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Synthesis and Characterization of Homoleptic Zintl Anions \([(\text{Pn}_7)\text{M(\text{Pn}_7)})^4^-\] (\text{M/Pn} = \text{Pb/As, Zn/Bi})

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The formation and follow-up chemistry of P$_7^{2-}$ has been intensively studied in the recent decades. In contrast, corresponding investigations of its heavier polycyclic polyphosphide congeners Pn$_7^{2-}$ (Pn = As, Sb, Bi), especially Bi$_7^{2-}$, have been done to a much lesser extent. In our report, we add to these rare studies, by reporting new coordination compounds with As$_7^{2-}$ and Bi$_7^{2-}$, respectively. Addition of Pb$_2$ to a solution of K$_3$As$_4$ in ethane-1,2-diamine (en) afforded the heterometallic cluster anion [(As$_5$)Pb(As$_7$)]$^{4-}$ (with an 8% co-crystallization of [PbAs$_3$]$_2$ en) (1). A similar reaction of [ZnPh$_3$]$_2$ with a pyridine (py) solution of the ternary solid ‘K$_3$Ga$_2$Bi$_4$’, which was previously shown to release Ga and polybismuthide units in situ under certain reaction conditions, resulted in the formation of [K(crypt-222)]$_2$[(Bi$_3$)Zn(Bi$_3$)] 2.5py (2), comprising the related heterometallic anion [Bi$_3$(Zn(Bi$_3$))]$^{4-}$. 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$_7^{2-}$.

Introduction

The nortricyclic-type anion P$_7^{2-}$ as well as its functionalized derivatives have been particularly well known as alternative phosphorous sources in coordination chemistry besides white phosphorous (P$_4$) itself[4–7] P$_7^{2-}$ and its heavier As and Sb analogues can be synthesized by dissolving the corresponding Zintl phases K$_3$Pn$_4$ in polar solvents, while analogous synthesis procedures are unsuccessful for the heaviest homologue of this series, Bi$_7^{2-}$. Consequently, the latter was long believed to be non-existent. In 2015, this assumption was disproven, when the anion as its [K(crypt-222)]$^+$ salt (crypt-222 = 4,7,13,16,21,24-hexaaza-1,10-diazabicyclo[8.8.8]hexacosane) was obtained with the assistance of a Lewis-acidic transition metal complex and pyridine (py).[8]

When interacting with d-/p-block metal precursors in solution, Pn$_7^{2-}$ (Pn = P, As) anions tend to maintain their original topology and act as a) two-electron (2-e) donor ($\eta^1$, Figure 1a), such as in the protonated [M$_2$(HP$_2$)$_2$]$^{4+}$ (M = Ag, Au; Figure 1d),[9] b) four-electron donor ($\eta^2$, Figure 1b), like in [Zn($\eta^2$-Pn)$_2$]$^{3-}$ (Pn = P, As; Figure 1e),[10] or c) six-electron donor ($\eta^3$, Figure 1c), as in [Fe($\eta^3$-HP$_2$)$_2$]$^{4+}$ (Figure 1f),[11] which can also be regarded as a mild activation of the Pn$_7^{2-}$ cage. Two Pn$_7^{2-}$ cages can also be bridged by one or two heteroatoms: e) [TP$_n$P$_2$]$^{4-}$ (TP$_n$ = Sn/P, Sn/As, Pb/Pb) or [MAs$_3$]$^{4+}$ (M = Zn, Hg), f) [MM'As$_3$]$^{4+}$ (M = Nb, Ta; M' = Cu, Ag). Color code: P (rose), P/As (tan), As (sky blue), T (orange), transition metal (black).

Figure 1. Top: Schematic representation of known coordination modes of Pn$_7^{2-}$ (Pn = P, As): a) $\eta^1$/[M($\eta^1$(HP$_2$)$_2$)]$^{4+}$ (M = Ag, Au), e) $\eta^2$/[Zn($\eta^2$-Pn)$_2$]$^{3-}$ (Pn = P, As), f) $\eta^3$/[Fe($\eta^3$-HP$_2$)$_2$]$^{4+}$. Bottom: Phosphorus-rich molecules based on (Pn$_3$) units: g) P$_3$As$_4$, and selected examples for Pn$_7^{2-}$ cages connected via one or two heteroatoms: e) [TP$_n$P$_2$]$^{4-}$ (TP$_n$ = Sn/P, Sn/As, Pb/Pb) or [MAs$_3$]$^{4+}$ (M = Zn, Hg), f) [MM'As$_3$]$^{4+}$ (M = Nb, Ta; M' = Cu, Ag). Color code: P (rose), P/As (tan), As (sky blue), T (orange), transition metal (black).
As$_x$(Mes)$_y$]$^{2-}$.

Additionally, the existence of (protonated) binary nortricyclane-type anions was reported, (SiPh$_3$)$_2$$^2_2$ (Pn = P, As), 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$_3^{2-}$ cage becomes increasingly difficult with the heavier pnictogens being involved.$^{[5,17]}$ This applies to the Bi$_3^{2-}$ cage, in particular. On the one hand, this species requires the presence of a certain amount of Lewis-acidic $^{[16]}$-$^{[18]}$ to heterometallic species, such as $[\text{Ru(cod)}]_2$Bi$_3^{2-}$, $[\text{U@Bi}_3^{2-}]$, $[\text{Zn@Bi}_3^{2-}]$, and $[\text{Th@Bi}_3^{2-}]$. So far, the only way of using Bi$_3^{2-}$ 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) coordination compounds of the Bi$_3^{2-}$ molecule, $[(\text{Bi}_3^{2-})\text{Cd}^{2+}]^{3-}$, which was synthesized through oxidative degradation of the binary anion (TBI)$_3^{2-}$.$^{[20]}$ Another example is the mono-adduct $[\text{Bi}_3\text{M}_3^{2+}(\text{CO})_3]^{2-}$ ($\text{M} = \text{Co}, \text{Rh}$), which resulted from redox reactions of $\text{K}_3\text{Bi}_4$ with $[\text{CpCo(CO)}_3]_2[\text{Rh(CO)}_2(\text{acac})]$ (acac = acetylacetonate).$^{[23]}$

In the work, we report on three new family members by reporting the anions $[(\text{As}_3\text{Pb})\text{As}_3]^{3+}$, $[\text{PbAs}_5]^{3+}$, and $[(\text{Bi}_3\text{Zn})\text{Bi}_4]^{4-}$, which were isolated as their $\text{K}[(\text{crypt}-222)]$ salts $\text{K}_3[(\text{crypt}-222)]_2[(\text{As}_3\text{Pb})\text{As}_3]_{12.0(0)3}$en (1) and $\text{K}[(\text{crypt}-222)]_2[(\text{Bi}_3\text{Zn})\text{Bi}_4]_{2.5}$Spy (2). The syntheses are illustrated in Scheme 1 and described in detail below.

**Results and Discussion**

The reaction of $\text{K}_3\text{As}_5$ 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 $[(\text{As}_3\text{Pb})\text{As}_3]^{2+}$ and $[\text{PbAs}_5]^{3+}$, sharing the same anion site in a 9:2 ratio in compound $\text{K}_3[(\text{crypt}-222)]_2[(\text{As}_3\text{Pb})\text{As}_3]_{12.0(0)3}$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 composition $'\text{K}_4\text{Ga}_4\text{Bi}_4'_{2+}\text{K}_3\text{Ga}_4\text{Bi}_4'_{2+}$ when reacted with $[\text{ZnPh}_3]^{2+}$ py, yielded $[(\text{Bi}_3\text{Zn})\text{Bi}_4]^{2+}$ in the compound $\text{K}[(\text{crypt}-222)]_2[(\text{Bi}_3\text{Zn})\text{Bi}_4]_{2.5}$Spy (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$_3^{2-}$ anion.

**Compound 1 crystallized as red crystals alongside colorless $\text{K}[(\text{crypt}-222)]$.** A compound with the nominal composition $'\text{K}[(\text{crypt}-222)]_2[\text{PbAs}_5]^{3+}'$ was reported to form in reactions between $\text{K}_3\text{As}_5$ and PbI$_2$ in the presence of crypt-222/en, yet, while a series of signals according to the composition $[\text{PbAs}_5]^{3+}$ 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 $[\text{As}_3\text{PbAs}_3]^{3+}$ with 92% occupancy (Figure 2a). However, this anion shares the same crystal site with a related $[\text{PbAs}_5]^{3+}$ 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$_3^{2-}$ units: In the majority species, $[\text{As}_3\text{PbAs}_3]^{3+}$, a single, three-connected Pb$_2^{2+}$ ion connects two As$_3^{2-}$ cages, while in $[\text{PbAs}_5]^{3+}$, the two units are connected by

\[
\text{K}_3[(\text{crypt}-222)]_2[(\text{As}_3\text{Pb})\text{As}_3]_{12.0(0)3}\text{en (1)}
\]

\[
\text{K}_3[(\text{crypt}-222)]_2[(\text{Bi}_3\text{Zn})\text{Bi}_4]_{2.5}\text{Spy (2)}
\]

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

$\text{As} = \text{P}, \text{As} = \text{Pb}, \text{As} = \text{Bi}$

$\text{K}_3[(\text{crypt}-222)]_2[(\text{As}_3\text{Pb})\text{As}_3]_{12.0(0)3}\text{en (1)}$

$\text{K}_3[(\text{crypt}-222)]_2[(\text{Bi}_3\text{Zn})\text{Bi}_4]_{2.5}\text{Spy (2)}$

$\text{K}_3[(\text{crypt}-222)]_2[(\text{As}_3\text{Pb})\text{As}_3]_{12.0(0)3}\text{en (1)}$

$\text{K}_3[(\text{crypt}-222)]_2[(\text{Bi}_3\text{Zn})\text{Bi}_4]_{2.5}\text{Spy (2)}$

Figure 2. Molecular structures of the anions in compound 1. a) Both molecules overlaid, b) molecular structure of $[(\text{As}_3\text{Pb})\text{As}_3]^{2+}$ (92% occupancy), c) molecular structure of $[\text{PbAs}_5]^{3+}$ (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(3), 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$_7^{–}$ anion that coordinates the Pb$^{2+}$ ion. The molecular structure of [As$_5$PbAs$_5$]$^{–}$ exhibits three normal Pb–As distances (Pb1–As7 2.8142(13) Å, Pb1–As14 2.8600(10) Å) and one slightly elongated contact (Pb1–As8 3.0636(10) Å), as a consequence of an η$^{3}$-type coordination of the central Pb atom by one and an η$^{1}$-type coordination by the other As$_3^{–}$ moiety. We note here that the η$^{3}$-η$^{1}$-type coordination mode of Pn$_7^{–}$ is rather unusual. To date this mode has only been observed in the molecular architecture of [(As$_5$)Sn(As$_5$)]$^{3–}$, which is isosctructural to that of [(As$_5$)Pb-(As$_5$)]$^{3–}$.[11,12] The second anion, [PbAs$_4$]$^{3–}$, shares one of the (As$_5$) unit (As8–As14) with the anion [(As$_5$)Pb(As$_5$)]$^{3–}$, while the second seven-atom cage exhibits an inverted orientation. Overall, the built-up of [PbAs$_4$]$^{3–}$ is isostructural with that of the reported [TpPn$_3$]$^{3–}$ species (M/Pn = Sn/P, Sn/As, Pb/P) and [MAs$_3$]$^{3–}$ (M = Zn, Hg).[9,10] Again, the Pb atom is three-connected, with Pb2–As distances of 2.726(4)–3.149(5) Å. The range is a bit wider than that observed for [As$_5$]Pb(As$_5$)]$^{3–}$, but the average value of the Pb–As bond lengths in [PbAs$_4$]$^{3–}$ (2.818 Å) and [(As$_5$)Pb(As$_5$)]$^{3–}$ (2.912 Å) agree well. They are a longer on average than reported for [As$_5$]M(As$_5$)Pb]$^{3–}$ (2.783 Å for M = Nb; 2.7825 Å for M = Ta).[20] 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 polymeric units maintain their structures and nuclearities (C$_m$) or breaking one of the basal Pn–Pn single bond, yielding a norbornadiene-like C$_n$ geometry. While the activation route of the heavier Sb$_7^{3–}$ anion is usually unpredictable, the nortricyclane-type (Sb$_7$) unit can still be observed in [Sb$_5$(Me$_2$CO)$_3$]$^{3–}$ (M = Cr, Mo, W),[22–26] [(Sb$_5$)Zn$_{16}$]$_{16}^{3–}$,[11] [Au$_4$Sb$_6$]$^{3+}$,[29] and [Ge$_2$Sb$_6$]$^{3–}$.[30] In addition, an binary anion of the composition [Zn$_n$Sb$_m$]$^{3–}$ was reported that can be viewed as a combination of two heteroatomic nortricyclane-like (ZnSb)$_n$ units.[31] However, whereas most of the (Pn)$_n$ units with Pn being P, As, or Sb were introduced into the heteroatomic clusters by reactions of the corresponding Pn$_7^{3–}$: the few heteroatomic species containing the homologous (Bi)$_n$ moiety could only be accessed in an indirect way. For each of the clusters [(Bi)$_4$Cd(Bi)$_3$]$^{3–}$, [(Bi)$_3$M$_2$(CO)$_6$]$^{3–}$ (M = Co, Rh), (Ge$_2$Bi)$_6$$^{3–}$, and (Ga$_2$Bi)$_6$$^{3–}$ the synthesis included the extraction of ternary Zintl anion, [K(crypt-222)]$_2$(TIB$_2$)-en in the presence of Lewis-acidic d-block or f-block metal complexes in en/crypt-222 or py/crypt-222.[20,21,24,25] 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 (Pb$_2$Bi)$_4$$^{3–}$ and [AuMePPh$_3$] in en/tol, py/tol, or py/THF afforded anions [Au$_n$(Pb$_2$Bi)$_y$]$_{15}^{3–}$, [Au$_n$(Pb$_2$Bi)$_y$]$^{3–}$, or (Pb$_2$Bi)$_y$$^{3–}$, respectively.[33] In this study, we therefore aimed at further variations of these reaction details in order to get access to new compounds featuring the rare (Bi)$_n$ unit. We chose to revisit the reaction between 'K$_4$GaBi$_4'$ and [ZnP$_2$], which previously yielded [K$_3$ZnP$_2$(Bi)$_4$]$^{3–}$ when applying en/tol/3-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 [Zn$_{11}$Bi$_7$]$^{5–}$ (Figure 3, top right).[16] These findings indicate the subtle, yet still poorly understood, impact of solvent on structure selection and stability in this reaction space. The [Bi$_6$]ZnP$_2$(Bi)$_4$$^{3–}$ anion in 2 (Figure 3, bottom) possesses the same topology as the homologous [(Bi)$_4$Cd(Bi)$_3$]$^{3–}$ anion,[33] but the structures differ in detail. In 2, the two (Bi)$_6$ cages are rotated against each other around the Zn$^{2+}$ ion by 85.03(4)$^\circ$, which results in a closer approximation of a tetrahedral coordination environment than in [(Bi)$_4$Cd(Bi)$_3$]$^{3–}$ (79.43(2)$^\circ$). 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](https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/ejic.202300514)
[(Bi₃ZnBi₄)]⁺ are similar to those observed in [K₂Zn₉Bi₁₀]⁺ and [Zn₈Bi₃]³⁻.[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 observed structural differences. More than the related Cd/Bi complex, which may explain the

As reflected by the reported reaction energies (Figure 5)[23] the [(Bi₃ZnBi₄)]⁺ complex is clearly disadvantaged as compared to a replacement of Zn⁺ with one of the softer central metal ions or ion dumbbells: 303.2 kJ/mol (Cd—Zn), 526.4 kJ/mol (Hg—Zn) and 183.3 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 [(Pn₅)M(Pn₅)]⁺ (M/Pn—Pb/As, Zn/Bi) that are related by their composition and molecular structures, but were accessed by different synthetic pathways as needed for the specific elemental combinations. The Pb/As-based anion co-crystallizes with small amounts of [PbAs₃]³⁻ on the same crystallographic site. [(As₅)Pb(As₅)]⁺ and [PbAs₃]³⁻ represent the first crystalline compounds comprising molecular Pb/As units. Despite a energetically disfavored situation as compared to heavier homologues, we achieved the synthesis and isolation of [(Bi₃ZnBi₄)]⁺ by varying the reaction/layering solvent as compared to previous studies with the starting material ‘K₅GaBi₄’ and [ZnPh₃], and by using the ternary starting material instead of [TIB₄]²⁻ for the reaction. We therefore not only add missing pieces to the series of homoleptic complexes of the Pn⁺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$_2$As$_5$[24a] and ‘K$_2$Ga$_5$Bi$_4$[24b] were prepared according to literature. PbI$_2$ and ZnPh$_2$ were commercially available from Aldrich. Samples were light shielded from ambient light throughout cluster syntheses.

Synthesis of [K$_2$as$_2$][crypt-222]$_2$[As$_5$Pb$_3$]$_2$[As$_3$Pb]$_3$[en]$_3$ (1): 80 mg (0.125 mmol) of K$_2$As$_5$, 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 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 1 formed at the wall of the Schlenk tube in approx. 15% yield.

Synthesis of [K(crypt-222)][(Bi$_2$)Zn(Bi$_3$)][2.5 py] (2): 80 mg (0.07 mmol) of the nominal composition ‘K$_3$Ga$_5$Bi$_4$’, 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 supplemental 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. All figures were created using Diamond 4.0.[41]

Supporting Information

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

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Conflict of Interests

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Variations of the coordination of nor-tricyclane-type 7-atom polypnictides to metal ions were achieved upon reactions of either K₃As₇ with PbI₂ in ethane-1,2-diamine and subsequent layering with toluene or by reacting an extraction solution of ‘K₅Ga₂Bi₄’ in pyridine with [ZnPh₂] prior to layering with toluene. The two procedures were specific for the respective elemental combinations, and they afforded the second compound exhibiting the rare Bi₃³⁻ ion in the coordination sphere of transition metal ions.