**New Insights into the Application of the Valence Rules in Zintl
Phases—Crystal and Electronic Structures of $\text{Ba}_7\text{Ga}_4\text{P}_9$,
 $\text{Ba}_7\text{Ga}_4\text{As}_9$, $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$, and $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$.**

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Abstract

Crystals of three new ternary pnictides— $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_7\text{Ga}_4\text{P}_9$, and $\text{Ba}_7\text{Ga}_4\text{As}_9$ have been prepared by reactions of the respective elements in molten Al or Pb fluxes. Single-crystal X-ray diffraction studies reveal that the three phases are isotypic, crystallizing in the orthorhombic $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ -type structure (space group $Pmmn$, Pearson symbol $oP40$, $Z = 2$), for which only the prototype is known. The structure is based on $TrPn_4$ tetrahedra ($Tr = \text{Al}, \text{Ga}$; $Pn = \text{P}, \text{As}, \text{Sb}$), connected in an intricate scheme into 1D-ribbons. Long interchain $Pn-Pn$ bonds ($d_{\text{P-P}} > 3.0 \text{ \AA}$; $d_{\text{As-As}} > 3.1 \text{ \AA}$; $d_{\text{Sb-Sb}} > 3.3 \text{ \AA}$) account for the realization of 2D-layers, separated by Ba^{2+} cations. Applying the classic valance rules to rationalize the bonding apparently fails, and $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ has long been known as a metallic Zintl phase. Earlier theoretical calculations, both empirical and ab-initio, suggest that the possible metallic properties originate from filled anti-bonding $Pn-Pn$ states, and the special roles of the “cations” in this crystal structure. To experimentally probe this hypothesis, we sought to synthesize the ordered quaternary phases $\text{Ba}_6\text{Ca}Tr_4\text{Sb}_9$ ($Tr = \text{Al}, \text{Ga}$). Single-crystal X-ray diffraction work confirms $\text{Ba}_{6.145(3)}\text{Ca}_{0.855}\text{Al}_4\text{Sb}_9$ and $\text{Ba}_{6.235(3)}\text{Ca}_{0.765}\text{Ga}_4\text{Sb}_9$, with Ca atoms preferably substituting Ba on one of the three available sites. The nuances of the five crystal structures are discussed, and the chemical bonding in $\text{Ba}_7\text{Ga}_4\text{As}_9$ is interrogated by tight-binding linear muffin-tin orbital calculations.

Keywords: crystal structure, single-crystal X-ray diffraction, barium, antimony, arsenic.

Introduction

A variety of new ternary $AE-Tr-Pn$ pnictides ($AE = Ca, Sr, Ba$; $Tr = Al, Ga, In$; and $Pn = P, As, Sb$) have been reported in recent years, including $BaGa_2Pn_2$ [1], $Ba_2Ga_5As_5$, $CaGa_2Pn_2$, and $SrGa_2As_2$ [2], $AE_3Al_2Pn_4$ and $AE_3Ga_2Pn_4$ [3], $Ba_3Al_3Pn_5$ and $Ba_3Ga_3P_5$ [4], discovered by our group, and $BaGa_2Sb_2$ [5], $Ba_3Ga_4Sb_5$ [6], $BaIn_2P_2$ [7], $Ba_2In_5As_5$ [8], among others, reporting by teams from all over the world. In these compounds, significant differences in the electronegativities of the constituent elements imply complete electron transfer from electropositive alkaline-earth metals to (poly)anionic networks made up of electronegative metalloid elements, which form covalent bonds to attain closed-shell configuration. Such compounds can be classified as Zintl phases and are expected to be small band gap semiconductors [9,10]. Much of the interest in these pnictides relates to their electrical and thermal transport properties, which prove favorable in thermoelectric materials design. Several compounds in the $AE-Tr-Pn$ systems, e.g., Ca_3AlSb_3 and $Ca_5Al_2Sb_6$ [11,12] have been considered as environmentally friendly candidates for thermoelectric applications.

A common denominator among the above-mentioned compounds is the straightforward application of the Zintl-Klemm formalism to rationalize the bonding [9,10]. There also exist “unusual” Zintl phases which deviate from the norm. $Ba_7Ga_4Sb_9$ is such an example from the $AE-Tr-Pn$ systems, which have been the subject of our attention for the past decade. This compound was first synthesized and structurally characterized in the 1980s by Schäfer, Cordier, and co-workers [13]. Some years later, this seemingly trivial structure, based on layers of fused $GaSb_4$ tetrahedra, separated by Ba^{2+} cations, piqued the interest of R. Hoffmann and his group [14]. Two interesting

structural features can be brought up for a discussion here: (1) the atypically long Sb–Sb bond; and (2), based on the valence rules, it seemed not possible to distribute the 14 electrons provided by the Ba atoms to the $[\text{Ga}_4\text{Sb}_9]$ polyanionic framework. Calculations based on the extended Hückel theory on $[\text{Ga}_4\text{Sb}_9]^{14-}$ suggested localized bonding, and an extra electron located in an antibonding σ^* band pertaining to the 3.3 Å long Sb–Sb interactions (*vide infra*). Hoffmann and co-workers also suggested possible pairing distortion and potential metal-insulator transition, and those findings were confirmed in a subsequent paper, describing first-principle DFT calculations on the electronic structure of this compound [15]. The latter treatise by Alemany and Canadell paid closer attention to the cation-anion bonding in this “metallic” Zintl phase and confirmed that although “every cation plays important structural role, the electronic properties of this unusual structure with both one- and three-dimensional contributions to the Fermi surface are decided by just a small subset of the cations” [15]. Since for more than 20 years, the phase $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ appeared to be the only example of this interesting structural chemistry [13], the theoretical papers looking into the problem [14,15] encouraged experimentalist to look for more precedents. We took this challenge, and here, we report our findings—we present the crystal structures of $\text{Ba}_7\text{Al}_4\text{Sb}_9$, and of the first phosphide and arsenide examples of this unusual structure type, namely, $\text{Ba}_7\text{Ga}_4\text{P}_9$ and $\text{Ba}_7\text{Ga}_4\text{As}_9$. In addition, we also investigated two quaternary variants of the structure, $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($\text{Tr} = \text{Al}, \text{Ga}$), which show preferential Ca-occupation on a specific Ba-site (near full ordering of the cations). These finding corroborate the hypothesis raised by Alemany and Canadell that judicious cation substitutions could create a “normal” Zintl phase, but with tunable

transport properties [15]. The structural characteristics are analyzed alongside band structure calculations.

Experimental

Synthesis

Starting materials were K, Ca, and Ba pieces, Al granules, Ga and Pb ingots, red P powder, As lumps, and Sb shot, all with purities greater than 99.9% and purchased from Alfa-Aesar or Sigma-Aldrich. All reagents and products were handled within an argon-filled glove box with controlled oxygen and moisture level below 1 ppm. Single-crystals of $\text{Ba}_7\text{Al}_4\text{Sb}_9$, and $\text{Ba}_7\text{Ga}_4\text{Pn}_9$ ($\text{Pn} = \text{P}, \text{As}$) were first isolated from reactions attempted to extend the AETr_2Pn_2 and $\text{AE}_3\text{Tr}_2\text{Pn}_4$ series [1,2,3] through use of the Al or Pb fluxes. Mixtures of the elements were loaded into alumina crucibles covered on the top with quartz wool and placed within fused silica tubes, which were then evacuated and flame-sealed. The tubes with the elemental mixtures inside were heated to 960 °C at a rate of 60 °C/h, held at that temperature for 20 h (samples with Al flux) or 40 h (samples with Pb flux), cooled to 750 °C at a rate of 5 °C/h (for samples with Al flux) or to 500 °C at a rate of 30 °C/h (for samples with Pb flux). The molten metals were removed at 750 °C (Al flux) or at 500 °C (Pb flux) by centrifugation. Generally, the title compounds were obtained as the major phase in each of the above-mentioned reaction, with AlAs, AlSb, and some unidentified products as the most common impurity phases. Subsequent experiments starting from the stoichiometric mixtures of elements and Pb flux aimed at extending the two series yielded only two new pnictides Sr_3GaAs_3 and Ba_3GaAs_3 [16]. The quaternary variants of $\text{Ba}_7\text{Al}_4\text{Sb}_9$ and $\text{Ba}_7\text{Ga}_4\text{Sb}_9$, $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$ and $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$, were prepared by direct fusion of the respective elements at 960 °C. Similar reactions

with K and Na, aimed at the electron-precise quaternary compounds $\text{NaBa}_6\text{Ga}_4\text{Sb}_9$ and $\text{KBa}_6\text{Ga}_4\text{Sb}_9$, as proposed by Alemany and Canadell [15], were unsuccessful. We even tried $\text{KBa}_6\text{Al}_4\text{Sb}_9$ and $\text{NaBa}_6\text{Al}_4\text{Sb}_9$, but all the efforts so far resulted in the known compounds Ba_3AlSb_3 [17], Ba_3GaSb_3 [18], $\text{K}_2\text{Ga}_2\text{Sb}_3$ [19], as well as some other, yet unknown phases—work to identify all the products is currently ongoing.

Structure Determination

X-ray powder diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer using filtered Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The data were gathered in θ – θ scan mode ($2\theta_{\text{max}} = 70^\circ$) with step-size 0.05° and 1 sec/step counting time. The data were analyzed with the JADE 6.5 software package. The extreme air-sensitivity of the studied samples hindered the match between the experimental and simulated powder patterns (see Supporting Information). Nonetheless, the reasonable agreement of positions/intensities of most strong peaks suggests that the phases can be obtained in quantitative yields.

For the purpose of solving and refining the crystal structures, intensity data were collected on the single-crystal diffractometer. First, since the crystals were air-sensitive, they were picked under an optical microscope in the glove box and mounted on glass fibers using Paratone-N oil. Next, the crystals were quickly transferred onto the goniometer of a Bruker SMART CCD-based diffractometer, equipped with a sealed Mo $K\alpha$ source. The protective inert atmosphere and temperature (200(2) K) were maintained by a stream of cold nitrogen gas. Full spheres of intensity data were collected using ω scans with a scan width of 0.4° and an exposure time of 12 s per frame in 4 batches. Data collection and integration of the intensity data were done with SMART/SAINT programs

[20], and semi-empirical absorption corrections based on the equivalent reflections were applied using SADABS [21]. Space group determination—uniquely *Pmmn*, sorting and merging the reflections, structure solution (direct methods) and refinements (full-matrix least squares on F^2 method) were carried out with the use of SHELX [22]. Refined parameters included the scale factor and atomic positions with the corresponding anisotropic displacement parameters. Before the final refinement steps, the atomic positions were labeled in accordance with the $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ -type structure [13] and standardized (the unit cell was transformed into b , a , $-c$, with the origin being shifted by $\frac{1}{2} 0 \frac{1}{2}$). The final difference Fourier maps in all refined structures were flat, with highest maxima and deepest minima not larger than ca. $\pm 1\text{--}2 \text{ e}^-/\text{\AA}^3$. The residual density was higher, ca. $\pm 3\text{--}4 \text{ e}^-/\text{\AA}^3$, for the $\text{Ba}_7\text{Ga}_4\text{P}_9$ crystal structure, which clearly is an artifact of the observed small positional disorder (related to the possible pairing distortion—*vide infra*).

A few noteworthy details follow. Refinements for $\text{Ba}_7\text{Al}_4\text{Sb}_9$ proceeded in a straightforward manner; all atomic sites were found to be fully occupied and to have reasonable thermal displacement parameters. Refinements for $\text{Ba}_7\text{Ga}_4\text{Pn}_9$ ($\text{Pn} = \text{P}, \text{As}$) provided some evidence for positional disorder, detailed later in the text. Refinements for the Ca-substituted $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ antimonides ($\text{Tr} = \text{Al}, \text{Ga}$) revealed a nearly ordered distribution of Ca atoms over the three alkaline-earth sites, with occupancies: 1.002(2) Ba / 0.000(2) Ca at the 1st cation site, 1.001(2) Ba / 0.000(2) Ca at the 2nd cation site, and 0.854(3) Ca / 0.146(3) Ba at the third site for the Al-containing compound. The occupancies for $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$ were: 0.997(2) Ba / 0.003(2) Ca, 0.998(2) Ba / 0.002(2) Ca, and 0.765(3) Ca / 0.235(3) Ba, respectively. Because the Ca atoms are clearly not

favored at the first two sites, the proceeding refinements were performed with Ba1 and Ba2 sites being assigned as Ba atoms, and Ba3/Ca3 as mixed-occupied. This resulted in the following refined formulas: $\text{Ba}_{6.145(3)}\text{Ca}_{0.855(3)}\text{Al}_4\text{Sb}_9$ and $\text{Ba}_{6.235(3)}\text{Ca}_{0.765(3)}\text{Ga}_4\text{Sb}_9$, which throughout the text are simplified to the stoichiometric formulas $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$ and $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$. No attempts were made to study the whether or not additional Ca uptake is possible, and the eventual stoichiometry breadth in $\text{Ba}_{7-x}\text{Ca}_x\text{Al}_4\text{Sb}_9$ and $\text{Ba}_{7-x}\text{Ca}_x\text{Ga}_4\text{Sb}_9$.

The crystallographic information pertaining to $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_7\text{Ga}_4\text{P}_9$, $\text{Ba}_7\text{Ga}_4\text{As}_9$, $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$ and $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$ is provided in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Selected interatomic distances are tabulated in Table 3. CIFs have also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers CSD-429585 for $\text{Ba}_7\text{Ga}_4\text{P}_9$, CSD-429586 for $\text{Ba}_7\text{Ga}_4\text{As}_9$, CSD-429587 for $\text{Ba}_7\text{Al}_4\text{Sb}_9$, CSD-429588 for $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$, and CSD-429589 for $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$. Crystallographic data for $\text{Ba}_7\text{Ga}_4\text{Pn}_9$ ($\text{Pn} = \text{P}, \text{As}$), where the positional disorder is modeled as split sites have been provided as supporting information.

Electronic Structure Calculations

To compare the chemical bonding in the newly identified phosphide and arsenide with the findings of Hoffmann and co-workers [14], and Alemany and Canadell [15] on the crystal chemistry of the $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ antimonide, tight-binding linear muffin tin orbital (TB-LMTO) calculations were performed. We chose to do electronic band structure calculations on $\text{Ba}_7\text{Ga}_4\text{As}_9$ only; the $\text{Ba}_7\text{Ga}_4\text{P}_9$ crystal structure exhibits more severe

positional disorder, and the average structure may not be a good discussion point. The calculations were done within the local density and atomic spheres approximation with use of the Stuttgart TB-LMTO-ASA program (version 4.7) [23]. The basis sets included Ba 6s/6p/5d/4f, Ga 4s/4p/4d, and As 4s/4p/4d orbitals, with the Ba 6p, Ga 4d, and As 4d orbitals being downfolded. Integration in reciprocal space was carried out with an improved tetrahedron method over 112 irreducible k -points within the first Brillouin zone. The total and partial density-of-states (DOS) were plotted and studied. To interrogate the chemical bonding, crystal orbital Hamilton populations (COHP) [24] of selected interactions were also analyzed.

Results and Discussion

Structures and chemical bonding

The antimonide $\text{Ba}_7\text{Al}_4\text{Sb}_9$, its quaternary variants $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($Tr = \text{Al}, \text{Ga}$), the first phosphide and arsenide examples of this unusual structure type— $\text{Ba}_7\text{Ga}_4\text{P}_9$ and $\text{Ba}_7\text{Ga}_4\text{As}_9$, are all isotypic and crystallize in the orthorhombic space group $Pmmn$ (No. 59, Pearson symbol $oP40$) with the $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ -type structure [13], for which only the archetype has been known up until now. There are ten crystallographically unique atoms are present in the asymmetric unit—three alkaline earth metals, two triels, and five pnictogens (Table 2). As exemplified by $\text{Ba}_7\text{Ga}_4\text{As}_9$ in Fig. 1(a), the crystal structure is based on GaAs_4 tetrahedra, which by sharing corner As atoms are fused into complex $[\text{Ga}_4\text{As}_9]$ polyanionic chains, with Ba cations separating the chains. Fig. 1(b) shows the most recognizable motif of the polyanionic framework, the $[\text{Ga}_4\text{As}_{11}]$ bicyclic ring, whose skeletal structure resembles the bicyclo-3.3.1-nonane. Connecting these $[\text{Ga}_4\text{As}_{11}]$ bicyclic rings by sharing the terminal pnictogens As3 and As4, a $[\text{Ga}_4\text{As}_9]$ chain forms

with alternating bi-cyclic rings and 4-membered rings running along the crystallographic a axis (Note that in the older literature, the a and the b axes are interchanged [13-15]). The structure has been previously discussed, and we will only provide a brief description.

Within the polyanionic framework, the $Tr-Pn$ distances match very well with the sums of their single-bonded covalent radii. For example, the Ga-As distances fall into the range from 2.423 Å to 2.576 Å, well-comparable with the sum of their Pauling radii ($r_{Ga}=1.24\text{Å}$, $r_{As}=1.21\text{ Å}$) [25], as well with those reported for compounds with similar bonding pattern: $d_{Ga-As}=2.506\text{-}2.565\text{ Å}$ in $BaGa_2As_2$ [1], $d_{Ga-As}=2.512\text{ Å}$ in $CaGa_2As_2$ [2], and $d_{Ga-P}=2.478\text{-}2.659\text{ Å}$ in $Ba_2Ga_5As_5$ [2]. The Ga-P and Al-Sb distances are also within the norms (Table 3), suggesting covalent bonding character of the $Tr-Pn$ interactions. Special attention needs to be paid to the long $Pn3-Pn4$ contacts in all structure, namely $d_{P3-P4}=3.012\text{ Å}$ in $Ba_7Ga_4P_9$ (average structure, devoid of disorder model), $d_{As3-As4}=3.135\text{ Å}$ in $Ba_7Ga_4As_9$, and $d_{Sb3-Sb4}=3.303\text{ Å}$ in $Ba_7Al_4Sb_9$. Although these distances are, in general, much longer than the closer $Pn-Pn$ contacts in the structures, as well as the intralayer distances in the structures of the respective elements [26], they still signify bonding interactions. For example, one can find the above metrics to be comparable with the distances between the layers in the elemental crystal structures of red phosphorous and grey arsenic [26]. Similarly long Sb-Sb interactions (e.g., 3.0-3.3 Å) can be found in several examples in the literature— La_3ZrSb_5 and La_3HfSb_5 [27] with $d_{Sb-Sb}=3.175\text{ Å}$ and 3.169 Å , respectively, $CeAgSb_2$ with $d_{Sb-Sb}=3.085\text{ Å}$ [28], and even the binary Li_2Sb , where both long and short Sb-Sb contacts exist: $d_{Sb-Sb}=2.97\text{ Å}$, 3.26 Å [29]. Long As-As and P-P bonds in compounds are less common, but are not without precedents, e.g., $Eu_{14}MnP_{11}$ and $Eu_{14}MnAs_{11}$ [30]. Interestingly, the latter two

structures, in contrast to their Sb analogue, show enlarged thermal displacement parameters of P and As. This is noted here since in the $\text{Ba}_7\text{Ga}_4\text{P}_9$ and $\text{Ba}_7\text{Ga}_4\text{As}_9$ structures, the elongation of the displacement parameters of $Pn3$ and $Pn4$ sites could be modeled as two split sites, each with 50% occupancy. As shown in Figure 2, the split model leads to more reasonable thermal displacement parameters, as well as modulation on the P3–P4 and As3–As4 distances, which now range from 2.382 to 3.677 Å for d_{P3-P4} and from 2.672 to 3.603 Å for $d_{As3-As4}$. Further analysis of the long $Pn3-Pn4$ interactions will be provided in the section dealing with the electronic structure.

Cations and their roles in the chemical bonding

Before turning our attention to the Ca substituted compounds, a short discussion on the cation coordination is also in order. As listed in Table 3, there are three unique cation sites in the structure. The coordination polyhedra of Ba1 and Ba3 both resemble that of a distorted octahedron, where Ba is coordinated by six Pn atoms. On the other hand, Ba2 is coordinated by 7 Pn atoms, forming a pentagonal bi-pyramid. The Ba– Pn distances span a wide range for every cation site; however, the average Ba– Pn distances are found to follow a general trend: $d_{Ba2-Pn} > d_{Ba1-Pn} > d_{Ba3-Pn}$ for all the title compounds. Taking $\text{Ba}_7\text{Al}_4\text{Sb}_9$ as an example, the average distances between Ba1–Sb, Ba2–Sb, and Ba3–Sb are 3.607 Å, 3.660 Å, and 3.462 Å, respectively, with the average d_{Ba3-Sb} being much shorter than the other two. Note that only Ba2 polyhedron contains $Pn3$ and $Pn4$, which form a long bond and have significant impact on the electronic structure at the Fermi level (*vide infra*).

Two quaternary variants $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($Tr = \text{Al, Ga}$), with very interesting coloring on the cation sites were successfully synthesized and structurally characterized

as a part of this study. The refinements on both of them show that Ca has a clear preference for the Ba3 site, with essentially no Ca incorporation at the Ba1 or Ba2 sites. Based on the analysis above, it seems natural that the smaller Ca prefers the Ba3 site, since the volume of the Ba3 polyhedron is the smallest (on average, Ba3–Sb distances are shorter than the Ba1–Sb and Ba2–Sb distances). A more sophisticated explanation on the Ca cation preference has been revealed by the theoretical work of Alemany and Canadell [15], which shows that among the three cations in $\text{Ba}_7\text{Ga}_4\text{Sb}_9$, Ba3 has the smallest positive Mulliken charge, i.e., the largest atomic orbital population (AOP). Therefore, following G. J. Miller's arguments in his review on the atomic orbital populations, one is to expect that the more electronegative Ca (compared with Ba) will prefer the electron-rich site, i.e., the Ba3 site, to minimize the site energy [31]. Although we did not calculate the AOPs at the different Ba sites in the isoelectronic and isostructural $\text{Ba}_7\text{Al}_4\text{Sb}_9$, the crystallographic data suggest that this structure will follow the same trends, a conjecture which is fully corroborated by the observed Ca-site preference in $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$.

Another interesting observation pertaining to $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($Tr = \text{Al}, \text{Ga}$) is that the certain bonds respond differently to the contraction of the unit cell volume due to inclusion of the smaller Ca ($\text{Ba}^{2+} = 1.36 \text{ \AA}$; $\text{Ca}^{2+} = 1.14 \text{ \AA}$ [32]). The substitution of ca. 10% of the Ba atoms by Ca does lead to ca. 2.5% smaller unit cell volume (Table 1: $V = 1398 \text{ \AA}^3$ in $\text{Ba}_7\text{Al}_4\text{Sb}_9$ and $V = 1365 \text{ \AA}^3$ in $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$). The contraction is in all three directions. Despite that, not all of the bond distances in $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$ are shorter than those in the parent compound. For example, the Al1–Sb2, Al1–Sb5, Ba1–Sb1, Ba1–Sb2, Ba2–Sb1 distances are longer (Table 3). Even though Ca is not involved in any of these

interactions, it is apparent that the small local environment changes cannot be rationalized by geometric considerations alone. The discriminating factor here, likely, is the higher Pauling scale electronegativity of Ca ($\chi_{\text{Ca}} = 1.0$; $\chi_{\text{Ba}} = 0.9$) [25]), which causes subtle changes in their orbital overlaps. This, in turn, leads to small modifications in the bond distances by virtue of modulating the electron density. Similar discussions on the bonding and the roles of the cations in Zintl phases have been a topic in several other articles [33-36].

Electron count and electronic structure

Following the octet rule and the Zintl formalism, an electron transfer (14 e⁻/f.u.) from the least electronegative Ba (or Ca) to the *Tr-Pn* polyanion leads to the definition of a “metallic Zintl phase”, i.e., the “13-“ charge on the $[\text{Tr}_4\text{Pn}_9]^{13-}$ slabs is not fully compensated (i.e., the oxidation numbers will be: $4 \times \text{Tr}^{3+} + 7 \times \text{Pn}^{3-} + 2 \times \text{Pn}^{2-}$). Applying the idea of the formal charge, whereby the covalency of the *Tr-Pn* interactions is exaggerated yields to the same conclusion—taking the multiplicity of each site into account, the polyanionic $[\text{Tr}_4\text{Pn}_9]$ sub-lattice can be rationalized as: $(4b\text{-Tr}^{1-})_4(1b\text{-Pn}^{2-})_2(2b\text{-Pn}^{1-})_5(3b\text{-Pn}^0)_2$, where the abbreviations 1b-, 2b-, 3b-, and 4b- denote 1-, 2-, 3-, and 4-bonded atoms.

From the above, it is apparent that there is one extra electron provided by the cations, which is not needed for covalent bonding. Notice that here, we implicitly assumed that the previously mentioned *Pn3–Pn4* “bonds” represent 2-center 2-electron covalent interactions, despite their unusual length (Table 3). Off course, for such unconventional interactions, bond order is nebulous, and the assignment of charges can be questioned. Applying the bond valence sum method for example suggests bond order

of about 0.1 to 0.3, confirming that there is almost no electron density shared between $Pn3$ and $Pn4$ (Table S4 in supporting information). In other words, the latter two pnictogen atoms can also be considered as formally Pn^{3-} , leading to a net “15–” charge on the $[Tr_4Pn_9]$ polyanions. Hence, in such terms, the title compounds should be viewed as electron-deficient.

Clearly, the classic electron counting rules fail to provide a reasonable picture of the chemical bonding. Based on computational results obtained by the extended Hückel method, R. Hoffmann and co-workers pointed that the extra electron (i.e., treating localized bonding within $[Ga_4Sb_9]^{14-}$) is located in an antibonding σ^* band pertaining to the 3.3 Å long Sb3–Sb4 interactions [14]. More interestingly, this study suggested that such bonding pattern is susceptible to pairing distortion, similar to the Jahn-Teller distortion in molecular systems [37]. R. Hoffmann encouraged follow up experimental studies and we believe we have found clues in the structures of $Ba_7Ga_4P_9$ and $Ba_7Ga_4As_9$, which could help unravel possible distortions—there are extremely elongated anisotropic displacement parameters for $Pn3$ and $Pn4$ in $Ba_7Ga_4Pn_9$ ($Pn = P, As$). For example, U^{33} are almost 8-9 larger compared to U^{11} and U^{22} , which allows these sites to be split in a model refinement. In all Sb-based structures, this split is somewhat concealed, probably because Sb is a heavy element that might favor hypervalent bonding, while the lighter pnictogen atoms (in our case for P and As) involved in this type of interactions, clearly indicate the tendency toward a pairing distortion. Below we provide our electronic structure calculations for the undistorted (idealized) $Ba_7Ga_4As_9$ structure and compare it with the previously studied $Ba_7Ga_4Sb_9$ [14,15].

The density of states (DOS) diagram of $\text{Ba}_7\text{Ga}_4\text{As}_9$ is shown on the left panel of Figure 3, with contributions from different electronic states in different energy ranges. In the energy range from -12.0 to -9.5 eV, the DOS predominately originate from the contributions of the As $4s$ states. The energy window from -6.5 to -5 eV corresponds to the mixture of the Ga $4s$ states and As $4p$ states. The states from -4 eV up to the Fermi level are associated with the mixing states from the As $4p$ and Ga $4p$ levels, with substantial contributions from the Ba $5d$ states. Mixing of the Ba d and As p states indicates significant covalency of the Ba–As bonding, which characteristic is also revealed for the Ba–Sb bonding in $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ [15]. In contrast with the narrow minimum around the Fermi level in $\text{Ba}_7\text{Ga}_4\text{Sb}_9$, a much wider minimum is observed in $\text{Ba}_7\text{Ga}_4\text{As}_9$, which could be linked to the more electronegative As, as compared to Sb, which understandably will lead to widening the gap. The Fermi level is located within this wide minimum, suggesting that $\text{Ba}_7\text{Ga}_4\text{As}_9$ is a poor metal.

The COHP curves are also projected in the same energy window (Figure 3, right panel). As seen from the plot, the strongest bonding interactions are found between Ga and As, which agrees with their covalent bonding character. While the Ba–Ga interactions are almost negligible, the Ba–As COHP curve indicates significant p – d mixing, especially in the energy range near the Fermi level. This is indicative of the important role of Ba in stabilizing the crystal structure and optimizing the overall bonding interactions, rather than being just spectators and/or space fillers. The As–As interactions, originated from the long As3–As4 bond, show antibonding character around the Fermi level. Note the significant As3 and As4 contributions to the DOS at the Fermi

level, this half-filled antibonding band is expected to play an important role in determining the transport properties, which are worth further investigation.

4. Conclusions

Reported were the synthesis and characterization of five new ternary pnictides: $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_7\text{Ga}_4\text{Pn}_9$, ($\text{Pn} = \text{P}, \text{As}$) and the nearly ordered quaternary derivatives of $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($\text{Tr} = \text{Al}, \text{Ga}$). They all adopt the $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ -type structure, and are representatives of the rare “electron-rich” Zintl phases, only a few examples of which come from the AE-Tr-Pn systems. The experimentally determined structures of $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($\text{Tr} = \text{Al}, \text{Ga}$) confirm the unique roles of the cations, suggested by Alemany and Canadell from a comprehensive DFT-study on the electronic structure [15]. The long Pn-Pn bonds, subject of two prior computational studies based on $\text{Ba}_7\text{Ga}_4\text{Sb}_9$, are also shown to produce an antibonding band crossing the Fermi level, according to the electronic band structure of $\text{Ba}_7\text{Ga}_4\text{As}_9$. The latter crystal structure shows the hallmarks of a pairing distortion. Currently, our efforts are focused on the syntheses and characterization of other members of this family, particularly the alkali metal substituted $\text{Ba}_7\text{Tr}_4\text{Sb}_9$ ($\text{Tr} = \text{Al}, \text{Ga}$), which are expected to be “normal” Zintl phases with interesting physical properties. The suggested metal-to-insulator transition continues to be sought experimentally at low temperature, although the prospects of identifying such transition are grim—the very high air- and moisture-sensitivity of the crystalline materials hampers all property measurements and calls for the use of specialized sample environments that are not commonly available.

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Figure Captions

Figure 1. Combined ball-and-stick and polyhedral representation of the crystal structure of $\text{Ba}_7\text{Ga}_4\text{As}_9$, viewed approximately down the direction of the b -axis. The dark blue, light blue, and violet circles are Ba1, Ba2, and Ba3 atoms, respectively, the green circles are Ga atoms, and the red circles are As atoms. (b) The $[\text{Ga}_4\text{As}_9]^{14-}$ polyanionic sublattice of $\text{Ba}_7\text{Ga}_4\text{As}_9$. (c) The small four-member rings (see text for further details).

Figure 2. The four-member rings involving the long As3–As4 bond, shown with anisotropic displacement parameters: (a) averaged model; (b) split model. The ellipsoids are drawn at 95% probability level and are a strong indicator of positional disorder (even more so for P3–P4 in $\text{Ba}_7\text{Ga}_4\text{P}_9$). Relevant distances: $d_{\text{As3–As4}}=3.13(1)$ Å, $d_{\text{As31–As41}}=2.672(4)$ Å, $d_{\text{As31–As42}}=3.123(4)$ Å. For $\text{Ba}_7\text{Ga}_4\text{P}_9$, $d_{\text{P3–P4}}=3.01(2)$ Å, while $d_{\text{P31–P41}}=2.38(1)$ Å, $d_{\text{P31–P42}}=3.02(1)$ Å.

Figure 3. Band structure of $\text{Ba}_7\text{Ga}_4\text{As}_9$. The left panel shows the DOS diagrams and the two right panels are COHP curves for selected bond interactions. The Fermi level is set at the energy reference of 0 eV.

Table 1. Selected single-crystal data collection and structure refinement parameters for Ba₇Ga₄P₉, Ba₇Ga₄As₉, Ba₇Al₄Sb₉, Ba₆CaAl₄Sb₉, and Ba₆CaGa₄Sb₉. All five structures are with the orthorhombic space group *Pmmn* (No. 59) with two formula units per cell. All five data sets are collected with graphite-monochromated Mo *K*α, λ = 0.71073 Å at temperature 200(2) K.

Empirical formula	Ba ₇ Ga ₄ P ₉	Ba ₇ Ga ₄ As ₉	Ba ₇ Al ₄ Sb ₉	Ba _{6.145(3)} Ca _{0.855} Al ₄ Sb	Ba _{6.235(3)} Ca _{0.765} Ga ₄ S
Formula weight, g·mol ⁻¹	1518.99	1914.54	2165.05	2081.89	2261.61
Crystal dimensions (μm)	400 × 500 × 500	400 × 500 × 700	400 × 600 × 800	400 × 800 × 1200	500 × 700 × 1500
<i>a</i> , Å	9.877(2)	10.184(2)	10.8020(11)	10.7666(5)	10.7883(6)
<i>b</i> , Å	16.548(4)	16.987(4)	18.0575(18)	17.9378(9)	17.9110(10)
<i>c</i> , Å	6.6395(15)	6.8012(14)	7.1677(7)	7.0975(4)	7.0621(4)
<i>V</i> , Å ³	1085.2(4)	1176.5(5)	1398.1(2)	1370.73(12)	1364.60(13)
ρ _{calcd} , g·cm ⁻³	4.65	5.40	5.14	5.04	5.50
μ (Mo <i>K</i> α), cm ⁻¹	180.0	285.5	183.2	176.4	215.6
2θ (Mo <i>K</i> α) range	4.80°–56.58°	4.66°–55.90°	4.40°–56.58°	4.42°–61.78°	4.40°–61.64°
Unique data with $F_o^2 > 2\sigma(F_o^2)$	1336 (<i>R</i> _{int} = 0.041)	1366 (<i>R</i> _{int} = 0.047)	1676 (<i>R</i> _{int} = 0.037)	2028 (<i>R</i> _{int} = 0.036)	2017 (<i>R</i> _{int} = 0.035)
Variables	60	60	60	61	61
GOF on <i>F</i> ²	1.061	1.040	1.089	1.110	1.134
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.034	0.024	0.019	0.020	0.020
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.087	0.051	0.039	0.036	0.037
<i>R</i> ₁ [all data] ^a	0.037	0.029	0.024	0.024	0.024
<i>wR</i> ₂ [all data] ^a	0.090	0.053	0.040	0.038	0.038
(Δρ) _{max} / (Δρ) _{min} , e·Å ⁻³	3.44 / –4.57	2.26 / –3.19	0.94 / –1.67	1.00 / –2.05	1.10 / –0.95

^a *R*₁ = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|; *wR*₂ = [Σ[*w*(*F*_o² – *F*_c²)²]/Σ[*w*(*F*_o²)²]]^{1/2}, where *w* = 1/[σ²*F*_o² + (*A*·*P*)² + (*B*·*P*)], and *P* = (*F*_o² + 2*F*_c²)/3; *A*, *B* – weight coefficients.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}^{a} for $\text{Ba}_7\text{Ga}_4\text{P}_9$, $\text{Ba}_7\text{Ga}_4\text{As}_9$, $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_6\text{CaAl}_4\text{Sb}_9$, and $\text{Ba}_6\text{CaGa}_4\text{Sb}_9$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
$\text{Ba}_7\text{Ga}_4\text{P}_9$					
Ba1	4e	1/4	0.53447(4)	0.55058(9)	0.0118(2)
Ba2	8g	0.02724(5)	0.62490(3)	0.06012(6)	0.0123(2)
Ba3	2a	1/4	1/4	0.5992(2)	0.0187(2)
Ga1	4e	1/4	0.12772(7)	0.2324(2)	0.0095(2)
Ga2	4f	0.5738(1)	1/4	0.4259(2)	0.0165(3)
P1	8g	0.0436(2)	0.1237(1)	0.4388(3)	0.0126(4)
P2	4e	1/4	0.0136(2)	0.0232(4)	0.0127(5)
P3 ^b	2b	1/4	3/4	0.301(2)	0.064(3)
P4 ^b	2b	1/4	3/4	0.847(2)	0.069(3)
P5	2a	1/4	1/4	0.0449(6)	0.0125(7)
$\text{Ba}_7\text{Ga}_4\text{As}_9$					
Ba1	4e	1/4	0.53487(3)	0.54821(7)	0.0169(1)
Ba2	8g	0.02586(3)	0.62491(2)	0.05516(4)	0.0164(1)
Ba3	2a	1/4	1/4	0.59320(9)	0.0145(1)
Ga1	4e	1/4	0.12552(5)	0.2347(1)	0.0129(2)
Ga2	4f	0.57269(8)	1/4	0.4297(1)	0.0177(2)
As1	8g	0.04134(5)	0.12087(3)	0.44208(8)	0.0141(1)
As2	4e	1/4	0.01174(5)	0.0197(1)	0.0163(3)
As3 ^b	2b	1/4	3/4	0.3002(3)	0.0392(4)
As4 ^b	2b	1/4	3/4	0.8392(3)	0.0428(4)
As5	2a	1/4	1/4	0.0466(1)	0.0139(2)
$\text{Ba}_7\text{Al}_4\text{Sb}_9$					
Ba1	4e	1/4	0.53709(2)	0.54422(5)	0.0147(1)
Ba2	8g	0.02308(2)	0.62563(1)	0.04804(3)	0.0136(1)
Ba3	2a	1/4	1/4	0.58682(7)	0.0134(1)
Al1	4e	1/4	0.12311(9)	0.2407(2)	0.0111(3)
Al2	4f	0.5724(2)	1/4	0.4400(3)	0.0147(4)
Sb1	8g	0.04182(2)	0.11894(1)	0.45389(4)	0.0124(1)
Sb2	4e	1/4	0.00835(2)	0.01972(5)	0.0129(1)
Sb3	2b	1/4	3/4	0.29089(9)	0.0221(1)
Sb4	2b	1/4	3/4	0.8300(1)	0.0238(1)
Sb5	2a	1/4	1/4	0.04731(8)	0.0126(1)
$\text{Ba}_6\text{CaAl}_4\text{Sb}_9$					
Ba1	4e	1/4	0.54121(2)	0.54202(4)	0.0139(1)
Ba2	8g	0.02058(2)	0.62639(1)	0.04737(3)	0.0127(1)
Ba3 ^c	2a	1/4	1/4	0.5806(1)	0.0121(3)
Al1	4e	1/4	0.12511(8)	0.2366(2)	0.0110(3)
Al2	4f	0.57015(14)	1/4	0.4431(2)	0.0149(3)

Sb1	8g	0.04894(2)	0.12124(1)	0.46197(3)	0.0121(1)
Sb2	4e	1/4	0.00669(2)	0.02183(5)	0.0118(1)
Sb3	2b	1/4	3/4	0.28880(8)	0.0193(1)
Sb4	2b	1/4	3/4	0.82606(8)	0.0221(1)
Sb5	2a	1/4	1/4	0.02578(7)	0.0121(1)
<hr/>					
Ba ₆ CaGa ₄ Sb ₉					
Ba1	4e	1/4	0.54125(2)	0.53866(4)	0.0148(1)
Ba2	8g	0.01853(2)	0.62647(1)	0.04295(3)	0.0125(1)
Ba3 ^d	2a	1/4	1/4	0.5724(1)	0.0113(3)
Ga1	4e	1/4	0.12499(3)	0.23684(7)	0.0109(1)
Ga2	4f	0.56778(5)	1/4	0.44373(8)	0.0141(1)
Sb1	8g	0.04773(2)	0.12004(1)	0.46202(3)	0.0129(1)
Sb2	4e	1/4	0.00581(2)	0.02178(4)	0.0117(1)
Sb3	2b	1/4	3/4	0.28913(7)	0.0179(1)
Sb4	2b	1/4	3/4	0.82609(8)	0.0210(1)
Sb5	2a	1/4	1/4	0.02494(7)	0.0127(1)

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

^b In a different refinement model, these two sites were split to two symmetry equivalent positions with 50% occupancy each. The corresponding U_{eq} values decrease 3-4 fold, as seen from the CIFs provided as supporting information.

^c Occupancy of 0.855(3) Ca and 0.145(3) Ba.

^d Occupancy of 0.765(3) Ca and 0.235(3) Ba.

Table 3. Selected interatomic distances (Å) and angles (°) in Ba₇Ga₄P₉, Ba₇Ga₄As₉, Ba₇Al₄Sb₉, Ba₆CaAl₄Sb₉, and Ba₆CaGa₄Sb₉.

	Ba ₇ Al ₄ Sb ₉	Ba ₇ Ga ₄ P ₉	Ba ₇ Ga ₄ As ₉	Ba ₆ CaAl ₄ Sb ₉	Ba ₆ CaGa ₄ Sb ₉
Ba1–Pn1 (×2)	3.4816(4)	3.255(2)	3.3078(9)	3.5243(3)	3.5083(3)
Ba1–Pn2	3.5057(6)	3.237(3)	3.303(1)	3.5122(5)	3.5145(5)
Ba1–Pn1 (×2)	3.6626(5)	3.400(2)	3.4692(9)	3.6742(4)	3.6607(4)
Ba1–Pn2	3.8479(6)	3.591(3)	3.680(1)	3.7908(5)	3.7463(5)
Ba2–Pn2	3.4501(4)	3.186(2)	3.2644(8)	3.4399(3)	3.4455(3)
Ba2–Pn1	3.6402(5)	3.386(2)	3.4510(9)	3.5631(4)	3.5701(3)
Ba2–Pn2	3.6636(4)	3.346(2)	3.4420(8)	3.6521(3)	3.6431(3)
Ba2–Pn1	3.6674(5)	3.400(2)	3.4879(9)	3.6929(4)	3.6389(4)
Ba2–Pn4	3.6734(5)	3.335(5)	3.447(1)	3.6722(3)	3.6711(3)
Ba2–Pn3	3.7526(5)	3.418(5)	3.536(1)	3.7355(3)	3.7622(3)
Ba2–Pn5	3.7699(4)	3.503(1)	3.5898(7)	3.6977(2)	3.6766(3)
Ba3–Pn5	3.3007(8)	2.959(4)	3.084(1)	3.159(1)	3.196(1)
Ba3–Pn1 (×4)	3.4007(4)	3.108(2)	3.2222(7)	3.2757(4)	3.2844(3)
Ba3–Pn5	3.8670(8)	3.681(4)	3.717(1)	3.159(1)	3.866(1)
Tr1–Pn2	2.608(2)	2.345(3)	2.423(2)	2.615(1)	2.6198(6)
Tr1–Pn5	2.678(2)	2.376(2)	2.471(1)	2.694(1)	2.6932(6)
Tr1–Pn1 (×2)	2.720(1)	2.457(2)	2.5516(8)	2.6924(9)	2.7016(4)
Tr2–Pn1 (×2)	2.6709(9)	2.392(2)	2.4833(8)	2.6451(8)	2.6434(4)
Tr2–Pn3	2.720(2)	2.513(8)	2.576(2)	2.715(2)	2.7247(7)
Tr2–Pn4	2.725(2)	2.514(9)	2.570(2)	2.720(2)	2.7378(7)
Pn3–Pn4	3.303(1)	3.01(2)	3.13(1)	3.2843(8)	3.2700(8)
Ba1– Tr1	3.619(2)	3.416(1)	3.460(1)	3.688(2)	3.6618(6)
Ba2– Tr1	3.604(1)	3.357(1)	3.4320(8)	3.5426(9)	3.5067(4)
Ba3– Tr1 (×2)	3.379(2)	3.167(1)	3.227(1)	3.314(2)	3.2601(8)
Ba3– Tr2 (×2)	3.638(2)	3.399(2)	3.469(1)	3.583(2)	3.5466(6)

Figure1

Figure2

Figure3

The four new Zintl phases— $\text{Ba}_7\text{Al}_4\text{Sb}_9$, $\text{Ba}_7\text{Ga}_4\text{P}_9$, and $\text{Ba}_7\text{Ga}_4\text{As}_9$, and their quaternary variants $\text{Ba}_6\text{CaTr}_4\text{Sb}_9$ ($Tr = \text{Al, Ga}$)—crystallize in the $\text{Ba}_7\text{Ga}_4\text{Sb}_9$ structure type. The structures are based on $TrPn_4$ tetrahedra (a perspective of the crystal structure is shown, as viewed along the c axis)