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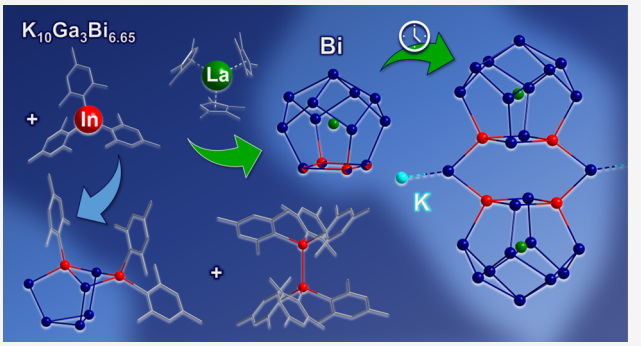
Effect of La^{3+} on the Formation of Endohedral Zintl Clusters Featuring In/Bi Shells

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Cite This: https://doi.org/10.1021/acs.inorgchem.4c00192
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ABSTRACT: Investigating the interactions of f-block metal ions with p-block polyanions in multinary cluster compounds is becoming increasingly attractive but remains a challenge in terms of both the synthetic approach and the control of the structures that are formed during the syntheses. So far, two types of reactions were dominant for the formation of corresponding clusters: the reaction of binary anions of p-block elements in 1,2-diamino-ethane (*en*) solutions or the reaction of organobismuth compounds with corresponding f-block metal complexes in THF. Herein, we report the synthesis of $[La@In_2Bi_{11}]^{4-}$ (**1**) and its doubly μ-Bi-bridged analogue in the doubly [K(crypt-222)]$^+$-coordinated $\{[K(crypt\text{-}222)]_2[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{4-}$ (**2**) as their [K(crypt-222)]$^+$ salts $[K(crypt\text{-}222)]_4$**1** and $[K(crypt\text{-}222)]_4$**2**, respectively, achieved by reactions of $[InMes_3]$ and $[La(C_5Me_4H)_3]$ (Mes = mesityl, C_5Me_4H = tetramethylcyclopentadienyl) with $K_{10}Ga_3Bi_{6.65}$/crypt-222 (crypt-222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in *en*. In the absence of $[La(C_5Me_4H)_3]$, the otherwise unchanged reactions afford the anions $[Bi_6(InMes)(InMes_2)]^{3-}$ (**3**) and $[Mes_3In{-}InMes_3]^{2-}$ (**4**) instead, which can be isolated as their [K(crypt-222)]$^+$ salts $[K(crypt\text{-}222)]_3$**3** and $[K(crypt\text{-}222)]_2$**4**·tol (tol = toluene), respectively. The $\{Bi_6\}$ fragment observed in anion **3** is assumed to be one of the key intermediates not only toward the formation of **1** and **2** but also on the way to more general bismuth rich compounds.



INTRODUCTION

Polar intermetallic compounds, also known as Zintl phases, generally represent compounds composed of s-block elements and p-block (semi)metal elements and can be transferred into Zintl salts by extraction with a cation-sequestering agent. Anionic clusters that are prepared by reactions of a Zintl phase or a Zintl salt with d-block or f-block metal compounds in solution are consequently referred to as Zintl clusters.[1−5]

Introducing d-block metal ions into Zintl clusters has resulted in a tremendously large number of new binary or ternary cluster anions featuring novel architectures and uncommon heterometallic bonding situations. In contrast, Zintl clusters comprising f-block metal cations—both from lanthanides or actinides, have remained rare. They represent p-block (semi)metal anions combined with one or more ions of f-block metals. Binary clusters have been reported as inverse sandwich complexes $[(LLn)_2Bi_6]^{2-}$ (L = Cp* = C_5Me_5; Ln = Y, Tb or Dy) obtained by reactions of $[Cp^*_2Ln(BPh_4)]$ with $[BiPh_3]$ in the presence of KC_8 in THF,[6,7] or as endohedral clusters $[Ln@Sb_{12}]^{3-}$ (Ln = La, Y, Ho, Er, or Lu)[8] and $[An@Bi_{12}]^{q-}$ (An/q = U/3, Th/4).[9,10] Ternary Zintl clusters have been exclusively obtained as endohedral clusters, which were synthesized by reactions of ternary Zintl solids or binary Zintl anions of the respective triel (Tr), tetrel (Tr), or pentel (Pn) elements with f-block organometallics in 1,2-diamino-ethane (*en*). The pioneering work showcased the fullerane-type species $[Eu@Sn_6Bi_8]^{4-}$, in which Eu^{2+} is embedded in an $\{Sn_6Bi_8\}^{6-}$ cage.[11] Later, f-block metal ions were encapsulated into a series of binary Tr/Bi (Tr = Ga, In, Tl), Tt/Bi (Tt = Sn, Pb) or Sn/Sb cages.[1,12] These studies resulted in the isolation of 13 atom shells such as $[Sm@Ga_{3-x}H_{3-2x}Bi_{10+x}]^{3-}$ (x = 0, 1), in which a massive charge overload at the (formally) "Ga^{2-}" sites is partially compensated by protonation,[13] or $[An@Tl_2Bi_{11}]^{3-}$ (An = U, Th).[9,10] The group 14/group 15 element combinations resulted in the formation of 13 atom and 14 atom cages (in many cases cocrystallizing on the same anionic sites of the respective crystal structure), such as $[Ln@Sn_4Bi_9]^{4-}$/$[Ln@Sn_7Bi_7]^{4-}$ (Ln = La, Ce),[14] $[Ln@Pb_{13-x}Bi_x]^{q-}$/$[Ln@Pb_{14-x}Bi_x]^{q-}$ (Ln = La, Ce, Nd, Sm, Gd, Tb; x/q = 9/4 or 10/3 for the 13 atom cages; x/q = 7/4 or 8/3 for the 14 atom cages),[15] $[U@Pb_4Bi_9]^{3-}$/$[U@Pb_7Bi_7]^{3-}$,[9] and $[U@Sn_6Sb_8]^{3-}$/$[U@Sn_7Sb_7]^{4-}$.[12] An extraordinary case was

Special Issue: Ligand-Metal Complementarity in Rare Earth and Actinide Chemistry

Received: January 16, 2024
Revised: February 25, 2024
Accepted: March 6, 2024

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reported for the cluster anion $\{[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{6-}$ (**A**) that crystallized as $[K([2.2.2]crypt)]_6\{[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}\cdot 3en\cdot 3tol$; $[K([2.2.2]crypt)]_6$**A**$\cdot 3en\cdot 3tol$).[16] The anion represents a $(\mu\text{-}Bi)^+$-bridged dimer of the hypothetical cluster anion "$[La@In_2Bi_{11}]^{4-}$", allowing for a reduction of the charge overload at the (formally) "In^{2-}" sites by the bridge, ending up with an "$In^-{-}Bi^-{-}In^-$" situation at this place. No monomeric species have been reported for the Ln/In/Bi elemental combination to date.

Studying Zintl clusters in general is motivated not only by the interesting geometrical and electronical structures and the insights into chemical bonding between metal atoms[17−20] but also by first hints toward catalytic properties, demonstrated recently on related p-block-based or p-/d-block-based species,[21−25] in which the Zintl compounds were used for bond activation in the catalytical hydrogenation of cyclic alkenes, for carbonyl or CO_2 reduction, and also for olefin isomerization.

Based on the previous observations made with the elemental combinations Ga/Bi and Tl/Bi, both of which always led to binary 13-atom cages with or without protonation for local charge reduction, while the In/Bi combination yielded exclusively a μ-Bi-bridged dimeric version, and the recent reports about Zintl cluster anions using f-block organometallics, we were interested in finding out which elemental combination would result in the products from a combination of a Ga/Bi-based Zintl solid with an organometallic In source in reactions with f-block compounds.

RESULTS AND DISCUSSION

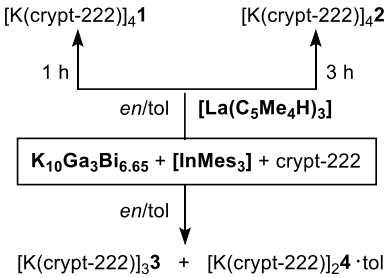
In this work, we report reactions of the Zintl phase $K_{10}Ga_3Bi_{6.65}$[26] with $[InMes_3]$ (Mes = mesityl) and $[La(C_5Me_4H)_3]$ (C_5Me_4H = tetramethylcyclopentadienyl) in the presence of crypt-222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in *en*, yielding $[La@In_2Bi_{11}]^{4-}$ (**1**; 1 h reaction time; approximately 15% yield) and $\{[K(crypt\text{-}222)]_2[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{4-}$ (**2**; 3 h reaction time; approximately 10% yield) as their $[K(crypt\text{-}222)]^+$ salts $[K(crypt\text{-}222)]_4$**1** and $[K(crypt\text{-}222)]_4$**2**, respectively. As detailed further below, the cluster formation strongly depends on the presence of the lanthanide cation, as demonstrated in the corresponding control experiments: In the absence of $[La(C_5Me_4H)_3]$ under otherwise unchanged reaction conditions yielded $[Bi_6(InMes)(InMes_2)]^{3-}$ (**3**) and $[Mes_3In{-}InMes_3]^{2-}$ (**4**) as their $[K(crypt\text{-}222)]^+$ salts $[K(crypt\text{-}222)]_3$**3** and $[K(crypt\text{-}222)]_2$**4**·tol (tol = toluene), respectively (Scheme 1).

All four compounds were obtained as single crystals. They were characterized by means of single-crystal X-ray diffraction (SCXRD) and energy-dispersive X-ray spectroscopy (EDS, Figures S5−S7).

Anion **1** represents the first In/Bi endohedral cluster that does not exhibit a dimeric structure. It can therefore be considered an intermediate on the pathway toward clusters **A** and **2** that crystallizes upon longer reaction times. The syntheses of **3** and **4** indicate, first, the necessity of the La^{3+} ion for the formation of the 13-vertex cluster shells found in A, **1** and **2**, and they confirm the dominance of In−Bi versus Ga−Bi interactions in the ternary Ga/In/Bi reaction space also in the absence of Lewis acidic La^{3+}.

Compound $[K(crypt\text{-}222)]_4$**1** (Tables S1−S3, Figures S1 and S5) crystallizes in the monoclinic space group type $P2_1/c$. The molecular structure of anion **1** (Figure 1a) is very similar

Scheme 1. Overview of the Synthesis of the Four Compounds Presented in This Work[a]



[a]By treatment of $K_{10}Ga_3Bi_{6.65}$ with $[InMes_3]$ in *en*/crypt-222 in the presence of $[La(C_5Me_4H)_3]$, yielding $[K(crypt\text{-}222)]_4$**1** and $[K(crypt\text{-}222)]_4$**2**, or in the absence of the f-block metal compound, yielding $[K(crypt\text{-}222)]_3$**3** and $[K(crypt\text{-}222)]_2$**4**·tol, respectively, upon subsequent layering with toluene.

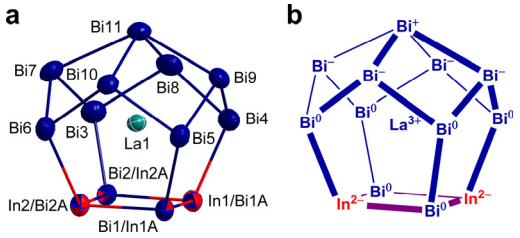


Figure 1. a) Side view of the molecular structure of $[La@In_2Bi_{11}]^{4-}$ anion **1**, as found in the single-crystal structure of $[K(crypt\text{-}222)]_4$**1** (displacement ellipsoids of heavy atoms set at 50% probability). Selected distances (Å) in **1**: In−Bi 2.9540(16)−3.0558(18), Bi−Bi 2.9974(13)−3.4903(16), La···In/Bi 3.1396(15)−3.4930(18). b) Formal charge assignment for **1**, in analogy to quantum chemical studies on this cluster type reported in refs 14−16.

to those of other reported clusters based on monomeric 13-atom cages, $[Sm@Ga_{3-x}H_{3-2x}Bi_{10+x}]^{3-}$ (x = 0, 1), and $[An@Tl_2Bi_{11}]^{3-}$ (An = U, Th). As in these clusters, the four atoms in the base vertices in **1** are distributed over the four sites with a 50:50 occupancy of In:Bi atoms. La^{3+} is located in the center of the 13-vertex cage. Besides the cluster shown in Figure 1a, the unit cell of $[K(crypt\text{-}222)]_4$**1** comprises a second cluster molecule that shows a 90:10 rotational disorder of two of these cages (see Figure S1). The In−Bi and Bi−Bi distances are similar to the ones observed in related cages. As determined based on detailed quantum chemical investigations about this kind of endohedrally filled 13-atom cages,[14−16] the charges are formally distributed in **1** as illustrated in Figure 1b, which demonstrates the high charge accumulation at the In sites.

In order to find out whether the energetically preferred, μ-Bi-bridged cluster dimer $\{[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{6-}$ (**A**) would also form eventually and whether the 13-vertex cluster **1** could reasonably be considered an intermediate during its formation, we prolonged the reaction time from 1 to 3 h. We were indeed successful in isolating the anion as species **2** (Figure 2a) in the $[K(crypt\text{-}222)]^+$ salt $[K(crypt\text{-}222)]_4$**2**. In contrast to the situation in the crystal structure of the compound comprising anion **A** (Figure 2b), each μ-Bi site in **2** directly coordinates to one $[K(crypt\text{-}222)]^+$ cation, which is significantly closer to the cluster (shortest Bi/In···K distance: 3.95 Å) than the other four $[K(crypt\text{-}222)]^+$ cations (shortest Bi/In···K distance: 6.03 Å); the sum formula of **2** therefore comprises two $[K(crypt\text{-}222)]^+$ units. This additional K···(μ-Bi) interaction seems to affect the cluster

https://doi.org/10.1021/acs.inorgchem.4c00192
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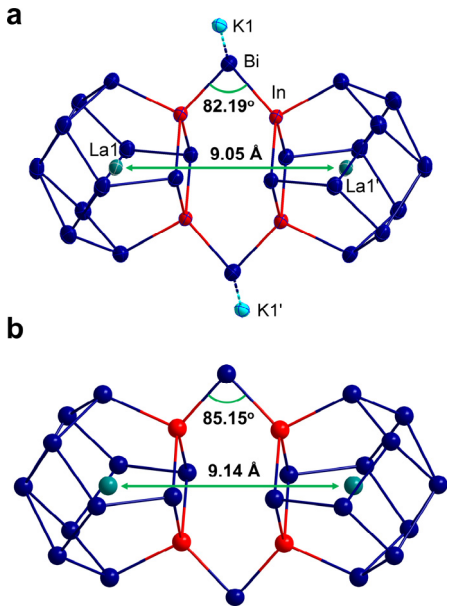


Figure 2. a) Side view of the molecular structure of the $\{[K(crypt\text{-}222)]_2[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{4-}$ anion (**2**), as found in the single-crystal structure of $[K(crypt\text{-}222)]_4$**2** (displacement ellipsoids of heavy atoms set at 50% probability. The crypt-222 molecules from $[K(crypt\text{-}222)]^+$ cations are omitted for the sake of clarity. Selected distances (Å) in **2**: In−Bi 2.838(2)−3.041(2), Bi−Bi 2.9808(18)−3.4502(18), La···In/Bi 3.132(2)−3.5093(19), K1···Bi: 3.950(6). b) Structure of $\{[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{6-}$ (**A**) from $[K([2.2.2]crypt)]_6$**A**·3en·3tol.

structure, which is reflected by a smaller In−(μ-Bi)−In angle (82.19° in **2** vs 85.15° in **A**) and a shorter La1···La1′ distance (9.05 Å in **2** vs 9.14 Å in **A**). This slight compression of the cluster dimer along the La1···La1′ axis accords with the corresponding vibrational (stretching) mode that was reported to exhibit the smallest wavenumber (10 cm^{-1}) according to DFT calculations.[16] The "compressed dimer" structure of **2** therefore gives indirect evidence for this soft mode to exist for $\{[La@In_2Bi_{11}](\mu\text{-}Bi)_2[La@In_2Bi_{11}]\}^{6-}$, as small effects of the packing of cations and anions in the crystal have a notable impact on the mentioned structural parameters.

The group 13 elements possess a rather unusual role as a Lewis base in this cluster species. This is attributed to the relatively high (formal) charge of 2− (see Figure 1b), which they do not easily cope with given their relatively small electron affinities of 0.30 eV (Ga), 0.38 eV (In), and 0.32 eV (Tl), as compared with that of Bi (0.94 eV).[27−29] Compensation of this excess charge was shown to occur in different ways. In the Ga−In−Tl series, the Ga atoms have the smallest radius and, thus, accumulate the largest charge density. The corresponding basicity is strong enough to enable deprotonation of an amine (*en*) to afford $[Sm@Ga_{3-x}H_{3-2x}Bi_{10+x}]^{3-}$.[13] The Tl atoms, on the other hand, are considerably larger and can compensate well for the additional negative charge without external compensation, as observed in $[An@Tl_2Bi_{11}]^{3-}$ (An = U, Th).[9,10] The In atoms are in between the two extremes, so partial charge dissipation via a μ-Bi-bridge (as observed in **A** and **2**) or no external charge compensation (as observed in **1**) is a possible scenario as demonstrated in this work.

DFT calculations of mode protonation reactions, according to eqs 1 and 2, with minimal model compounds $[TrH_3]^{2-}$ (Tr = B, Al, Ga, In, Tl) and protonation agents NH_3 or *en*, support these suggestions (see Table 1).

$$[TrH_3]^{2-} + NH_3 \rightarrow [TrH_4]^- + (NH_2)^- \quad (1)$$

$$[TrH_3]^{2-} + H_2NCH_2CH_2NH_2 \rightarrow [TrH_4]^- + (H_2NCH_2CH_2NH)^- \quad (2)$$

Table 1. Reaction Energies (in kJ·mol^{-1}) for Protonation Reactions of Model Compounds $[TrH_3]^{2-}$ (for Tr = Al, Ga, In, Tl) with NH_3 or $H_2NCH_2CH_2NH_2$ (*en*) according to eqs 1 and 2

	$[BH_3]^{2-}$	$[AlH_3]^{2-}$	$[GaH_3]^{2-}$	$[InH_3]^{2-}$	$[TlH_3]^{2-}$
NH_3	−160	−50	−24	+38	+110
en	−161	−51	−25	+37	+109

The calculations were done without symmetry restrictions (C_1) of the molecules using the program system TURBOMOLE v7.4,[30] the TPSSH functional,[31] and dhf-TZVP basis sets[32] including corresponding auxiliary bases[33] and effective core potentials.[34] The conductor-like screening model (COSMO) was applied for compensation of negative charges.[35] The reaction energies calculated for the two reactions are very similar for a given Tr element, indicating, first, that both amines have equal protonation properties toward the model species, Second, the reaction demonstrates very well that a compensation of the charge overload (e.g., by protonation) is highly energetically preferrable for the species comprising smaller Tr atoms (Tr = B, Al, and Ga), while it is unfavorable in case of the model compounds with the larger Tr atoms (In, Tl), in agreement with the fact that anion **1** is not protonated in contrast to its Ga analogue. However, the interaction with the less acidic, larger μ-Bi atom seems to be a suitable bonding partner, as exemplified by the subsequent formation of cluster **2**.

We were also interested in exploring whether the La^{3+} ions (a) have an impact on the formation of the cage-type cluster structures or whether they would also without, and (b) whether they affect the competition between Ga and In ions in the multinary reaction system.

Both questions were answered by the reaction of $K_{10}Ga_3Bi_{6.65}$ with $[InMes_3]$ in the absence of $[La(C_5Me_4H)_3]$. The experiment allowed the isolation of $[Bi_6(InMes)(InMes_2)]^{3-}$ (**3**, Figure 3a) and $[Mes_3In{-}InMes_3]^{2-}$ (**4**, Figure 3b) as their $[K(crypt\text{-}222)]^+$ salts $[K(crypt\text{-}222)]_3$**3** and $[K(crypt\text{-}222)]_2$**4**·tol in approximately 25% or 2% yield, respectively, from the same reaction. Regarding question (a), it can be stated that 13- or 14-atom cages are not formed and seem to be reliant on the presence of and interaction with the (stabilizing) inner La^{3+} ion−in line with previous assumptions.[15] Question (b) cannot be directly answered, but the observations suggest that the preference of In/Bi or polybismuth architectures over Ga/Bi or Ga/In/Bi species is not affected by the Lewis acidic La^{3+} ions; under both circumstances, Ga atoms are not incorporated in the crystalline products and rather serve as reducing agents, in accordance with Ga possessing the lowest electron affinity of the three p-block (semi)metals involved (see above).

Anion **3** can be described as being based on a binary nortricyclane-type $\{InBi_6\}$ cage, with the In atoms occupying the apical position. Another In atom is coordinated by two of

https://doi.org/10.1021/acs.inorgchem.4c00192
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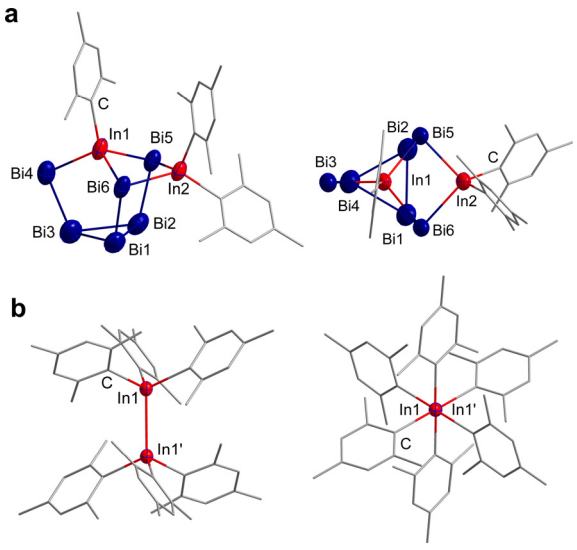


Figure 3. Side view of the molecular structures of the $[Bi_6(InMes)(InMes_2)]^{3-}$ (**3**; a) and $[Mes_3In{-}InMes_3]^{2-}$ (**4**; b) anions, as found in the single-crystal structures of $[K(crypt\text{-}222)]_3$**3** and $[K(crypt\text{-}222)]_2$**4**·tol, respectively. Displacement ellipsoids of heavy atoms were set at 25% probability for **3** (exhibiting limited crystal quality) and 50% probability for **4**; H atoms are omitted for clarity. Selected distances (Å) and angles (deg) in **3**: In−Bi 2.884(4)−2.982(3), Bi−Bi 2.896(3)−3.090(3), In−C 2.30(2); Bi−Bi−Bi 60.58(7)−100.91(8), Bi−Bi−In 92.53(8)−94.22(10), Bi4−In1−Bi(5,6) 111.60(11), 112.81(11), Bi5−In1−Bi6 92.80(8), Bi5−In2−Bi6 93.54(9), Bi−In1−C 108.1(7)−116.9(5), Bi−In2−C 101.7(7)−131.2(5). Selected distances [Å] and angles [deg] in **4**: In1−In1′ 2.9756(11), In−C 2.280(5)−2.296(5); In−In−C 111.67(12)−114.07(13).

the two-coordinated Bi atoms, thereby forming a butterfly shaped $\{In_2Bi_2\}$ ring that expands the polycyclic architecture. Both In atoms are additionally coordinated by one of the originally present Mes substituents, which suggests that anion **3** is likely an intermediate during the formation of larger In/Bi cages upon release of the remaining Mes groups that crystallized owing to a fairly suitable charge/size relationship in comparison with the $[K(crypt\text{-}222)]^+$ counterion complexes; the crystal quality is rather poor though. The structural arrangement not only refers to the famous nortricyclane-type Zintl clusters Pn_7^{3-} of all group 15 elements (Pn = P−Bi) but also is reminiscent of the recently reported multinary Zintl cluster $[(Bi_6)Zn_3(TlBi_5)]^{4-}$ with the same underlying $\{Bi_6\}$ subunit, which was formed in a reaction of $[K(crypt\text{-}222)]_2(TlBi_3)$·en with $[ZnPh_2]$.[36] The coordination of the extra-cyclic In atom, on the other hand, is reminiscent of recent coordination compounds of the Bi_7^{3-} anion, $[(Bi_7)M(Bi_7)]^{4-}$ (M = Zn, Cd), that were formed in similar reactions.[36,37] Cluster **3** therefore indicates the dominance of this structural motif also upon the combination of the ternary solid with a p-block organometallic.

Dianion **4** occurs as a side product, which demonstrates nicely, however, that the In atoms undergo a stepwise reduction under the given rection conditions. Starting from $[InMes_3]$ with formally In(III), anion **4** exhibits an In−In bond, which was achieved upon formation of pseudo-group 14 groups "$[InMes_3]^-$" through highly reductive $K_{10}Ga_3Bi_{6.65}$, and the reductive coupling of these fragments yielded the homologue of a distannane.

CONCLUSION

In conclusion, we synthesized two La^{3+}-centered In/Bi-based endohedral Zintl clusters from a yet unexplored reaction space combining a ternary Zintl solid, $K_{10}Ga_3Bi_{6.65}$, and a p-block organometallic, $InMes_3$, with $[La(C_5Me_4H)_3]$. The polyhedral cluster shells are obtained only in the presence of Lewis acidic Ln^{3+} ions, as confirmed by corresponding reactions undertaken in the absence of the f-block metal complex, which yielded salts of $[Bi_6(InMes)(InMes_2)]^{3-}$ and $[Mes_3In{-}InMes_3]^{2-}$ exhibiting other architectures, with the first one representing a potential snapshot of the formation of larger bismuth-rich clusters and both potentially serving as new starting materials for such species. Our studies show that In can be integrated into ternary Zintl clusters from an organometallic source to afford compounds that have otherwise not bee accessible so far. In this regard, our contribution provides a new strategy toward the isolation of novel multinary Zintl clusters. In addition, the results indicate that the In/Bi combination is preferred over the Ga/Bi combination under all of the reaction conditions explored herein, most probably by the better fit of atomic radii and the smaller heteropolarity, both of which seem to stabilize the heterometallic cage.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c00192.

Synthesis details, single crystal X-ray crystallography (SCXRD), energy-dispersive X-ray spectroscopy (EDS) analysis, details of quantum chemical investigations (PDF)

Accession Codes

CCDC 2323911−2323914 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through the Collaborative Research Centre "4f for Future" (CRC 1573, project number 471424360), project A3. The work was cofunded by the European Union (ERC, BiCMat, 101054577). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them.

■ ABBREVIATIONS

crypt-222, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane; *en*, ethane-1,2-diamine; Mes, 1,3,5-trimethylbenzene; tol, toluene

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