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Synthesis and Characterization of Homoleptic Zintl Anions $[(Pn_7)M(Pn_7)]^{4-}$ ($M/Pn = Pb/As, Zn/Bi$)

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The formation and follow-up chemistry of P_7^{3-} has been intensely studied in the recent decades. In contrast, corresponding investigations of its heavier polycyclic polypnictide congeners Pn_7^{3-} ($Pn = As, Sb, Bi$), especially Bi_7^{3-} , have been done to a much lesser extent. In our report, we add to these rare studies, by reporting new coordination compounds with As_7^{3-} and Bi_7^{3-} , respectively. Addition of PbI_2 to a solution of K_3As_7 in ethane-1,2-diamine (en) afforded the heterometallic cluster anion $[(As_7)Pb(As_7)]^{4-}$ (with an 8% co-crystallization of $[PbAs_{15}]^{3-}$ on the same site), in compound $[K_{3.92}(\text{crypt-222})_4][(As_7)Pb-$

$(As_7)]_{0.92}[PbAs_{15}]_{0.08} \cdot 3en$ (1). A similar reaction of $[ZnPh_2]$ with a pyridine (py) solution of the ternary solid 'K₅Ga₂Bi₄', which was previously shown to release Ga and polybismuthide units *in situ* under certain reaction conditions, resulted in the formation of $[K(\text{crypt-222})_4][(Bi_7)Zn(Bi_7)] \cdot 2.5py$ (2), comprising the related heterometallic anion $[(Bi_7)Zn(Bi_7)]^{4-}$. The former represents the first Pb–As binary Zintl anions obtained via solution chemistry, and the latter adds one more piece to the remarkably rare coordination compounds reported for Bi_7^{3-} .

Introduction

The nortricyclane-type anion P_7^{3-} as well as its functionalized derivatives have been particularly well known as alternative phosphorous sources in coordination chemistry besides white phosphorous (P_4) itself.^[1–3] P_7^{3-} and its heavier As and Sb analogues can be synthesized by dissolving the corresponding Zintl phases K_3Pn_7 in polar solvents, while analogous synthesis procedures are unsuccessful for the heaviest homologue of this series, Bi_7^{3-} . Consequently, the latter was long believed to be non-existent. In 2015, this assumption was disproved, when the anion as its $[K(\text{crypt-222})]^+$ salt (crypt-222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained with the assistance of a Lewis-acidic transition metal complex and pyridine (py).^[4]

When interacting with d-/p-block metal precursors in solution, Pn_7^{3-} ($Pn = P, As$) anions tend to maintain their original topology and act as a) two-electron (2-e) donor (η^1 , Figure 1a), such as in the protonated $[M_2(HP_7)_2]^{2-}$ ($M = Ag, Au$; Figure 1d),^[5]

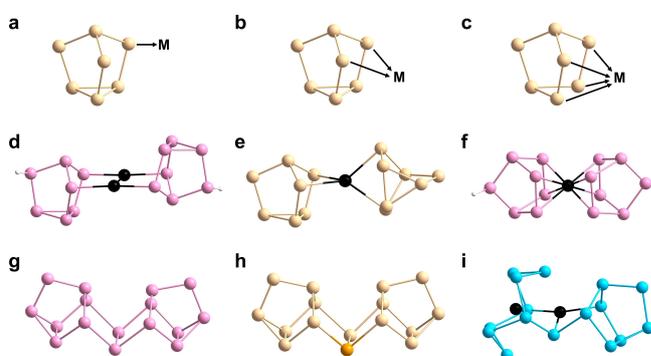


Figure 1. Top: Schematic representation of known coordination modes of Pn_7^{3-} ($Pn = P, As$): a) η^1 , b) η^2 , c) η^4 . Center: Examples for said coordination modes: d) $\eta^1/[M_2(HP_7)_2]^{2-}$ ($M = Ag, Au$), e) $\eta^2/[Zn(\eta^2-Pn_7)_2]^{3-}$ ($Pn = P, As$), f) $\eta^4/[Fe(\eta^4-HP_7)_2]^{2-}$. Bottom: Pnictogen-rich molecules based on $\{Pn_7\}$ units: g) P_{16}^{2-} and selected examples for Pn_7^{3-} cages connected via one or two heteroatoms: e) $[TtPn_{15}]^{3-}$ ($Tt/Pn = Sn/P, Sb/As, Pb/P$) or $[MAS_{15}]^{3-}$ ($M = Zn, Hg$), f) $[MM'As_{16}]^{4-}$ ($M = Nb, Ta; M' = Cu, Ag$). Color code: P (rose), P/As (tan), As (sky blue), Tt (orange), transition metal (black).

b) four-electron donor (η^2 , Figure 1b), like in $[Zn(\eta^2-Pn_7)_2]^{3-}$ ($Pn = P, As$; Figure 1e),^[6] or c) six-electron donor (η^4 , Figure 1c), as in $[Fe(\eta^4-HP_7)_2]^{2-}$ (Figure 1f),^[7] which can also be regarded as a mild activation of the Pn_7^{3-} cage. Two Pn_7^{3-} cages can also be bridged by one or two heteroatoms: a (formal) isoelectronic replacement of two bridging P atoms of the polyphosphide P_{16}^{2-} (Figure 1g)^[8] by a group 14 atom (Tt, charged -1) results in the species $[TtP_{15}]^{3-}$ ($Tt = Sn, Pb$; Figure 1h).^[9] There are also examples involving transition metal atoms connected to the Pn_7^{3-} units, like $[MAS_{15}]^{3-}$ ($M = Zn, Hg$).^[10,11] A series of structurally related anions have been observed in $[MM'As_{16}]^{4-}$ ($M = Nb, Ta; M' = Cu, Ag$; Figure 1i).^[12]

In spite of the dominance of retained Pn_7^{3-} cages in reaction products using these units, there are also some reports of their fragmentation upon corresponding treatment, such as $[Co(\eta^5-P_5)\{\eta^2-P_2H(\text{Mes})\}]^{2-}$,^[13] $[As@Ni_{12}@As_{20}]^{3-}$,^[14] or $[Co(\eta^3-As_3)\{\eta^4-$

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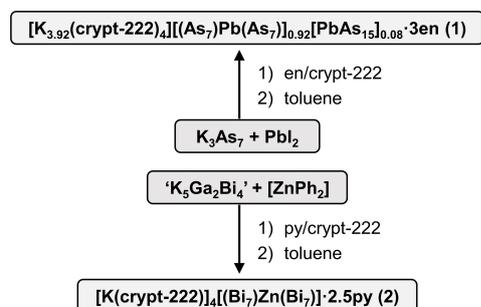
$\text{As}_4(\text{Mes})_2\text{]}^{2-}$.^[15] Additionally, the existence of (protonated) binary nortricyclane-type anions was reported, $(\text{SiPn}_6\text{H}_2)^{2-}$ (Pn = P, As).^[16] In which one of the Pn atoms was replaced with Tt⁻, together indicating that even these two cages are labile in some regard.

In contrast, as the Pn–Pn bond dissociation energies decrease notably from P to Bi, the maintenance of the Pn_7^{3-} cage becomes increasingly difficult with the heavier pnictogens being involved.^[1,17] This applies to the Bi_7^{3-} cage, in particular. On the one hand, this species requires the presence of a certain amount of (Lewis-acidic) d-block metal atoms to form. On the other hand, facile cluster rearrangement is observed for Bi-based Zintl anions with d-/f-block metal compounds, giving rise to heterometallic species, such as $[\mu^2\eta^3\text{-Bi}_3\text{W}(\text{CO})_3\text{W}(\text{CO})_4]^{3-}$,^[17b] $[\text{Zn}_9\text{Bi}_{11}]^{5-}$,^[18] $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$,^[19] $[\{\text{Ru}(\text{cod})\}_4\text{Bi}_{18}]^{4-}$,^[20] $[\text{U}@\text{Bi}_{12}]^{3-}$,^[21a] and $[\text{Th}@\text{Bi}_{12}]^{4-}$.^[21b] So far, the only way of using Bi_7^{3-} as a coordinating ligand has been its in-situ generation in the presence of the corresponding d-block metal ions. This was exemplified by the synthesis of the first (and so far only) homoleptic complex with the Bi_7^{3-} molecule, $[(\text{Bi}_7)\text{Cd}(\text{Bi}_7)]^{4-}$, which was synthesized through oxidative degradation of the binary anion $(\text{TlBi}_3)^{2-}$.^[22] Another example is the mono-adduct $[\text{Bi}_7\text{M}_3(\text{CO})_3]^{2-}$ (M = Co, Rh), which resulted from redox reactions of K_3Bi_4 with $[\text{CpCo}(\text{CO})_2]/[\text{Rh}(\text{CO})_2(\text{acac})]$ (acac = acetylacetonate).^[23]

In this work, we report on three new family members by reporting the anions $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$, $[\text{PbAs}_{15}]^{3-}$, and $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$, which were isolated as their $[\text{K}(\text{crypt-222})]^+$ salts $[\text{K}_{3.92}(\text{crypt-222})_4][(\text{As}_7)\text{Pb}(\text{As}_7)]_{0.92}[\text{PbAs}_{15}]_{0.08}\cdot 3\text{en}$ (1) and $[\text{K}(\text{crypt-222})]_4[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]\cdot 2.5\text{py}$ (2). The syntheses are illustrated in Scheme 1 and described in detail below.

Results and Discussion

The reaction of K_3As_7 ^[24a] with PbI_2 in ethane-1,2-diamine (en) and subsequent layering with toluene (tol) resulted in the co-crystallization of the heterometallic cluster anions $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$ and $[\text{PbAs}_{15}]^{3-}$, sharing the same anion site in a 92:8 ratio in compound $[\text{K}_{3.92}(\text{crypt-222})_4][(\text{As}_7)\text{Pb}(\text{As}_7)]_{0.92}[\text{PbAs}_{15}]_{0.08}\cdot 3\text{en}$ (1). As outlined above, the other reaction system involving bismuth required an in-situ generation of the nortricyclane-type cage. The ternary solid of the nominal



Scheme 1. Illustration of the syntheses of compounds 1 and 2. Side products are not given; they are detailed in the text.

composition ' $\text{K}_5\text{Ga}_2\text{Bi}_4$ '^[24b] when reacted with $[\text{ZnPh}_2]$ in py, yielded $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ in the compound $[\text{K}(\text{crypt-222})]_4[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]\cdot 2.5\text{py}$ (2) after layering by tol. The former two represent the first crystalline compounds comprising Pb/As binary Zintl anions that were obtained via wet chemistry. The latter provides one more piece to the remarkably small collection of coordination compounds of the Bi_7^{3-} anion.

Compound 1 crystallized as red crystals alongside colorless $[\text{K}(\text{crypt-222})]$. A compound with the nominal composition " $[\text{K}(\text{crypt-222})]_3[\text{PbAs}_{15}]$ " was reported to form in reactions between K_3As_7 and PbI_2 in the presence of crypt-222/en, yet, while a series of signals according to the composition $\{\text{PbAs}_{15}\}$ were detected by means of ESI-MS in DMF, but the obtained products was unsuitable for single-crystal X-ray diffraction.^[9] According to our single-crystal X-ray diffraction (SCXRD) study of compound 1 (see Figures S1 and S3, Tables S1 and S2), the refinement indeed requires some extra attention, as two anions share the same crystallographic site (Figure 2): one anion is well defined and can be ascribed to $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$ with 92% occupancy (Figure 2a). However, this anion shares the same crystal site with a related $[\text{PbAs}_{15}]^{3-}$ anion at 8% occupancy (Figure 2b). This is in agreement with the observation of a slight under-occupation of one of the K^+ sites (K1), while the cryptand molecule remains fully occupied. The two anions differ by the central part that bridges two As_7^{3-} units: In the majority species, $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$, a single, three-connected Pb^{2+} ion connects two As_7^{3-} cages, while in $[\text{PbAs}_{15}]^{3-}$, the two units are connected by

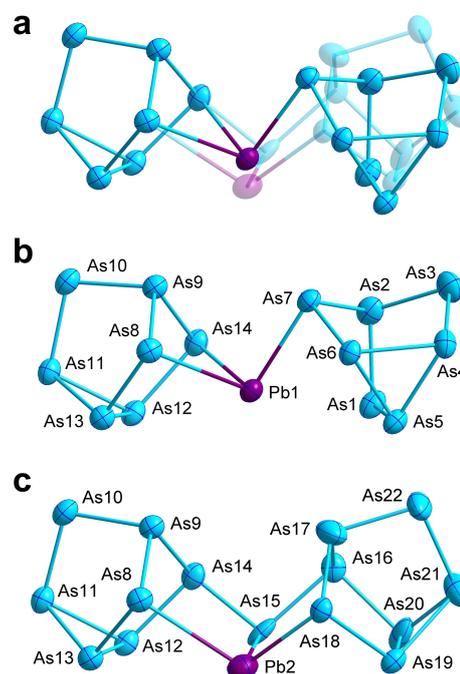


Figure 2. Molecular structures of the anions in compound 1. a) Both molecules overlaid, b) molecular structure of $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$ (92% occupancy), c) molecular structure of $[\text{PbAs}_{15}]^{3-}$ (8% occupancy). Thermal displacement ellipsoids are drawn at the 50% probability level. Selected interatomic distances [Å] and angles [°]: Pb1–As7 2.8142(12), Pb1–As8 3.0636(10), Pb1–As14 2.8600(10), Pb2–As8 3.149(5), Pb2–As15 2.726(14), Pb2–As18 2.741(13), As14–As15 2.242(11), As15–As16 2.448(18); As7–Pb1–As8 93.85(3), As7–Pb1–As14 94.53(3), As8–Pb2–As18 103.3(3), As8–Pb2–As15 97.3(3), As18–Pb2–As15 96.6(4), As14–As15–As16 99.0(5).

a Pb–As dumbbell, which at the same time serves to link the two seven-vertex units into a larger As_{15}^{5-} anion that coordinates the Pb^{2+} ion. The molecular structure of $[\text{As}_7\text{PbAs}_7]^{4-}$ exhibits three normal Pb–As distances [Pb1–As7 2.8142(13) Å, Pb1–As14 2.8600(10)] and one slightly elongated contact [Pb1–As8 3.0636(10) Å], as a consequence of an η^2 -type coordination of the central Pb atoms by one and an η^1 -type coordination by the other As_7^{3-} moiety. We note here that the $\eta^2:\eta^1$ -type coordination mode of Pn_7^{3-} is rather unusual. To date this mode has only been observed in the molecular architecture of $[(\text{As}_7)\text{Sn}(\text{As}_7)]^{4-}$, which is isostructural to that of $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$.^[1,25] The second anion, $[\text{PbAs}_{15}]^{3-}$, shares one of the $[\text{As}_7]$ unit (As8–As14) with the anion $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$, while the second seven-atom cage exhibits an inverted orientation. Overall, the built-up of $[\text{PbAs}_{15}]^{3-}$ is isostructural with that of the reported $[\text{TtPn}_{15}]^{3-}$ species (M/Pn=Sn/P, Sn/As, Pb/P) and $[\text{MAs}_{15}]^{3-}$ (M=Zn, Hg).^[9–11] Again, the Pb atom is three-connected, with Pb2–As distances of 2.726(14)–3.149(5) Å. The range is a bit wider than that observed for $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$, but the average value of the Pb–As bond lengths in $[\text{PbAs}_{15}]^{3-}$ (2.818 Å) and $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$ (2.912 Å) agree well. They are a longer on average than reported for $[\text{As}_3\text{M}(\text{As}_3\text{Pb}_3)]^{3-}$ (2.7836 Å for M=Nb; 2.7826 Å for M=Ta).^[26] Both the bond lengths and the coordination environments of the atoms suggest that all bonds within the two anions in **1** are (polar) covalent in nature, with a slight polarization of the electron density of the Pb–As bonds towards the more electronegative As atom (cf. EN(Pb): 1.55 and EN(As): 2.20 according to the Allred-Rochow scale). This allows to alternatively understand the cluster anions in terms of the *pseudo*-element concept, with all three connected As atoms being formally uncharged, and the two-connected As atoms as well as the three-connected Pb atoms being formally charged -1 , which leads to the very same net charge of the two anions.

As mentioned above, the interaction of solutions of Pn_7^{3-} (Pn=P, As) with d-block or p-block metal compounds typically result in compounds in which the polypnictogen units maintain their structures and nuclearities (C_{3v}) or breaking one of the basal Pn–Pn single bond, yielding a norbornadiene-like C_{2v} geometry. While the activation route of the heavier Sb_7^{3-} anion is usually unpredictable, the nortricyclane-type $\{\text{Sb}_7\}$ unit can still be observed in $[\text{Sb}_7\text{M}(\text{CO})_3]^{3-}$ (M=Cr, Mo, W),^[27,28] $[(\text{Sb}_7)\text{Zn}(\text{Sb}_7)]^{4-}$,^[11] $[\text{Au}_2\text{Sb}_{16}]^{4-}$,^[29] and $[\text{Ge}_4\text{Sb}_{14}]^{4-}$.^[30] In addition, a binary anion of the composition $[\text{Zn}_2\text{Sb}_{12}]^{4-}$ was reported that can be viewed as a combination of two heteroatomic nortricyclane-like $\{\text{ZnSb}_6\}$ units.^[31] However, whereas most of the $\{\text{Pn}_7\}$ units with Pn being P, As, or Sb were introduced into the heteroatomic clusters by reactions of the corresponding Pn_7^{3-} ,^[32] the few heteroatomic species containing the homologous $\{\text{Bi}_7\}$ moiety could only be accessed in an indirect way. For each of the clusters $[(\text{Bi}_7)\text{Cd}(\text{Bi}_7)]^{4-}$, $[\text{Bi}_7\text{M}_3(\text{CO})_3]^{2-}$ (M=Co, Rh), $(\text{Ge}_4\text{Bi}_{14})^{4-}$, and $(\text{Ga}_2\text{Bi}_{16})^{4-}$ the synthesis included the extraction of ternary solids of the nominal compositions 'K₂GeBi' or 'K₅Ga₂Bi₄' or the reaction of a salt of a binary Zintl anion, $[\text{K}(\text{crypt-222})]_2(\text{TlBi}_3) \cdot \text{en}$ in the presence of Lewis-acidic d-block or f-block metal complexes in en/crypt-222 or py/crypt-222.^[20,23,24,33] According to other reports on the formation and crystallization of the

bismuth-rich cluster anions, the product spectrum can be significantly influenced by the choice of the solvents used as reaction medium or layering solvent.^[34] For example, the reaction between $(\text{Pb}_2\text{Bi}_2)^{2-}$ and $[\text{AuMePPh}_3]$ in en/tol, py/tol, or py/THF afforded anions $[\text{Au}\{\eta^2\text{-}(\text{Pb}_2\text{Bi}_2)\}_2]^{3-}$, $\{[\text{AuPb}_5\text{Bi}_3]_2\}^{4-}$, or $(\text{PbBi}_3)^-$, respectively.^[3,35] In this study, we therefore aimed at further variations of these reaction details in order to get access to new compounds featuring the rare $\{\text{Bi}_7\}$ unit. We chose to revisit the reaction between 'K₅Ga₂Bi₄' and $[\text{ZnPh}_2]$, which previously yielded $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$ when applying en/tol/crypt-222 (Figure 3, top left).^[19] By using the combination py/tol/crypt-222, we were able to isolate compound **2** (see Figure S2, Tables S1, S3, and S4), which crystallizes as black block-type crystals. Notably, the same reaction in en/THF/crypt-222 leads to the formation of the previously reported cluster $[\text{Zn}_9\text{Bi}_{11}]^{5-}$ (Figure 3, top right).^[18] These findings indicate the subtle, yet still poorly understood, impact of solvent on structure selection and stability in this reaction space. The $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ anion in **2** (Figure 3, bottom) possesses the same topology as the homologous $[(\text{Bi}_7)\text{Cd}(\text{Bi}_7)]^{4-}$ anion,^[23] but the structures differ in detail. In **2**, the two $\{\text{Bi}_7\}$ cages are rotated against each other around the Zn^{2+} ion by 85.03(4)°, which results in a closer approximation of a tetrahedral coordination environment than in $[(\text{Bi}_7)\text{Cd}(\text{Bi}_7)]^{4-}$ (79.43(2)°). The Bi–Bi and Zn–Bi bond lengths (2.9087(9)–3.0456(10) and 2.802(2)–2.840(2) Å, respectively) in

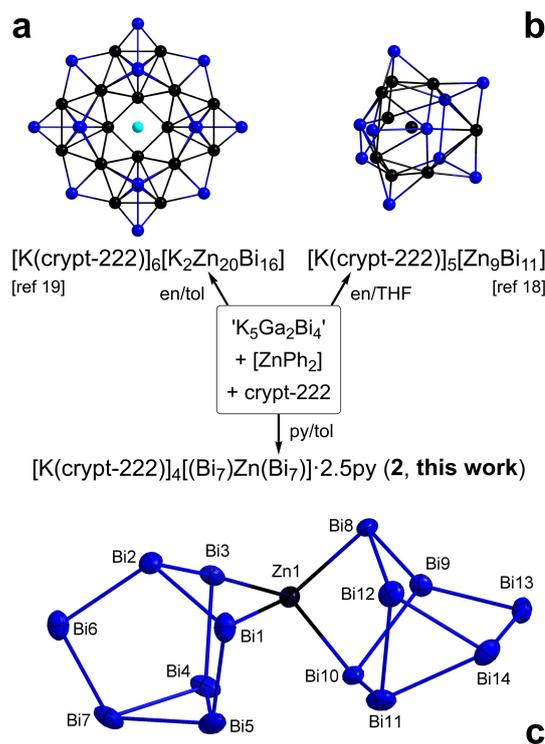


Figure 3. Summary of reported and new reactions of 'K₅Ga₂Bi₄' with $[\text{ZnPh}_2]$ using different reaction and layering solvents to afford different cluster anions. a) Formation of $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$,^[19] b) formation of $[\text{Zn}_9\text{Bi}_{11}]^{5-}$,^[18] c) formation of $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ (in **2**). Color code: Bi (blue), Zn (black), K (light turquoise). Selected interatomic distances [Å] and angles of the anion in **2** [°]: Bi–Bi 2.9086(9)–3.0840(16), Zn–Bi 2.786(7)–2.840(2); Bi2–Zn1–Bi3 98.06(6), Bi3–Zn1–Bi8 123.67(7), Bi3–Zn1–Bi10 108.89(6), Bi1–Zn1–Bi8 115.16, Bi1–Zn1–Bi10 113.66(6), Bi8–Zn1–Bi10 98.02(5).

$[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ are similar to those observed in $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$ and $[\text{Zn}_9\text{Bi}_{11}]^{5-}$.^[18,19] Given the essentially identical electronegativities of Zn and Bi atoms (EN(Zn): 1.66 and EN(Bi): 1.67 according to the Allred-Rochow scale), the bonds within the anion in **2** can again be described as being predominantly covalent – naturally more than the related Cd/Bi complex, which may explain the observed structural differences.

Notably, despite the same elemental ratio of the anions in **1** (majority component) and **2**, the structures clearly differ by the different connectivity of the central atoms (Pb: 3, Zn: 4).

For Bi-rich cluster compounds, spectroscopic monitoring of processes in solution is essentially impossible owing to missing NMR handles. Although time-dependent electrospray-ionization (ESI) mass spectrometry has been used to get some insight, the real-time detection is still seriously hindered by the extremely fast reaction and the large number of signals.^[34,36] In this regard, a comparison of related structures (also from different reaction set-ups) can help to get an idea of reaction steps. In this case, the coordination activity of the $\{\text{Bi}_7\}$ unit in $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ (Figure 4, left) can be topologically connected to a reported compound, $[(\text{Bi}_6)\text{Zn}_3(\text{TlBi}_5)]^{4-}$,^[23] which contains a partially formed $\{\text{Bi}_7\}$ cage (Figure 4, right). From this reaction, a cluster like the one in compound **2** was not observed, and in the case of compound **2**, we do not observe a corresponding Zn/Bi/Ga cluster; however, one might assume that in the absence of Tl, hence in the presence of the much more weakly bonded Ga–Bi system, an intermediate like the one reported for Zn/Tl/Bi might have formed and underwent a rapid cluster rearrangement to the more favorable structure of the anion in **2**. It is known that, owing to the mismatch of atomic sizes, Ga atoms are much more readily released from binary Zintl anions than other atoms from the homologous In/Bi or Tl/Bi systems or from related elemental combinations like Sn/Bi or Pb/Bi, which tend to form ternary clusters together with d-block or f-block metal compounds.^[33,37–41] In this regard, ‘ $\text{K}_5\text{Ga}_2\text{Bi}_4$ ’ again showed to be a suitable reactant for the generation of Bi-rich molecular assemblies in general, and the construction of $\{\text{Bi}_7\}$ cages in particular.

It is worth noting that, compared to the reported synthesis and crystallization of $[(\text{Bi}_7)\text{Cd}(\text{Bi}_7)]^{4-}$,^[23] the Zn^{2+} complex is actually less favored. This was shown by calculating the reaction energies of the following exchange reactions [Eq. (1)]:

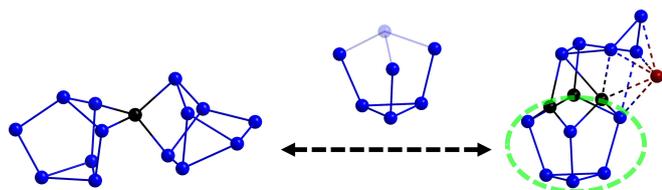
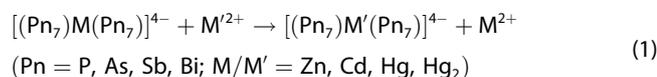


Figure 4. Illustration of the topological relationship between $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ in **2** (left) and $[(\text{Bi}_6)\text{Zn}_3(\text{TlBi}_5)]^{4-}$ (right) with the Bi_7^{3-} anion (center). Color code: Bi (blue), Zn (black), Tl (dark red).

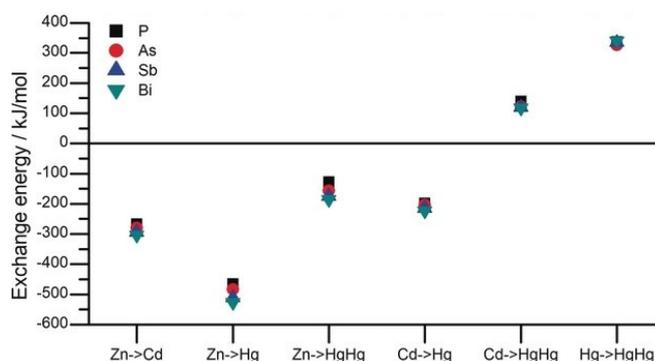


Figure 5. Reaction energies (given in kJ/mol) calculated for the exchange reactions indicated in Equation (1). Pn = P, As, Sb, Bi; M/M' = Zn, Cd, Hg, Hg₂. The involved atom types Pn and M/M' are denoted by colored symbols and at the horizontal axes. Reproduced with permission from Wiley-VCH.

As reflected by the reported reaction energies (Figure 5),^[23] the $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ complex is clearly disadvantaged as compared to a replacement of Zn^{2+} with one of the softer central metal ions or ion dumbbells: 303.2 kJ/mol (Cd→Zn), 526.4 kJ/mol (Hg→Zn) and 185.3 kJ/mol (Hg₂→Zn). Note that the relatively lower stability of the anion in **2** as compared to the homologous species does not mean that its absolute stability is not sufficient for its synthesis; it just suggests that its preparation and isolation may be more challenging, which underlines the importance of creating suitable synthesis pathways for this compound, as achieved in this work.

Conclusions

We reported the synthesis and the characterization of two homoleptic Zintl anions $[(\text{Pn}_7)\text{M}(\text{Pn}_7)]^{4-}$ (M/Pn = Pb/As, Zn/Bi) that are related by their composition and molecular structures, but were accessed by different synthesis pathways as needed for the specific elemental combinations. The Pb/As-based anion co-crystallizes with small amounts of $[\text{PbAs}_{15}]^{3-}$ on the same crystallographic site. $[(\text{As}_7)\text{Pb}(\text{As}_7)]^{4-}$ and $[\text{PbAs}_{15}]^{3-}$ represent the first crystalline compounds comprising molecular Pb/As units. Despite an energetically disfavored situation as compared to heavier homologues, we achieved the synthesis and isolation of $[(\text{Bi}_7)\text{Zn}(\text{Bi}_7)]^{4-}$ by varying the reaction/layering solvent as compared to previous studies with the starting material ‘ $\text{K}_5\text{Ga}_2\text{Bi}_4$ ’ and $[\text{ZnPh}_2]$, and by using the ternary starting material instead of $(\text{TlBi}_3)^{2-}$ for the reaction. We therefore not only add missing pieces to the series of homoleptic complexes of the Pn_7^{3-} (Pn = P, As, Sb, Bi) Zintl anions, but also provide some more knowledge of preconditions for and possible steps of the still largely unexplored processes during cluster growth.

Experimental Section

General synthesis methods: All manipulations and reactions were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques. All solvents were dried and freshly distilled prior to use; crypt-222 (Kryptofix®, Merck) was dried in vacuo for at

least 18 hours. K_3As_7 ^[24a] and $'K_5Ga_2Bi_4$ ^[24b] were prepared according to literature. PbI_2 and $ZnPh_2$ were commercially available from Aldrich. Samples were shielded from ambient light throughout cluster syntheses.

Synthesis of $[K_{3.92}(crypt-222)_4][(As_7)Pb(As_7)]_{0.92}[PbAs_{15}]_{0.08} \cdot 3en$ (1): 80 mg (0.125 mmol) of K_3As_7 , 141 mg (0.374 mmol) of crypt-222 and 27 mg (0.06 mmol) of PbI_2 were combined in a Schlenk tube and dissolved in ethane-1,2-diamine (en, 3 mL). The reaction mixture was allowed to stir for 3 hours. The resulting dark red solution was filtered through a standard glass frit, carefully layered with toluene (3 mL), and stored for crystallization at 5 °C. After 14 days, crystals of compound 1 formed at the wall of the Schlenk tube in approx. 15% yield.

Synthesis of $[K(crypt-222)]_4[(Bi_7)Zn(Bi_7)] \cdot 2.5py$ (2): 80 mg (0.07 mmol) of the nominal composition $'K_5Ga_2Bi_4$, 128 mg (0.342 mmol) of crypt-222 and 7 mg (0.03 mmol) of $ZnPh_2$ were combined in a Schlenk tube and dissolved in pyridine (en, 3 mL). The reaction mixture was allowed to stir for 3 hours. The resulting dark red solution was filtered through a standard glass frit, carefully layered with toluene (3 mL), and stored for crystallization at 5 °C. After 14 days, crystals of compound 2 formed at the wall of the Schlenk tube in approx. 10% yield.

X-ray diffraction analyses: Deposition Numbers 2287434 (for 1) and 2287436 (for 2) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. Details of the structure solution and refinement as well as additional structural figures are provided in the Supporting Information.^[42–44] All figures were created using Diamond 4.0.^[45]

Supporting Information

Further details of single-crystal X-ray diffraction analyses,²⁰⁷Pb-NMR spectroscopy, and micro-X-ray fluorescence spectroscopy (μ -XFS).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Bismuth · Lead · Zinc · Structure elucidation · Zintl clusters

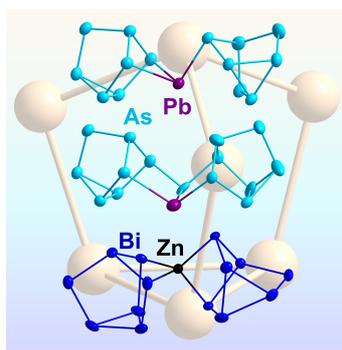
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RESEARCH ARTICLE

Variations of the coordination of nor-tricyclane-type 7-atom polynictides to metal ions were achieved upon reactions of either K_3As_7 with PbI_2 in ethane-1,2-diamine and subsequent layering with toluene or by reacting an extraction solution of ' $K_5Ga_2Bi_4$ ' in pyridine with $[ZnPh_2]$ prior to layering with toluene. The two procedures were specific for the respective elemental combinations, and they afforded the second compound exhibiting the rare Bi_7^{3-} ion in the coordination sphere of transition metal ions.



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Synthesis and Characterization of Homoleptic Zintl Anions $[(Pn_7)M-(Pn_7)]^{4-}$ ($M/Pn = Pb/As, Zn/Bi$)



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