Phosphorus Chemistry

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P_8^{8-} Polyanion with Phosphorus Atoms in Three Different Formal Oxidation States Stabilized by a Combination of Ag^+ and Hg^{2+} Cations[**]

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Phosphorus is among the few elements that feature a large variety of allotropic modifications, polyanions, and clusters.[1,2] The discovery of elemental phosphorus lies far in the past but scientists continue to make exciting new experimental findings, among which the recent discovery of fibrous phosphorus ought to be mentioned.[3] Extensive research is also devoted to theoretical calculations of seemingly limitless varieties of phosphorus clusters.[4] Among these clusters, however, highly charged clusters and polyanions are poorly studied because of their lower stability. As a rule, the bonding in phosphorus clusters and polyanions is of two-center, two-electron type, and the formal oxidation states can be easily assigned to each phosphorus atom according to the number of homonuclear bonds it makes.[5] Typically, the clusters and polyanions are constructed by phosphorus atoms

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that have two different oxidation numbers. Polyanions with three different oxidation states are merely exceptions found only in the infinite branched chains of transition-metal polyphosphides.[6] Herein we report a highly charged phosphorus polyanion P_8^{8-} that features phosphorus atoms with three different oxidation numbers. This polyanion was stabilized in a framework of the new compound $Hg_4Ag_5P_8Cl_5$ by a combination of the Ag^+ and Hg^{2+} ions, which have the same coordination geometries but different charges and are linked to phosphorus atoms of different oxidation state.

The silver–mercury phosphide chloride $Hg_4Ag_5P_8Cl_5$ was obtained by an ampoule synthesis, and the crystal structures of two polymorphs (monoclinic from a low-temperature synthesis and orthorhombic from a high-temperature synthesis) were determined.[7] The P_8^{8-} polyanion in the fully ordered monoclinic structure consists of a six-membered ring in a chair conformation with two equatorial P atoms in 1,4-positions (Figure 1). The P–P bond lengths range from 2.18 to 2.20 Å, which is typical for a single P–P bond.[1] All P atoms exhibit slightly distorted tetrahedral coordination geometries, although their formal oxidation states differ. The P1 atom of the six-membered ring forms three homonuclear bonds to two phosphorus atoms within the ring and to one equatorial phosphorus atom; thus, it is assigned a formal oxidation state of zero. The tetrahedral coordination geometry of this atom is completed by an additional bond to a silver atom. The P2 atom, which also belongs to the six-membered ring, is linked to two phosphorus atoms and two metal atoms (one silver atom and one mercury atom); hence, it has an oxidation state of –I. The equatorial P3 atom forms one homonuclear bond, is further connected to three metal atoms (two mercury atoms and one silver atom), and has an oxidation state of –II. Thus, phosphorus in a lower oxidation state of –II is preferentially linked to mercury, whereas phosphorus in the higher oxidation state of zero has only silver as a neighbor. Taking into account the typical oxidation states of mercury (with no Hg–Hg bonding), silver, and chlorine, one obtains the charge-balanced formulation $Hg_4^{2+}Ag_5^{+}P1_2^{0}P2_4^{-}P3_2^{2-}Cl_5^{-}$.

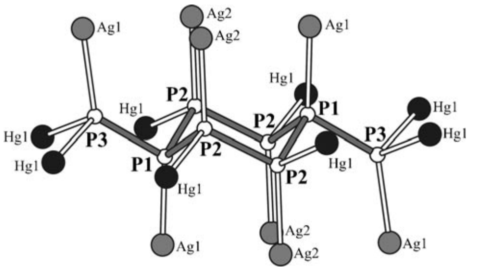

Figure 1. Geometry of the P_8^{8-} polyanion and its coordination by metal atoms in the monoclinic structure of $Hg_4Ag_5P_8Cl_5$: P1–P2 2.185(2) Å, P2–P2 2.200(3) Å, P1–P3 2.183(3) Å.

In the monoclinic structure, the P_8^{8-} polyanions are linked by mercury atoms to form layers within the *ab* plane, where they are produce a checkered pattern (Figure 2a). These layers are connected along the *c* axis through silver atoms (Figure 2b). One silver atom (Ag3) is disconnected from the phosphorus polyanion, and its coordination can be described as a 4+2 array of six chlorine atoms. The structure of the layer can be viewed as the result of disassembly of the corrugated 2D net from the structure of gray arsenic by insertion of mercury and chlorine atoms. Such a gray arsenic structure is unique. Another type of alternation is the structures of metal triphosphides MP_3 (M = In, Ge, Sn),[8] in which the metal atoms replace phosphorus atoms in such a way that the separated P_6 chairs retain the structural motif of gray arsenic. Many other compounds exhibit the black phosphorus, rather than gray arsenic, structure, which features buckled layers of atoms. In various binary and ternary pnictides, diverse modes of removing a fraction the phosphorus atoms from the buckled layer lead to various 2D and 1D substructures.[9]

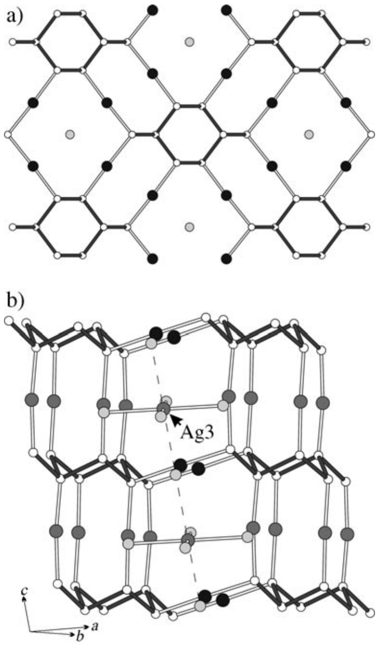

Figure 2. Crystal structure of the monoclinic structure of $Hg_4Ag_5P_8Cl_5$: a) projection of a layer along the (001) plane; b) general view. Black Hg, dark gray Ag, light gray Cl, white P.

The major difference between the two polymorphs of $Hg_4Ag_5P_8Cl_5$ is the packing of the phosphorus layers (Figure 3). Whereas the monoclinic structure features identical layers that propagate along the *c* axis, the orthorhombic structure has two types of layers that are mirror reflections of each other and alternate along the *c* axis. Another noticeable distinction between these two polymorphs is the occupancy of the metal-atom positions. The monoclinic structure is fully ordered: the silver and mercury atoms occupy different sites in the network as described above. Conversely, two of the metal positions in the orthorhombic structure are jointly occupied by silver and mercury, while one position remains fully occupied by silver only.

Band-structure calculations (Figure 4) performed for the fully-ordered monoclinic form show that, although the assignment of the oxidation states is merely a formality, the P1 atoms indeed possess the lowest negative charge, whereas the P3 atoms exhibit the highest negative charge, which is in accordance with their oxidation numbers. The analysis of the

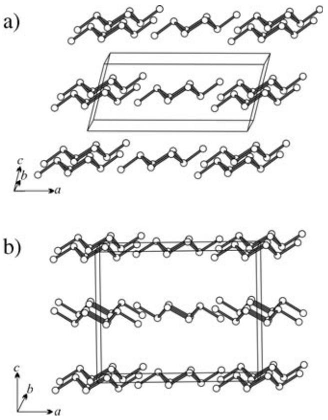

Figure 3. Interlayer ordering of phosphorus atoms in the monoclinic (a) and orthorhombic (b) forms of $Hg_4Ag_5P_8Cl_5$.

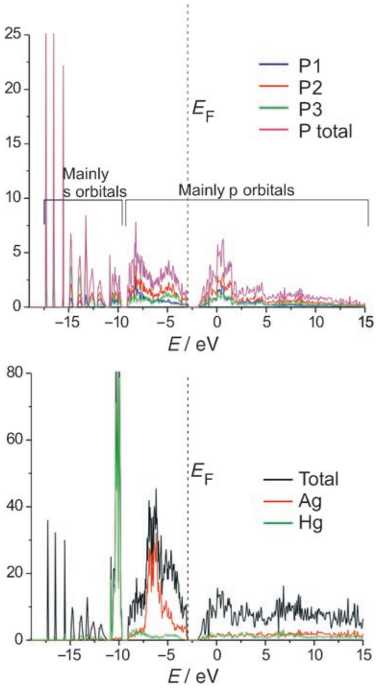

Figure 4. DOS plots for the monoclinic form of $Hg_4Ag_5P_8Cl_5$.

orbital interactions revealed that the P–M bonding involves mainly interactions of the phosphorus p orbitals with the mercury s and p orbitals and the silver d and s orbitals. However, the states in the vicinity of the Fermi level are composed mainly of chlorine p orbitals (not shown) and silver d orbitals. Therefore, the states of the P_8^{8-} polyanion should not contribute significantly to the electrical properties of the compound (calculated band-gap width E_g is 1.0 eV).

The crystal structures of three compounds reported earlier,[10] namely, $Hg_7Ag_2P_8I_6$, $Hg_7Ag_2P_8Br_6$, and $Hg_6Ag_3P_8AgBr_6$, have already provided examples of Ag^+ and Hg^{2+} ions linked to phosphorus atoms with different oxidation numbers. In particular, mercury is bound only to the P^{-II} atoms of the P_2^{4-} units, whereas silver prefers the P^{-I} atoms of the P_6^{6-} rings. In this work, the linking of Ag^+ and Hg^{2+} ions to differently charged phosphorus atoms has led to the stabilization of the P_8^{8-} polyanion in $Hg_4Ag_5P_8Cl_5$. The presence of phosphorus atoms in different oxidation states linked to different metal atoms seems to provide the stability for highly charged P_8^{8-} polyanion. It is expected that other combinations of cations that stabilize phosphorus atoms in different oxidation states will lead to the isolation of new phosphorus clusters and polyanions of even higher complexity.

Experimental Section

Mercury, red phosphorus, and silver chloride were mixed in the molar ratio 4:8:5 (1 g total), vacuum-sealed in quartz ampoules (inner diameter 8 mm), and heated for 5 days. The annealing temperature was set at 675 and 775 K for the monoclinic and orthorhombic forms, respectively. The X-ray diffraction patterns of the products (STADI-P (STOE), Cu$K_{\alpha1}$ radiation) were identical to those calculated from the corresponding crystal data and did not reveal the presence of any impurities. Single crystals for the structural determination were selected from the respective samples. Band-structure calculations were performed for the monoclinic form of $Hg_4Ag_5P_8Cl_5$ by using the TB-LMTO-ASA approach with the TB-LMTO-47 code.[11] Before the calculation of the density of states (DOS), the self-consistent field (SCF) calculations were performed for 267 k-points in the irreducible wedge of the Brillouin zone.

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[7] Crystal data of the monoclinic form (**1**): space group $C2/m$ (no. 12), $a=14.490(2)$, $b=10.9043(15)$, $c=6.2863(9)$ Å, $\beta=104.094(2)°$, $V=963.4(2)$ Å^3, $Z=2$, $\rho_{\mathrm{calcd}}=6.090$ g cm^{-3}; 4119 reflections, 1185 of which were independent ($R_{\mathrm{int}}=0.0215$), $T=173$ K, ω scans (0.3° width, total 1850 frames), Mo$_{K\alpha}$ radiation, $\lambda=0.71069$ Å, $2\theta_{\max}=56.58°$, crystal dimensions $0.07\times0.06\times0.04$ mm^3, empirical absorption correction (SADABS,[12a] min./max. transmission: 0.1759/0.3114, $\mu=38.047$ mm^{-1}). Structure solution: full-matrix least-squares procedure on $|F^2|$ (Bruker SHELXTL Version 6.12,[12b] 1136 reflections with $F>4\sigma(F)$) with 60 free parameters; $R1=0.0262$, $wR2=0.0639$; min./max. residual electron density 2.600/−2.854 e Å^{-3}; Crystal data of

orthorhombic form (**2**): space group *Cmcm* (no. 63), $a = 11.1426(6)$, $b = 14.5064(8)$, $c = 11.8444(6)$ Å, $V = 1914.52(18)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 6.129$ g cm^{-3}; 8202 reflections, 1271 of which were independent ($R_{\text{int}} = 0.0244$), $T = 173$ K, ω scans (0.3° width, total 1850 frames), $\text{Mo}_{\text{K}\alpha}$ radiation, $\lambda = 0.71069$ Å, $2\theta_{\max} = 56.52°$, crystal dimensions $0.15 \times 0.14 \times 0.13$ mm^3, empirical absorption correction (SADABS, min./max. transmission: 0.0690/0.0825, $\mu = 38.291$ mm^{-1}). Structure solution: full-matrix least-squares procedure on $|F^2|$ (Bruker SHELXTL Version 6.12, 1246 reflections with $F > 4\sigma(F)$) with 72 free parameters; $R1 = 0.0216$, $wR2 = 0.0510$; min./max. residual electron density $1.944/-2.026$ e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-416360 (**1**) and CSD-416361 (**2**).

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