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ARTICLE

$K_{10}Ga_3Bi_{6.65}$ – The First Compound in the Ternary *A*-Ga-Bi System Comprising Cyclic Tris-meta Borate-Analogous $[Ga_3Bi_6]^{9–}$ Units and Bi_2 Dumbbells

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. $K_{10}Ga_3Bi_{6.65}$ is the first representative in the ternary system *A*-Ga-Bi (*A* = alkali metal). It contains $[Ga_3Bi_6]^{9–}$ anions with planar triangular-coordinated Ga atoms as the main structural feature, accompanied by isolated Bi–Bi dumbbells. Alkali metal cations are counterbalancing the charges and fill the space between the anionic units. According to the Zintl-Klemm concept charge balance is reached if an almost equal ratio of single and double-bonded Bi_2 dumbbells are present according to $(K^+)_{10}[Ga_3Bi_6]^{9–}([Bi\text{-}Bi]^{4–})_{1/6}([Bi{=}Bi]^{2–})_{1/6}$.

Introduction

Heteroatomic anions $[Tr_xPn_y]^{z–}$ as they occur in Zintl phases with different compositions, charges and bonding situations comprise a large number of representatives (*Tr* = Ga, In, Tl, *Pn* = P, As, Sb, Bi). The *Tr* atoms in these species are either in a trigonal planar environment as monomeric, dimeric or trimeric [$TrPn_3$] fragments, or they are arranged in condensed five-membered rings (Table S1, Supporting Information) and [$Tr@Pn_4$] tetrahedra, which then can be interconnected in different ways. Edge, face and corner sharing units lead to structures that can extend in various dimensions. The nature of the anionic framework of these structures is collectively related to the number, the size, and the charge of the cations and, in turn, to the atomic ratio in the $[Tr_xPn_y]^{z–}$ anion and its valence electron count. Consequently, the less reduced general anionic compositions $[Tr_xPn_y]^{z–}$ exhibit one-, two- or three-dimensional anionic frameworks.[1]

A large number of *A-Tr-Pn* systems, which contain isolated fragments, are located in the alkali metal-rich area of the ternary phase diagrams. The most simple unit is the trigonal planar $[TrPn_3]^{6–}$ anion which is isostructural to the trioxoborate(III) anion unit $BO_3^{3–}$, and in which the Ga or In atoms are covalently bound to three *Pn* atoms. We obtained the highly charged carbonate analogue $[SnBi_3]^{5–}$even from solution.[2] Phases with the highly charged $[TrPn_3]^{6–}$ anions consequently have a high alkali metal content for charge compensation, such as in Na_6GaPn_3 (*Pn* = P, As)[3,4] K_6InPn_3 (*Pn* = P, As),[5,6] and Cs_6GaSb_3[7] (Figure 1a). Phases with the heavier alkali metals like $Cs_6Ga_2P_4$,[8] Rb_3GaP_2,[9] and Cs_3GaAs_2[10] contain isolated dimeric anions $[Ga_2Pn_4]^{6–}$, which share two *Pn* atoms in an almost planar Ga_2Pn_2 butterfly-type ring structure with two Ga-*Pn* exo bonds (Figure 1b). The Ga-containing ternary $K_{20}Ga_6As_{12.66}$ and $K_{20}Ga_6Sb_{12.66}$[11] as well as quaternary phases $RbNa_8Ga_3P_6$ and $RbNa_8Ga_3As_6$[12] comprise cyclic trimers $[Ga_3Pn_6]^{9–}$ (*Pn* = P, As and Sb) in which three monomers formally share two *Pn* atoms each. The planar and slightly deformed Ga_3Pn_3 hexagon in the anion $[Ga_3Pn_6]^{9–}$ shows Ga atoms in a trigonal planar environment with three Ga–*Pn* exo bonds (Figure 1c).

Linking of the building units $TrPn_3$ also allows for the construction of one-dimensional infinite chains in ternary compounds. Almost planar five-membered rings consisting of two Ga and three *Pn* atoms, which are inter-connected by the terminal *Pn* atoms with a Ga–*Pn* exo bond, build a linear chain (Figure 2a) in K_2GaP_2,[13] A_2GaAs_2 (*A* = K, Rb),[14,15] and A_2GaSb_2 (*A* = K, Rb, Cs).[16–18] In case of the heavier homologue Tl, two compounds in the *A*/Tl/*Pn* systems are known with more complex heteroatomic chains including Tl–Tl bonds in Na_6TlSb_4[19] (Figure 2b) and Tl–Tl bonds beside *Pn*–*Pn* bonds in $K_6Tl_2Sb_3$[1] (Figure 2c), that are part of one-dimensionally linked six-membered rings.

Herein we report on a novel ternary compound that contains two different independent anionic units. Single crystals of $K_{10}Ga_3Bi_{6.65}$ were, along with copper gallides, first discovered as one of the products, obtained in an attempted synthesis of the K analogue of $Na_{12}Cu_{12}Sn_{21}$[20] and iso-valence electronic replacement of the tetrel Sn by the triel Ga and Bi. Later, $K_{10}Ga_3Bi_{6.65}$ was synthesized as the main product together with some residual binary KBi_2 in a high temperature reaction of the elements K, Bi and Ga with the ratio 10:3:6.

Experimental Section

Synthesis: The sample was prepared from the elements using 210.9 mg K, 124.4 mg Ga and 676.2 mg Bi, corresponding to an

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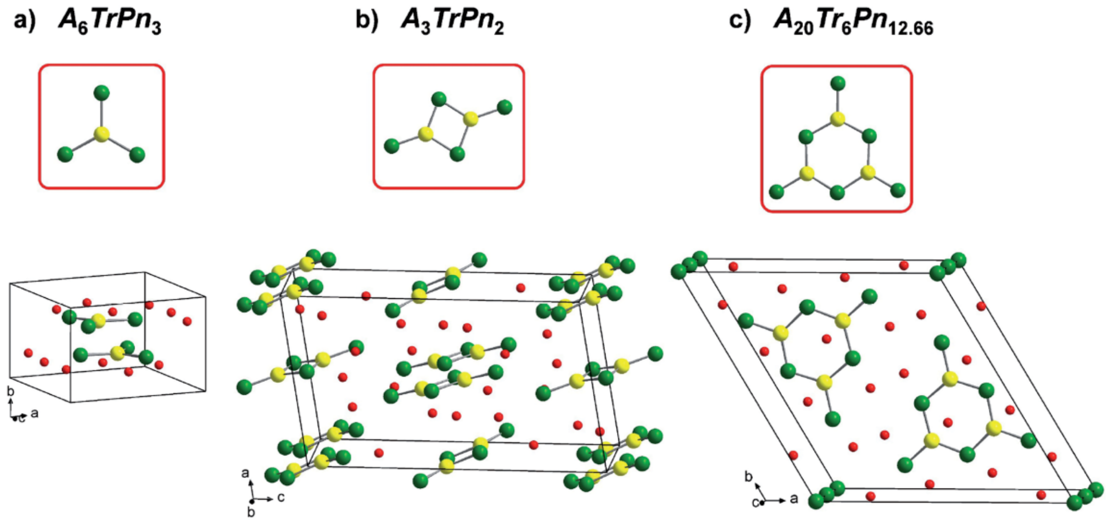

Figure 1. Alkali metal-rich compounds with isolated fragments in the ternary systems *A-Tr-Pn*. The trigonal planar anion $[TrPn_3]^{6-}$ and the structure of the compounds with the stoichiometry 6:1:3 (a), butterfly-like $[Ga_2Pn_4]^{6-}$ units in Ga compounds with the stoichiometry 3:1:2 (b), and the $[Ga_3Pn_6]^{9-}$ unit in $K_{20}Ga_6Pn_{12.66}$ (c). Top – isolated fragments, bottom – structures of the compounds. *A* atoms are shown in red, *Tr* in yellow and *Pn* in green color.

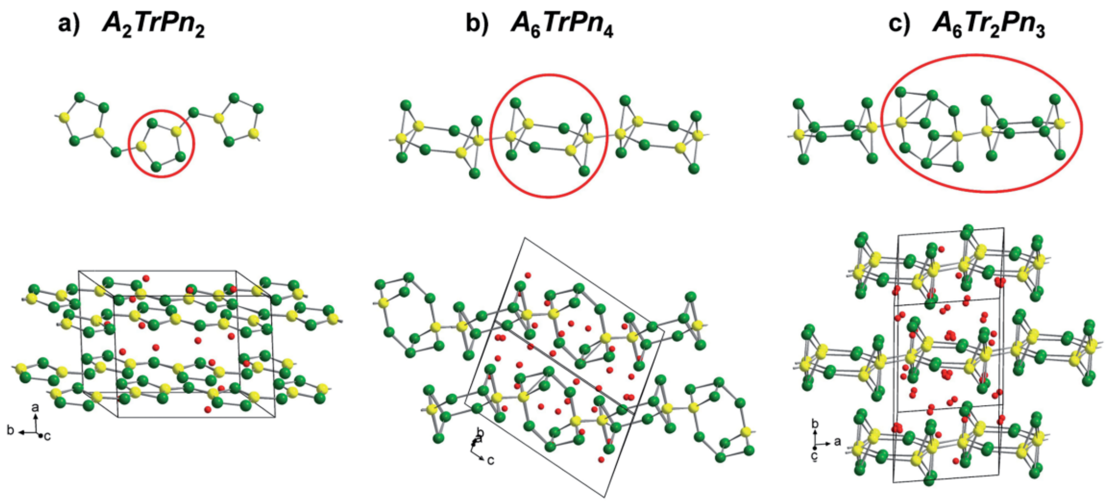

Figure 2. One-dimensional chains in *A–Tr–Pn* compounds. (a) Heteroatomic five-membered rings bridged through *Pn* atoms in K_2GaP_2. Chains of connected six-membered Tr_4Pn_2 and Tr_2Pn_4 rings in (b) Na_6TlSb_4 and (c) $K_6Tl_2Sb_3$, respectively.

atomic ratio K:Ga:Bi of 10:3:6. The reaction mixture was weighted in an Ar-filled glove box and then packed in a niobium ampoule, which was sealed afterwards. The ampoule was transferred into a silica tube and heated to 500 °C with a rate of 4°•min^{-1}, held at this temperature for 72 h, then slowly cooled (with a rate of 0.1°•min^{-1}) to 400 °C and finally quenched to room temperature. The PXRD analysis showed the presence of $K_{10}Ga_3Bi_{6.65}$ as the main phase with some residual binary KBi_2 (see Figure S1, Supporting Information) Because of the high absorption of the sample due to the presence of Bi, the sample had to be significantly diluted by diamond powder.

Structure Determination: Single crystals were picked from the reaction product in a glove box, and data collection was performed on a Stoe StadiVari diffractometer with an exposure time of 50 seconds and a detector distance of 60 mm. The structure was solved by Direct Methods in the hexagonal space group $P6_3/m$. A numerical absorption correction was carried out using the software packages X-Red and X-Shape,[21,22] showing an expected high absorption coefficient of 41.729 mm^{-1}. The refinement revealed three crystallographically independent Bi sites (two in Wyckoff position 6h and one in 2b), one Ga (6h) and three K atoms (all in Wyckoff position 6h). The electron deficiency in the Bi3 position is most likely due to a defect, resulting in an occupancy of 64.7 %. Partial defects were tested for all K positions, which led to lower occupation factors for the Bi3 position, but no sufficient difference was observed, suggesting no significant correlation between the K content and the defect in the Bi position. Crystallographic data and selected details of the structure refinement for the compound with the refined composition $K_{10}Ga_3Bi_{6.647(4)}$ are listed in Table 1, atomic parameters and anisotropic displacement parameters in Table 2 and Table 3, respectively.

Further details of the crystal structure investigations may be obtained from from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033;

Table 1. Crystallographic data and selected details of the structure refinement of $K_{10}Ga_3Bi_{6.647(4)}$.

	$K_{10}Ga_3Bi_{6.647(4)}$
Formula weight /g·mol^{-1}	3979.75
Space group	$P6_3/m$ (no. 176)
Z	2
Unit cell parameters	
a /Å	18.0393(9)
c /Å	5.4689(3)
Volume /Å^3	1541.2(2)
$D_{calcd.}$ /g·cm^{-3}	4.288
Abs. coeff. /mm^{-1}	41.729
F(000) (e)	1670
Crystal shape / color	block / silver
Temperature /K	150
Θ range /°	3.450–30.000
Range in *hkl*	±25, ±25, –7 to +5
Reflections collected	18200 (R = 0.0307)
Unique reflections	1653 (R_{int} = 0.0648)
Data / parameter	1653/43
GOF on F2	1.061
R_1, wR_2 [$I > 2\ \sigma(I)$]	0.0283, 0.0501
R_1, wR_2 (all data)	0.0463, 0.0542
Largest diff. peak/hole /e·Å^{-3}	1.969 and –2.386

e-mail: deposit@ccdc.cam.ac.uk) and can be obtained free of charge on quoting the depository number CSD-1965045.

EDX analysis of the measured crystal confirmed the presence of the all three elements. The atomic ratios only approximately confirm the composition obtained from the single crystal structure determination, due to the large standard deviation produced by the instrument (see Supporting Information).

Supporting Information (see footnote on the first page of this article): Table of structural data of compounds in the ternary systems *A-Tr-Pn* (*Tr* = Ga,In,Tl; *Pn* = P,As,Sb,Bi); Table with results of the EDX analysis of $K_{10}Ga_3Bi_{6.65}$ single crystal; Figure of powder X-ray diffractogram of "$K_{10}Ga_3Bi_6$" sample.

Results and Discussion

Crystal Structure

$K_{10}Ga_3Bi_{6.65}$ contains anionic [Ga_3Bi_6] units with covalently connected Ga and Bi atoms together with isolated anionic [Bi_2] dumbbells (Bi3–Bi3) (Figure 3). These units are separated by the potassium counterions.

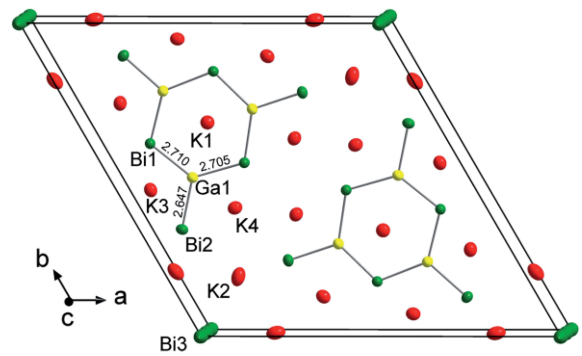

Figure 3. Unit cell of $K_{10}Ga_3Bi_{6.65}$. Gallium atoms are shown in yellow, bismuth in green and potassium in red color, the displacement ellipsoids are drawn at a 90 % probability level.

Three trigonal planar [$GaBi_3$] units with shared Bi atoms form a planar cyclic [Ga_3Bi_6] structure that contains three *exo*-cyclic Ga–Bi bonds with terminal Bi atoms (Figure 4a), in analogy to the cyclic tris-meta borate [B_3O_6]$^{6-}$. In addition, disordered Bi atoms are present that form due the site occupation factor (*sof*) Bi–Bi dumbbells. Alkali metal cations are counterbalancing the charges and fill the space among the anions. The heteroatomic hexagon is slightly distorted from regularity due to two different bond angles (Bi–Ga–Bi) = 125.47° and (Ga–Bi–Ga) = 114.53°. The sum of the three Bi–Ga–Bi angles including the external bond for all Ga atoms is 360.00°, revealing a planar coordination of the Ga by three Bi

Table 2. Atomic coordinates and equivalent isotropic displacement parameters /Å^2 for $K_{10}Ga_3Bi_{6.647(4)}$.

Atom	Wyckoff site	S.O.F.	x	y	z	U_{eq}
Bi1	6*h*	1	0.54902(2)	0.15899(2)	1/4	0.01337(9)
Bi2	6*h*	1	0.33572(2)	0.22619(2)	1/4	0.01400(9)
Bi3	2*b*	0.647(4)	0	0	0	0.145(2)
Ga	6*h*	1	0.50165(6)	0.27951(6)	1/4	0.0138(2)
K1	2*c*	1	1/3	2/3	1/4	0.0183(7)
K2	6*h*	1	0.0049(1)	0.1898(2)	1/4	0.0277(5)
K3	6*h*	1	0.0667(1)	0.4507(1)	1/4	0.0183(4)
K4	6*h*	1	0.2723(1)	0.3938(1)	1/4	0.0187(4)

Table 3. Anisotropic displacement parameters /Å^2 for $K_{10}Ga_3Bi_{6.647(4)}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi1	0.0113(1)	0.0112(1)	0.0172(1)	0.000	0.000	0.0054(1)
Bi2	0.0113(1)	0.0154(1)	0.0151(1)	0.000	0.000	0.0067(1)
Bi3	0.0198(6)	0.0198(6)	0.394(4)	0.000	0.000	0.0099(3)
Ga	0.0117(4)	0.0128(4)	0.0168(4)	0.000	0.000	0.0061(4)
K1	0.0197(1)	0.019(1)	0.0155(1)	0.000	0.000	0.0098(5)
K2	0.0190(1)	0.028(1)	0.0275(1)	0.000	0.000	0.0058(9)
K3	0.0168(9)	0.020(1)	0.0170(9)	0.000	0.000	0.0089(8)
K4	0.0221(1)	0.0180(9)	0.017(1)	0.000	0.000	0.0106(8)

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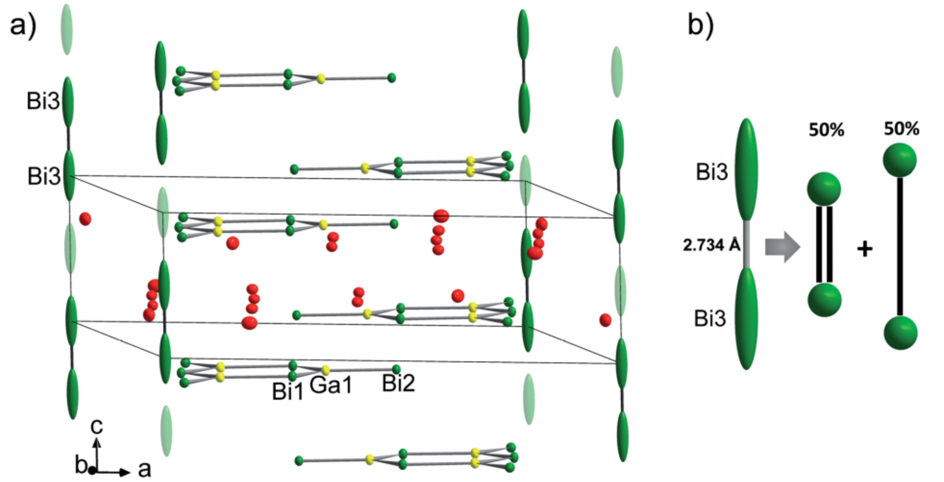


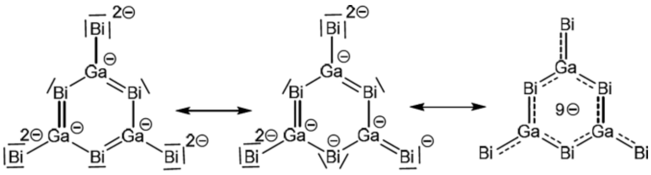
Figure 4. (a) The structure of $K_{10}Ga_3Bi_{6.65}$: the trigonal planar coordination of Ga atoms in the $[Ga_3Bi_6]^{9-}$ anion and the disordered $[Bi_2]^{3-}$ dumbbells are emphasized. The occupancy of Bi3 by 2/3 can be interpreted in a localized model of $[Bi_2]$ dumbbells and vacancies at the Bi3 position shown as green and transparent green ellipsoids, respectively. (b) Representation of the $[Bi_2]^{3-}$ dumbbells as a superposition of two types: $(Bi{=}Bi)^{2-}$ and $(Bi–Bi)^{4-}$ with shorter and longer Bi–Bi bonds. The gallium atoms are shown in yellow, bismuth in green and potassium in red color, the displacement ellipsoids are drawn at a 50% probability level.

Table 4. Interatomic distances of the $K_{10}Ga_3Bi_{6.647(4)}$.

Atom pairs		Distance /Å	Atom pairs		Distance /Å
Bi1	Ga1	2.705(1)	Bi2	Ga1	2.647(1)
	Ga1	2.710(1)	Ga1	Bi2	2.647(1)
Bi3	2 × Bi3	2.7345(2)		Bi1	2.705(1)
	2 × Bi3	3.7928(9)		Bi1	2.7096(9)
K1	2 × Ga1	3.7938(6)	K2	2 × Bi2	2.647(4)
	2 × Ga1	3.7940(7)		2 × Bi3	3.606(1)
	2 × Ga1	3.8980(3)		Bi2	3.647(3)
	2 × Bi1	3.8982(2)		K3	3.666(3)
	2 × Bi1	3.8992(3)		2 × K4	4.261(4)
	Bi1	4.424(2)		4 × K2	4.276(3)
	K3	4.424(2)		K4	4.348(2)
	K3	4.425(3)	K4	2 × Ga1	4.366(3)
	K3	4.473(3)		2 × Bi1	3.720(2)
	K4	4.475(2)		Bi2	3.726(1)
	K4	4.475(2)		2 × Bi2	3.730(3)
	K4	5.4689(3)		2 × K2	3.758(2)
	2×K1	3.649(2)		2 × K3	4.276(3)
K3	Bi1	3.689(2)		K3	4.293(3)
	2 × Ga1	3.704(1)		K2	4.316(4)
	2 × Bi1	3.739(2)		K1	4.366(3)
	2 × Bi2	4.261(4)		K3	4.475(2)
	K2	4.293(2)			
	2 × K4	4.316(4)			
	K4	4.424(2)			
	K1	4.550(3)			
	2 × K3	4.582 (3)			
	K4	5.4689(3)			
	2 × K3	2.705(1)			

atoms. The Ga–Bi distances are 2.710 and 2.647 Å within the hexagonal ring and the exo bond, respectively (Table 4) and are thus shorter than the sum of the covalent radii of 2.75 Å typical for Ga–Bi single bonds (1.24 and 1.51 Å for Ga and Bi, respectively[23]), but longer than the value calculated for a Ga–Bi double bond (2.58 Å[23]), indicative of a certain degree of electron delocalization within the anion (Scheme 1).

In contrast to the situation in the structures of the isostructural phases $K_{10}Ga_3As_{6.33}$ and $K_{10}Ga_3Sb_{6.33}$ (or $K_{20}Ga_6As_{12.66}$ and $K_{20}Ga_6Sb_{12.66}$ as reported in original paper),[11] the position of the non-bonded atom Bi3 in $K_{10}Ga_3Bi_{6.65}$ shows a significant higher occupancy. In $K_{10}Ga_3As_{6.33}$ and $K_{10}Ga_3Sb_{6.33}$ the corresponding position is occupied by 1/3 by As and Sb atoms, respectively. Assuming



Scheme 1. Two possible resonance structures resembling the fully delocalized π electron system of $[Ga_3Bi_6]^{9-}$.

a model with ordered *Pn* atoms no contact to other symmetry equivalent *Pn* atoms occurs. Due to the occupancy of this site by 2/3 of Bi3 in $K_{10}Ga_3Bi_{6.65}$ the formation of $[Bi_2]$ dumbbells with an average Bi–Bi distance of 2.734 Å is anticipated (Figure 4b). This distance is shorter than in the singly bonded $[Bi_2]^{2-}$ unit (1.51 × 2 = 3.02 Å[23]) and closer to range of doubly bonded $[Bi_2]^{-}$ (1.41 × 2 = 2.82 Å[23]) and even triply-bonded Bi_2 units (1.35 × 2 = 2.70 Å[23]). Bi–Bi distances in Zintl phases are generally longer due to the anionic charge located at the Bi atoms. Two-bonded Bi atoms in KBi[24] reveal Bi–Bi distances longer than 3 Å. The smallest anion has been described as a doubly-bonded Bi dumbbell $[Bi{=}Bi]^{2-}$ [25] in K_3Bi_2, while the tetrameric planar zigzag $[Bi_4]^{4-}$ unit[26] in K_5Bi_4 features a delocalized double bond. According to the 8-N rule both compounds contain an additional free electron which most likely is delocalized. $[Bi_2]$ dumbbells are found in several binary *A*–Bi (*A* = K, Cs) phases and show a Bi–Bi distance of 2.975 Å in Cs_3Bi_2.[27] K_5Bi_4[28] contains a planar zigzag $[Bi_4]^{4-}$ tetramer with six delocalized electrons. Both compounds contain according to the 8-N rule one additional electron which most likely is fully delocalized over the structure (metallic). Consequently, the rather short Bi–Bi distance of 2.734 Å in $K_{10}Ga_3Bi_{6.65}$ reveals a higher bond order than a single bond.

Despite the different atoms or the different connection of the Bi atoms in the $[Ga_3Bi_6]^{9-}$ subunits the potassium atoms form almost regular trigonal prismatic coordination polyhedra around the Ga and Bi atoms (Figure 5a). The prisms of one unit are linked within the *ab* plane by sharing rectangular faces. Further, the remaining Bi atoms (Figure 5b) are encapsulated by trigonal antiprisms of K atoms. In the unit cell, $[Ga_3Bi_6]^{9-}$ units are shifted by ½ in [001] direction with respect to each other. As a consequence the vertices of the prisms of one unit become caps of the outside rectangular faces of the prisms surrounding neighboring $[Ga_3Bi_6]^{9-}$ units (Figure 5c).

Discussion

According to the Zintl-Klemm concept and the (8-N) rule, the $[Ga_3Bi_6]$ unit contains three three-bonded (3b-Ga^0), three two-bonded (2b-Bi^{1-}) and three singly-bonded (1b-Bi^{2-}) atoms giving the polyanion $[Ga_3Bi_6]^{9-}$, and its charge is balanced by nine K cations. There are in average almost 2/3 Bi3 atoms per one $[Ga_3Bi_6]$ units resulting in the formula $K_{10}[Ga_3Bi_6]Bi_{2/3}$. Charge balance is reached, if an almost equal ratio of singly and doubly bonded Bi_2 dumbbells according to $[Bi\text{-}Bi]^{4-}$ and $[Bi{=}Bi]^{2-}$, respectively, are present, resulting in the overall formula

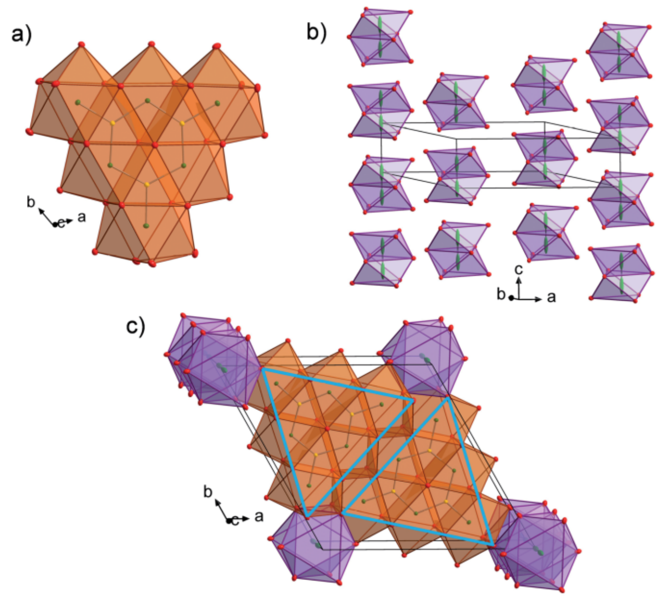


Figure 5. (a) Packing of trigonal prisms of K atoms around $[Ga_3Bi_6]^{9-}$ fragments, (b) trigonal antiprisms of K atoms sharing triangular faces and encapsulating atoms of $[Bi_2]$ dumbbells, and (c) both types of polyhedra. Gallium atoms are shown in yellow, bismuth in green and potassium in red color, the displacement ellipsoids are drawn at a 50 % probability level.

$(K^+)_{10}[Ga_3Bi_6]^{9-}([Bi\text{-}Bi]^{4-})_{1/6}([Bi{=}Bi]^{2-})_{1/6}$. Since the value obtained from the single crystal structure determination is slightly smaller (0.647(4) instead of 0.667), statistically a small amount of Bi_2 dumbbells might be replaced by isolated Bi^{3-} as anticipated for *Pn* atoms before in $K_{10}Ga_3As_{6.33}$ and $K_{10}Ga_3Sb_{6.33}$.

Note added in Proof: During the revision of this manuscript, it came to our attention that a compound with similar composition $K_{10}Ga_3Bi_{6.33}$ has been described in a PhD Thesis (S. Klos, Dissertation Thesis, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany, 2018). The lower Bi content does however not hint for Bi–Bi dumbbell formation.

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Keywords: Zintl-anion; Bismuth; Gallium; Crystal structure

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