Zintl Salts Ba$_2$P$_7$X (X = Cl, Br, and I): Synthesis, Crystal, and Electronic Structures

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Abstract: Two barium phosphide halides, Ba$_2$P$_7$Br and Ba$_2$P$_7$I, were synthesized and structurally characterized by single crystal X-ray diffraction. Both compounds crystallize in the monoclinic space group $P2_1/m$ (No. 11) and are isostructural to Ba$_2$P$_7$Cl. The crystal structures of Ba$_2$P$_7$X (X = Cl, Br, I) feature the presence of heptaphosphanortricyclane P$_7^{3-}$ clusters along with halogen anions and barium cations. According to the Zintl concept, Ba$_2$P$_7$X compounds are electron-balanced semiconductors. Quantum-chemical calculations together with UV-Visible spectroscopy confirm the title compounds are wide bandgap semiconductors. The bonding in the P$_7^{3-}$ clusters was analyzed by means of electron localization function. The elemental compositions were confirmed using energy dispersive X-ray spectroscopy.

Keywords: Zintl phase; crystal structure; P$_7$ cluster; heptaphosphanortricyclane; electronic structure; electron localization function

1. Introduction

Polyphosphides are known to form a variety of crystal structures with different elements [1–15]. From three-dimensional frameworks to isolated cages, phosphorous backbones form a wide range of stable structures. The P$_7^{3-}$ cluster, heptaphosphanortricyclane, heptaphosphatricyclo[2.2.1.0(2,6)]heptane, is a commonly present phosphorus fragment which is able to form binary and ternary compounds with different counter-cations, like A$_3$P$_7$ (A = alkali metal) or Ba$_3$P$_{14}$ [1–5]. The P$_7^{3-}$ clusters are quite stable.
and have been found in both solution and solid phases [1–5,15]. Heavier analogs of such clusters with As and Sb are also known [16–18].

Similar to other intermetallics, the electronic structures of polyphosphides can be rationalized by application of the Zintl concept [19,20]. Zintl theory implies the valence electrons of electropositive atoms are donated to more electronegative atoms. The latter realize their electron octet by forming 2c–2e chemical bonds and by having electron lone pairs. In A₃P₇, one electron is donated from each A atom to allow for the formation of the P₇³⁻ cage [4]. In Ba₃P₁₄, three Ba atoms donate two electrons each to allow for the formation of two P₇³⁻ cages [3]. An interesting example of a compound combining the P₇³⁻ Zintl anion with a classical chloride anion was reported by von Schnering and Menge in 1981 [21]. In the Ba₂P₇Cl Zintl salt, the total charge of two Ba²⁺ cations is compensated by a combination of Cl⁻ and P₇³⁻ anions. In this work, we expand the family of P₇³⁻ structures to include the isostructural Ba₂P₇Br and Ba₂P₇I. We report the synthesis, characterization, and chemical bonding of three Ba₂P₇X (X = Cl, Br, I) compounds.

2. Results and Discussion

2.1. Crystal Structure

Originally, Ba₂P₇I was discovered accidentally during attempts to grow large single crystals of BaP₃ utilizing I₂ as a transport reagent. After the crystal structure and composition were established, a sample of Ba₂P₇I was synthesized by the reaction of stoichiometric amounts of the elements at 1073 K. The bromine-containing analog was synthesized from barium, red phosphorus, and barium bromide at the same temperature. A summary of pertinent information related to single crystal X-ray diffraction unit cell parameters, data collection, and refinements is provided in Table 1. Energy-dispersive X-ray spectroscopy (EDS) investigations of the selected single crystals confirmed the presence of only the expected Ba, P, and X halogen elements.

| Composition | Ba₂P₇Cl | Ba₂P₇Br | Ba₂P₇I |
|-------------|---------|---------|---------|
| CSD number  | 426193  | 426194  | 426195  |
| Space Group | P2₁/m (No. 11) |         |         |
| Temperature [K] | 90(2) |         |         |
| λ [Å]      | Mo Kα, 0.71073 |         |         |
| a [Å]      | 6.329(1) | 6.294(1) | 6.3538(3) |
| b [Å]      | 6.805(1) | 6.835(1) | 6.8990(4) |
| c [Å]      | 11.709(2) | 11.850(2) | 12.0392(6) |
| β [deg]    | 95.267(2) | 95.819(2) | 95.915(1) |
| V [Å³]     | 502.2(1) | 507.2(2) | 524.93(5) |
| Z          | 2       | 2       | 2       |
| ρ [g cm⁻³] | 3.485   | 3.742   | 3.912   |
| μ [mm⁻¹]   | 9.099   | 12.868  | 11.392  |
| θ [deg.]   | 3.23 < θ < 30.66 | 3.25 < θ < 30.57 | 3.22 < θ < 30.58 |
| data/parameters | 1671/55 | 1671/55 | 1733/55 |
| R₁ (I > 2σ(I)) | 0.028  | 0.012  | 0.019  |
Table 1. Cont.

| Composition        | Ba$_2$P$_7$Cl | Ba$_2$P$_7$Br | Ba$_2$P$_7$I |
|--------------------|---------------|---------------|--------------|
| $wR_2(I>2\sigma(I))$ | 0.047         | 0.025         | 0.037        |
| Goodness-of-fit    | 1.087         | 1.202         | 1.117        |
| $\Delta \rho_{\text{max}}$ and $\Delta \rho_{\text{min}}$, e/Å$^3$ | 1.36 and −1.14 | 0.50 and −0.73 | 1.22 and −0.92 |

* More information can be obtained from Fachinformations-Zentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository CSD (Crystal Structure Database) numbers given above.

The new compounds, Ba$_2$P$_7$Br and Ba$_2$P$_7$I, are isostructural to the previously reported Ba$_2$P$_7$Cl (Figure 1) [21]. The crystal structure of Ba$_2$P$_7$X can be described as consisting of two distinct ionic layers, [Ba$_2$X$_2$]$^{2+}$ and [Ba$_2$(P$_7$)$_2$]$^{2-}$ stacked along the [001] direction (Figure 2a). According to the Zintl concept [19,20], the Ba$_2$P$_7$X compounds are electron balanced. The barium and halogen atoms realize their electron octet by donating and accepting two and one electrons, respectively. Phosphorus atoms bonded to three other phosphorus atoms should be P$^{0}$, realizing their electron octet by maintaining an electron lone pair. Phosphorus atoms bonded to two other phosphorus atoms should be P$^{1-}$, realizing their electron octet by maintaining two electron lone pairs. The P$_7^{-3}$ clusters contain four three-bonded phosphorus atoms (P1, P2, P5) and three two-bonded P atoms (P3, P4) (Figure 3a). Thus, the total charge per cluster is −3, (3b-P$_{\text{0}}$)$_4$(2b-P$_{\text{1-}}$)$_3$, and the charge-balanced formula is (Ba$^{2+}$)$_2$(P$_{\text{7}^{-3}}$)(X$^{-}$). In accordance with this formulation, the halogen atoms of Ba$_2$P$_7$X are surrounded by barium atoms in the first coordination sphere, while the phosphorus atoms are situated further apart. The P$_7^{-3}$ units are surrounded by barium atoms coordinating to the faces, edges, and corners of the cluster (Figure 3b). The Ba–P separations for all Ba$_2$P$_7$X are in the range of 3.3–3.6 Å. The shortest P–X interatomic separations are longer than 3.6 Å.

Figure 1. Crystal structure of Ba$_2$P$_7$X (X = Cl, Br, I) projected along the (a) [100] and (b) [010] directions. Ba: red; P: brown; X: green. The shortest Ba–X distance is indicated with a dashed line.
An interesting feature of the Ba$_2$P$_7$X crystal structure is the relative arrangement of its P$_7^{3-}$ fragments. All fragments are arranged parallel to each other in a head-to-head fashion. To the best of our knowledge, no other structures composed of the P$_7^{3-}$ anions are known to form with such straight linear arrangements of P$_7^{3-}$ anions. For example, in Ba$_3$P$_{14}$, the heptaphosphorantricyclone clusters are rotated with respect to each other (Figure 2b) [3]. Apparently, the presence of [Ba$_2$X$_2$]$_2^{2+}$ layers fixes the orientation of the P$_7^{3-}$ clusters, probably due to the repulsion between negatively charged species. The lack of halogen atoms in Ba$_3$P$_{14}$ allows for more structural flexibility, and the P$_7^{3-}$ clusters are free to face different directions.

In Ba$_2$P$_7$X, the P$_7^{3-}$ cluster is made up of only five symmetrically unique phosphorous atoms. Bond lengths and angles, and a general view of the P$_7^{3-}$ clusters are presented in Table 2 and Figure 3, respectively. The heptaphosphorantricyclone of Ba$_2$P$_7$X has $C_s$ local symmetry with a mirror plane containing the P1, P2, and P3 atoms. In Ba$_3$P$_{14}$, A$_3$M$_7$ (A = alkali metal), and ammonia solvates of alkali metal phosphides, the P$_7^{3-}$ heptaphosphorantricyclone clusters have $C_1$ local symmetry [3,4,15].
Table 2. P–P bond distances and angles in the crystal structures of Ba$_2$P$_7$X (X = Cl, Br, I).

| Atoms   | Distances (Å) | Angle Type | Angle (°) |
|---------|---------------|------------|-----------|
|         | Ba$_2$P$_7$Cl | Ba$_2$P$_7$Br | Ba$_2$P$_7$I |
| P1–P3   | 2.156(2)      | 2.1558(9)   | 2.156(1)   | ∠P1–P3–P2 | 97.51(8) | 97.65(3) | 97.77(6) |
| P1–P5   | 2.229(2)      | 2.2307(7)   | 2.233(1)   | ∠P2–P4–P5 | 99.53(7) | 99.53(3) | 99.47(4) |
| P2–P3   | 2.188(2)      | 2.1853(9)   | 2.188(1)   | ∠P1–P5–P4 | 105.44(7)| 105.23(3)| 104.88(5)|
| P2–P4   | 2.170(1)      | 2.1706(6)   | 2.180(1)   | ∠P1–P5–P5 | 58.26(4) | 58.38(1) | 58.41(2) |
| P4–P5   | 2.143(2)      | 2.1434(6)   | 2.154(1)   | ∠P5–P1–P5 | 63.49(7) | 63.24(3) | 63.19(5) |
| P5–P5   | 2.345(2)      | 2.339(1)    | 2.340(2)   | –          | –        | –        | –        |

The P$_7^{3–}$ clusters of Ba$_2$P$_7$X contain phosphorus atoms P1 and P5 in strained geometries, with angles in the basal triangle close to 60°. Other angles are significantly larger and closer to the typical tetrahedral angles found in most polyphosphide anions. In the P$_7^{3–}$ clusters of Ba$_3$P$_{14}$ and Li$_3$P$_7$, the P–P distances in the basal triangle are similar, 2.23–2.29 Å [3,4]. In Ba$_2$P$_7$X, the P–P bond perpendicular to the mirror plane is significantly elongated compared to the other two basal triangle bonds: $d$(P5–P5) = 2.34 Å, $d$(P1–P5) = 2.23 Å. The other bond lengths and angles in the Ba$_2$P$_7$X P$_7^{3–}$ clusters appear to be similar to those found in the crystal structures of Ba$_3$P$_{14}$ and Li$_3$P$_7$.

The local coordination of the barium and halogen atoms is shown in Figure 4. Five barium atoms form the first coordination sphere of the halogen atoms. Each barium atom is surrounded by 11 neighbors. Four halogen atoms and seven phosphorus atoms form irregular polyhedra around Ba1, while the Ba2 atoms are surrounded by 10 phosphorus atoms and only one halogen atom. As expected, with an increase of the halogen size from chlorine to iodine, the unit cell volume increases (Table 1). The P$_7^{3–}$ unit remains nearly the same in all three Ba$_2$P$_7$X compounds (Table 2). The shortest Ba–P distance also exhibits a minor variation upon a change in the halogen atom, with the shortest Ba2–P distance remaining the same in all compounds: 3.30–3.31 Å. An increase of the unit cell occurs mainly due to the increase in the shortest Ba–X distances from 3.14 Å (Cl) to 3.32 Å (Br) to 3.47 Å (I).

Figure 4. The local coordination of (a) halogen atoms and (b,c) barium atoms in Ba$_2$P$_7$X. The shortest Ba–X distance is indicated with dashed lines.
2.2. Electronic Structure

The electron balanced Zintl salts, Ba$_2$P$_7$X, are expected to exhibit semiconducting and diamagnetic properties. Band structure calculations were performed to verify this description (Figure 5). According to the calculations, the Ba$_2$P$_7$X compounds are wide band-gap semiconductors with indirect bandgaps $E_g = 1.71$ eV ($X = \text{Cl}$), 1.86 eV ($X = \text{Br}$), 1.91 eV ($X = \text{I}$). The results of calculations were verified with UV-Vis spectroscopy (vide infra). In the electronic structure of Ba$_2$P$_7$X, the top of the valence band is dominated by the contribution of phosphorus 3p orbitals, with both halogen and barium orbitals also contributing to the states near the Fermi level. The contribution of the halogen orbitals to the states near the Fermi level increases in the Cl–Br–I series. The bottom of the conduction band is comprised of phosphorus and barium orbitals with negligible contributions from halogen orbitals. The main contribution of halogen p-orbitals to the valence band is located between $-1$ and $-3$ eV.

**Figure 5.** Density of states (DOS) diagram for Ba$_2$P$_7$X, (a) $X = \text{Cl}$; (b) $X = \text{Br}$; and (c) $X = \text{I}$. Contributions from Ba, P, and X orbitals are shown in red, green, and blue colors, respectively.
To clarify the bonding in the $\text{P}_7^{3-}$ phosphorus clusters, we applied Electron Localization Function (ELF) analysis [22–25] to the Ba$_2$P$_7$I compound (Figure 6). According to the Zintl concept, single covalent $2e-2c$ bonds are expected to be present at short P–P interatomic separations. Additionally, one and two electron lone pairs are expected to be located on the two- and three-bonded phosphorus atoms, respectively. The ELF analysis indicates the presence of the expected number of electron lone pairs (Figure 6a). The two bonded phosphorus atoms, P4 and P3, have two electron lone pairs, while the three-bonded P1, P2, and P5 have only one electron lone pair. These results are similar to the results of ELF calculations for less symmetric P$_7^{3-}$ clusters [15].

**Figure 6.** Top: 3D isosurfaces of electron localization function ($\eta$) for the P$_7^{3-}$ phosphorus cluster in Ba$_2$P$_7$I, (a) $\eta = 0.91$; (b) $\eta = 0.83$; (c) $\eta = 0.765$. Bottom: coloring of the electron localization function distribution for the slices of the phosphorus cluster in Ba$_2$P$_7$I (d,e). The color bar is given in the right bottom corner.

Localization domains corresponding to the covalent two centered P–P interactions were found for all of the short interatomic separations (Figure 6b–e). The ELF maxima of the P1–P5 bonds were shifted from the lines connecting the P1 and P5 atoms. The ELF domain for the P5–P5 bond exhibited lower values of ELF (Figure 6c). This localization domain is also shifted from the line connecting the P5 atoms and it is not well separated from the domains corresponding to the electron lone pairs on the P5 atoms (Figure 6c–e). The P1–P5–P5 basal triangle, with a topology close to that of cyclopropane, is the most strained face of the P$_7^{3-}$ cluster. Angles of ~60° hamper the direct overlap of phosphorus orbitals. This explains the displacement of the bonding maxima from the lines connecting the atoms.

In ELF studies performed for the P$_7^{3-}$ clusters of the ammonia solvates of alkali metal phosphides, the heptaphosphanortricyclane units are less symmetric, with point group $C_1$ [15]. These units have
almost identical bonds, 2.26–2.30 Å, between phosphorus atoms forming a strained basal triangle. Three well-separated and similar localization domains were found displaced from the line connecting phosphorus atoms [15]. Heptaphosphanortricyclic units in Ba$_2$P$_7$X have a different geometry (Table 2) with shorter P1–P5 distances (2.23 Å) and longer P5–P5 distance (2.34 Å) than those distances present in ammonia solvate compounds [15]. This difference is probably due to the presence of a Ba atom coordinated to the P4–P5–P5–P4 square (Figure 3b) [21]. This is reflected in the bonding picture: the localization domains for P1–P5 bonds are well pronounced and remain separated from the lone pair domains, while the localization domain for the P5–P5 bond is less pronounced and is not separated from the domains corresponding to the lone pairs located on the P5 atoms (Figure 6e).

No ELF maxima were detected near the shortest Ba–X separations, which are indicated by the dashed lines in Figures 1 and 4. Presumably, all Ba–X interactions are electrostatic cation-anion interactions.

2.3. UV-Vis Spectroscopy

Ba$_2$P$_7$Cl, Ba$_2$P$_7$Br, and Ba$_2$P$_7$I are red, orange, and yellow-orange, respectively. Solid state UV-Visible spectroscopy was employed for experimental bandgap determinations.

According to the calculated Tauc plots [26,27], Ba$_2$P$_7$Cl has indirect optical transitions corresponding to a bandgap of 1.83(2) eV (Figure 7, Table 3). The calculated bandgap for this compound, 1.71 eV, is in reasonable agreement with the experimental data. Calculations predict the increase of the bandgaps in the Cl–Br–I series (Figure 5). This increase was observed experimentally and is consistent with the visual color change of the Ba$_2$P$_7$X analogs from red to yellow. The experimental indirect bandgaps of the bromine and iodine analogs, 1.92(4) eV and 1.89(2) eV, respectively, are approximately 0.1 eV larger than the Ba$_2$P$_7$Cl bandgap. In our UV-Vis experiments we were not able to detect the small predicted difference between the indirect bandgap values for Ba$_2$P$_7$Br and Ba$_2$P$_7$I, when estimated standard deviations are taken into account. A combination of the spectroscopic and calculation approaches indicates the compounds obtained are wide bandgap semiconductors.

**Figure 7.** Solid-state UV-Visible spectra of Ba$_2$P$_7$X (X = Cl, Br, I) compounds. (a) Kubelka-Munk diffuse reflectance; (b) and (c) Tauc plots for allowed direct and indirect transitions, respectively.
Table 3. Experimental and calculated values for the Ba$_2$P$_7$X bandgaps.

| Composition | Ba$_2$P$_7$Cl | Ba$_2$P$_7$Br | Ba$_2$P$_7$I |
|-------------|---------------|---------------|-------------|
| Direct Bandgap (eV) | 2.16(3) | 2.20(4) | 2.19(4) |
| Indirect Bandgap (eV) | 1.83(2) | 1.92(2) | 1.89(2) |
| Calculated Bandgap (eV) | 1.71 | 1.86 | 1.91 |

3. Experimental Section

All samples of Ba$_2$P$_7$Cl, Ba$_2$P$_7$Br, and Ba$_2$P$_7$I were prepared via solid-state reactions in evacuated and sealed silica ampoules. The samples were prepared in an Argon-filled glovebox with $p$(O$_2$) and $p$(H$_2$O) < 1 ppm. The starting materials: metallic barium (Sigma Aldrich, St. Louis, MO, USA, 99.9%), iodine (Alfa Aesar, Ward Hill, MA, USA, 99.9985%), and red phosphorous (Alfa Aesar, Ward Hill, MA, USA, 99%) were used as received. Barium bromide and barium chloride (Alfa Aesar, Ward Hill, MA, USA, 99.998% and 99%, respectively) were heated at 573 K overnight under an inert atmosphere to remove traces of water.

A single phase sample of Ba$_2$P$_7$I was synthesized by annealing stoichiometric amounts of the elements at 1073 K for 140 h. Samples of Ba$_2$P$_7$Cl and Ba$_2$P$_7$Br were prepared using metallic barium, phosphorous, and barium chloride or barium bromide in a 3:1 ratio under similar annealing conditions. In agreement with the previous report [21], Ba$_2$P$_7$Cl crystals have a red color. Ba$_2$P$_7$Br and Ba$_2$P$_7$I crystals exhibit orange and orange-yellow colors, respectively. The color of all Ba$_2$P$_7$X lightened upon grinding. Similar to other compounds containing the P$_7$$^{3-}$ phosphorus cluster, Ba$_2$P$_7$X degrades in air over time, and appears to quickly decompose in water, so samples were stored in an Argon-filled glovebox.

The samples were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer employing Cu K$_\alpha$ radiation. Elemental analysis of the selected single crystals was carried out on a Hitachi S4100T scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) microanalysis (Oxford INCA energy). Sample analysis confirmed the presence of only Ba, P, and X (X = Cl, Br, I). Solid-state UV-Visible spectroscopy (Thermo Scientific Evolution 220 Spectrometer) was employed for experimental bandgap determinations. For UV-Vis measurements, solid samples were ground into powders and gently pressed onto rough filter paper to form a thick layer of sample. Attempts to dissolve samples of Ba$_2$P$_7$X for solution-based UV-Vis measurements were unsuccessful. Samples of Ba$_2$P$_7$X were water sensitive, turning to amorphous yellow material when immersed. No visible color change was observed for immersion in ethanol, but as samples dried they turned brown.

Single crystal X-ray diffraction experiments were carried out at 90 K using a Bruker AXS SMART diffractometer with an APEX-II CCD detector and Mo K$_\alpha$ radiation. The data sets were recorded as $\omega$-scans at a 0.3° stepwidth and integrated with the Bruker SAINT software package [28]. A multiscan absorption correction was applied. The solution and refinement of crystal structures were carried out using the SHELX suite of programs [29]. The structures were solved in the P2$_1$/m space group and the final refinement was performed using anisotropic atomic displacement parameters for all atoms.

Density functional band structure calculations and bonding analyses were carried out using the tight binding—linear muffin tin orbitals—atomic sphere approximation (TB–LMTO–ASA) program
The Barth–Hedin exchange potential was employed for the local density approximation (LDA) calculations [31]. The radial scalar-relativistic Dirac equation was solved to obtain partial waves. A basis set containing Ba(6s,5d,4f), P(3s,3p), Cl(3p), Br(4p), and I(5p) orbitals was employed for a self-consistent calculation, with Ba(6p), P(3d), Cl(4s,3d), Br(5s,4d), and I(6s,5d,4f) functions being downfolded. The ELF ($\eta$) was evaluated with modules implemented within the TB–LMTO–ASA program package [22–24]. The ParaView program was used for visualization of ELF isosurfaces [32,33].

4. Conclusions

Two new compounds, Ba$_2$P$_7$Br and Ba$_2$P$_7$I, have been synthesized and their crystal structures have been determined by means of single crystal X-ray diffraction. In the crystal structure of Ba$_2$P$_7$X (X = Cl, Br, I) negatively charged layers of heptaphosphanortricyclane P$_7^{3-}$ clusters surrounded by barium cations are stacked along the [001] direction, alternating with positively charged Ba$_2$X$_2$ layers. According to the Zintl count and quantum-chemical calculations, Ba$_2$P$_7$X are electron-balanced semiconductors with wide bandgaps. UV-Vis spectroscopy confirms the semiconducting nature of Ba$_2$P$_7$X compounds. Analysis of the chemical bonding in P$_7^{3-}$ clusters by means of electron localization function indicates their bonding generally follows the Zintl counting scheme. However, for the basal triangle of phosphorus atoms, the ELF localization domains are displaced from the shortest interatomic separations.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Pöttgen, R.; Hönle, W.; von Schnering, H.G. Phosphides: Solid State Chemistry. In Encyclopedia of Inorganic Chemistry, 2nd ed.; King, R.B., Ed.; Wiley: Chichester, UK, 2005; volume 8, pp. 4255–4308.
2. Von Schnering, H.G.; Hoenle, W. Bridging chasms with polyphosphides. Chem. Rev. 1988, 88, 243–273.
3. Dahlmann, W.; von Schnering, H.G. Die Polyphosphide SrP$_3$ und Ba$_3$P$_{14}$. Naturwissenschaften 1973, 60, 429–429.
4. Manriquez, V.; Hönle, W.; von Schnering, H.G. Trilithiumheptaphosphid Li$_3$P$_7$: Darstellung, Struktur und Eigenschaften. Z. Anorg. Allg. Chem. 1986, 539, 95–109.
5. Scharfe, S.; Kraus, F.; Stegmaier, S.; Schier, A.; Fässler, T.F. Zintl ions, cage compounds, and intermetalloid clusters of group 14 and group 15 elements. Angew. Chem. Int. Ed. 2011, 50, 3630–3670.

6. Shatruk, M.M.; Kovnir, K.A.; Shevelkov, A.V.; Popovkin, B.A. Ag₃SnP₇: A polyphosphide with a unique (P₇) chain and a novel Ag₃Sn heterocluster. Angew. Chem. Int. Ed. 2000, 39, 2508–2509.

7. Lange, S.; Sebastian, C.P.; Zhang, L.; Eckert, H.; Nilges, T. Ag₃SnCupro [Ag₃Sn] tetrahedra embedded between adamantane-type [P₁₀] cages. Inorg. Chem. 2006, 45, 5878–5885.

8. Lange, S.; Bawohl, M.; Weihrich, R.; Nilges, T. Mineralization routes to polyphosphides: Cu₃P₂₀ and Cu₃InP₁₆. Angew. Chem. Int. Ed. 2008, 47, 5654–5657.

9. Dewalsky, M.V.; Jeitschko, W.; Wortmann, U. The metallic polyphosphide titanium nickel phosphide (Ti₂NiP₃). Chem. Mater. 1991, 3, 316–319.

10. Eisenmann, B.; Rößler, U. Ein Erdalkalimetallpolyphosphid ungewöhnlicher Zusammensetzung: Die Kristallstruktur von Ba₃P₉. Z. Anorg. Allg. Chem. 2003, 629, 459–462.

11. Chen, X.; Zhu, L.; Yamanaka, S. High-pressure synthesis and structural characterization of three new polyphosphides, α-SrP₃, BaP₆, and LaP₆. J. Solid State Chem. 2003, 173, 449–455.

12. Eschen, M.; Jeitschko, W. Au₂PbP₂, Au₂TlP₂, and Au₂HgP₂: Ternary gold polyphosphides with lead, thallium, and mercury in the oxidation state zero. J. Solid State Chem. 2002, 165, 238–246.

13. Kovnir, K.; Stockert, U.; Budnyk, S.; Prots, Y.; Baitinger, M.; Paschen, S.; Shevelkov, A.V.; Grin, Y. Introducing a magnetic guest to a tetrel-free clathrate: Synthesis, structure, and properties of Eu₄Ba₈–₉₄₄₃₀₃₀ (0 ≤ x ≤ 1.5). Inorg. Chem. 2011, 50, 10387–10396.

14. Fulmer, J.; Kaseman, D.C.; Dolyniuk, J.; Lee, K.; Sen, S.; Kovnir, K. BaAu₂P₄: Layered Zintl Polyphosphide with Infinite 1/2(P⁻) Chains. Inorg. Chem. 2013, 52, 7061–7067.

15. Kraus, F.; Korber, N. The Chemical Bond in Polyphosphides: Crystal Structures, the Electron Localization Function, and a New View of Aromaticity in P₄²⁻ and P₅⁻. Chem. A Eur. J. 2005, 11, 5945–5959.

16. He, H.; Tyson, C.; Bobev, S. New compounds with [As₇]³⁻ clusters: Synthesis and crystal structures of the Zintl phases Cs₂NaAs₇, Cs₂ZnAs₁₄ and Cs₂CdAs₁₄. Crystals 2011, 1, 87–98.

17. Knapp, C.M.; Large, J.S.; Rees, N.H.; Goicoechea, J.M. A versatile salt-metathesis route to heteratomic clusters derived from phosphorus and arsenic Zintl anions. Dalton Trans. 2011, 40, 735–745.

18. Hirschle, C.; Röhr, C. Darstellung und Kristallstruktur der Bekannten Zintl-Phasen Cs₃Sb₇ und Cs₄Sb₂. Z. Anorg. Allg. Chem. 2000, 626, 1992–1998.

19. Kauzlarich, S.M. Chemistry, Structure, and Bonding of Zintl Phases and Ion; John Wiley and Sons Ltd.: New York, NY, USA, 1996.

20. Miller, G.J.; Schmidt, M.W.; Wang, F.; You, T.S. Quantitative advances in the Zintl-Klemm formalism. Struct. Bond. 2011, 139, 1–55.

21. Von Schnering, H.G.; Menge, G.; Dibariumheptaphosphidchlorid Ba₂P₇Cl, eine Verbindung mit dem polycyclischen Anion P₇³⁻. Z. Anorg. Allg. Chem. 1981, 481, 33–40.

22. Becke, A.D.; Edgecombe, K.E. A simple measure of electron localization in atomic and molecular systems. J. Chem. Phys. 1990, 92, 5397–5403.
23. Savin, A.; Jepsen, O.; Flad, J.; Anderson, O.K.; Preuß, H.; von Schnering, H.G. Electron localization in solid-state structures of the elements: The diamond structure. *Angew. Chem. Int. Ed.* **1992**, *31*, 187–188.

24. Savin, A.; Nesper, R.; Wengert, S.; Fässler, T.F. ELF: The electron localization function. *Angew. Chem. Int. Ed.* **1997**, *36*, 1808–1832.

25. Kovnir, K.; Kolen’ko, Y.V.; Baranov, A.I.; Neira, I.S.; Sobolev, A.V.; Yoshimura, M.; Presniakov, I.A.; Shevelkov, A.V. Sn₄As₃ revisited: Solvothermal synthesis and crystal and electronic structure. *J. Solid State Chem.* **2009**, *182*, 630–639.

26. Morales, A.; Mora, E.; Pal, U. Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures. *Rev. Mex. Fis.* **S. 2007**, *53*, 18–22.

27. Nobbs, J.H. Kubelka—Munk theory and the prediction of reflectance. *Rev. Prog. Color. Relat. Top.* **1985**, *15*, 66–75.

28. SMART and SAINT. Bruker AXS Inc.: Madison, WI, USA, 2007.

29. Sheldrick, G. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122.

30. Jepsen, O.; Burkhardt, A.; Andersen, O.K. The Program TB-LMTO-ASA, Version 4.7; Max-Planck-Institut für Festkörperforschung: Stuttgart, Germany, 1999.

31. Barth, U.V.; Hedin, L. A local exchange-correlation potential for the spin polarized case. *J. Phys. C Solid State Phys.* **1972**, *5*, doi:10.1088/0022-3719/5/13/012.

32. Sandia National Labs, Kitware Inc., Los Alamos National Labs (USA). Paraview: Parallel visualization application, version 3.8.1 64 bit. Available online: http://paraview.org.

33. Baranov, A.I. *Visualization Plug-in for ParaView*, Version 3.4.11; Springer: Dresden, Germany, 2012.

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