(3)	4*f*	0.5514(5)	0.1713(1)	0.0214(4)	0.0131(5)
P(4)	4*f*	0.6480(5)	0.9937(1)	0.4682(4)	0.0119(5)
P(5)	4*f*	0.4807(5)	0.1298(1)	0.5964(4)	0.0119(5)
P(6)	4*f*	0.2426(5)	0.1175(1)	0.2849(4)	0.0129(5)
P(7)	4*f*	0.456(5)	0.1175(1)	0.7467(4)	0.0141(5)
P(8)	4*f*	0.1099(5)	0.0457(1)	0.2894(4)	0.0138(5)
P(9)	4*f*	0.5203(5)	0.0599(1)	0.7643(4)	0.0146(5)
P(10)	4*f*	0.7089(5)	0.9369(1)	0.0902(4)	0.0147(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Experimental details

3.1. Synthesis

HgI_2, AgI, red P, Hg, and Ag were used as starting materials. Red phosphorus was purified prior to use according to the procedure detailed elsewhere [12]. Different combinations of starting materials as well as different annealing regimes were tried to obtain a phase-pure sample. The synthesis temperature was varied from 675 to 875 K, the heating time was varied from 0.5 to 24 h, and the cooling time was modified from quenching into icy water to slow cooling at a rate of 5 K/h. In all cases no pure phase of $HgAg_6P_{20}I_2$ was obtained. The best yield (approximately 30%) was achieved by heating the mixture HgI_2:20P:6Ag at 675 K for 5 days with further furnace cooling. The phase analysis was carried out using a Huber G670 Image Plate Guinier Camera. It confirmed that the main admixture was Ag_3P_{11} in all cases.

3.2. Single crystal preparation

The mixture of starting materials taken in the molar ratio 41AgI:12Hg:88P was sealed under vacuum in a silica tube (length 6 cm, inner diameter 10 mm). The ampoule was annealed at 775 K for 5 days and then furnace cooled. The crystals for the X-ray diffraction experiments were mechanically picked from the multi-phase mixture.

3.3. Crystal structure determination

A suitable single crystal was mounted on a CAD 4 (Nonius) goniometer head for structure determination. Monoclinic unit cell parameters $a = 6.718(1)$ Å, $b = 27.701(6)$ Å, $c = 7.383(1)$ Å, and $\beta = 113.98(3)^\circ$ were refined based on 24 well-centered reflections in the angular range $12.2^\circ < \theta < 14.0^\circ$. The data set was collected at ambient temperature in the $\omega - 2\theta$ mode up to $26.5^\circ\ 2\theta$. A total of 2884 reflections were collected. A semiempirical absorption correction was applied to the data based on ψ-scans of four reflections having their χ angles close to 90°. The structure was successfully solved and refined in a centric space group $P2_1/m$ (No. 11). Positions of all atoms were found by direct methods (SHELXS-97) [13]. It was found that the Ag(4) atom residing on the 4*f* position had a physically impossible distance Ag(4)–Ag(4) 1.96 Å due to the $P2_1/m$ group symmetry and was consequently refined as half-occupied. It should be notified that lowering the symmetry to $P2_1$ could not eliminate the observed disorder. Final anisotropic refinement on F^2 (SHELXL-97) [13] led to $R1 = 0.0460$, and $wR2 = 0.1326$. Atomic parameters are given in Table 1.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 419630.

3.4. EDX analysis

EDX analysis was carried out using Supra 50VP (LEO) microscope with an EDS analytical equipment INCA Energy+ (Oxford). The same crystal as for the crystal structure determination was taken for the analysis. The obtained results (Hg:Ag:P:I = 3.5(3):21.0(4):69(3):6.5(2)) are in a good agreement with those calculated from the $HgAg_6P_{20}I_2$ formula (Hg:Ag:P:I = 3.45:20.69:68.96:6.90).

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