Zintl Ions Hot Paper

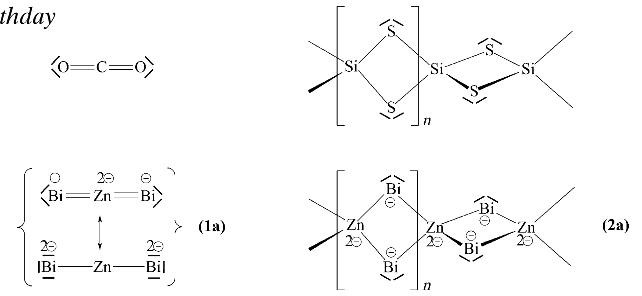
DOI: 10.1002/ange.201404343

Bi–Zn Bond Formation in Liquid Ammonia Solution: $[Bi{-}Zn{-}Bi]^{4-}$, a Linear Polyanion that is Iso(valence)-electronic to CO_2**

*Christian B. Benda, Tobias Köchner, Raphaela Schäper, Stephan Schulz, and Thomas F. Fässler**

Dedicated to Professor R. Nesper on the occasion of his 65th birthday

Abstract: *Reactions of the zinc(I) complex $[Zn_2(Mesnacnac)_2]$ (Mesnacnac = $[(2,4,6\text{-}Me_3C_6H_2)NC(Me)]_2CH$) with solid K_3Bi_2 dissolved in liquid ammonia yield crystals of the compound $K_4[ZnBi_2]\cdot(NH_3)_{12}$ (**1**), which contains the molecular, linear heteroatomic $[Bi{-}Zn{-}Bi]^{4-}$ polyanion (**1a**). This anion represents the first example of a three-atomic molecular ion of metal atoms being iso(valence)-electronic to CO_2 and being synthesized in solution. The analogy of the discrete $[Bi{-}Zn{-}Bi]^{4-}$ anion and the polymeric $^1_\infty[(ZnBi_{4/2})^{4-}]$ unit to monomeric CO_2 and polymeric SiS_2 is rationalized.*



Scheme 1. Comparison and analogy between various monomeric and polymeric 16 VE species: CO_2, SiS_2, and the two isomeric forms $[ZnBi_2]^{4-}$ (**1a**) and $^1_\infty[(ZnBi_{4/2})^{4-}]$ (**2a**) in $K_4[ZnBi_2]\cdot(NH_3)_{12}$ (**1**) and Ba_2ZnBi_2 (**2**),[8] respectively.

Beside the discussion on carbon dioxide as a greenhouse gas and on the importance of carbon dioxide as one of the most abundant carbon sources,[1] CO_2 represents a rather interesting case with respect to chemical bonding. The linear molecule with 16 valence electrons (VE) unequivocally exhibits two double bonds between C and O atoms. Multiple bond formation between heavier atoms in homologous molecules, however, is one of the most controversially discussed issues in chemistry.[2] Whereas CO_2 is best described with double bonds as is typical for elements of the second period, the bonding situation in the heavier homologue SiS_2 is less clear, and it is well-established that ionic contributions have a drastic influence on the chemical bond in monomeric SiS_2.[3] However, the consequence with respect to stability is indicated by the existence of allotropes under standard conditions: CO_2 is a monomeric gas with double bonds, which can be transformed to the structure of the quartz polymorph SiO_2 only under extreme conditions, such as high pressure and temperature.[4] By contrast, SiS_2 forms polymers with exclusively single-bonded atoms at ambient conditions,[5] and other modifications of SiS_2 can be realized only under more drastic conditions, such as solid argon matrix isolation techniques[6] and by electrical discharge experiments,[7] indicating linear and cyclic units of monomeric SiS_2, respectively (Scheme 1).

The concepts of multiple-bond formation between two main-group atoms have been extensively discussed in detail for many of the lighter main-group-element compounds that are iso(valence)-electronic to CO_2, such as $[C_3]^{4-}$, $[BN_2]^{3-}$, $[CN_2]^{2-}$, $[BC_2]^{5-}$, $[CBN]^{4-}$,[9,10] $[BePn_2]^{4-}$ (Pn = P, As, Sb),[11] and $[BPn_2]^{3-}$ (Pn = P, As).[12] Furthermore, the concept of CO_2-analogous molecules can also be extended to heavier homologues of the main-group elements as it was shown for several X=Y=X molecules, and multiple bonds are even formed to Group 11 and 12 metals.[13] Recently we have also shown the existence of the highly charged 16 VE species $[Sn{=}Zn{=}Sn]^{6-}$ in the intermetallic compounds Na_6ZnSn_2 and $Na_{20}Zn_8Sn_{11}$.[14] The three-atomic ions each have a linear structure, whereas the Zintl phase Ba_2ZnBi_2 is a rare example with a polymeric anion $^1_\infty[(ZnBi_{4/2})^{4-}]$,[8] which is isostructural to SiS_2. Interestingly, most of the anionic 16 VE species were synthesized by high-temperature solid-state reactions and exist (with alkali or alkaline-earth metal counterions) solely in neat solids, whereas only a few molecular ions such as $[NO_2]^+$, $[N_3]^-$, $[NS_2]^+$, and $[PCS]^-$ have been obtained in solution.[10]

We report herein on the synthesis of the first compound with an isolated linear $[ZnBi_2]^{4-}$ ion (**1a**) formed in solution under very mild reaction conditions by the reaction of the binary bismuthide K_3Bi_2 with the low-valent Zn^I compound $[Zn_2(Mesnacnac)_2]$ in liquid ammonia (Mesnacnac = $[(2,4,6\text{-}Me_3C_6H_2)NC(Me)]_2CH$).[15] $[Zn_2(Mesnacnac)_2]$ is a mild reducing agent that was shown to react under formation of Zn^{II} compounds.[16] Furthermore, $[Zn_2(Mesnacnac)_2]$ disproportionates in liquid ammonia with subsequent formation of Zn metal and Zn^{II} species.[17]

Triggered by our results on the formation of $[Bi_4]^{6-}$, which is the polyanion with the highest negative charge per atom obtained in solution,[18] and of the $^1_\infty[(Zn(\eta^3{:}\eta^3\text{-}Ge_9)]^{2-}$

---

[*] C. B. Benda, T. Köchner, Prof. Dr. T. F. Fässler
Department Chemie, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
E-mail: thomas.faessler@lrz.tum.de
R. Schäper, Prof. Dr. S. Schulz
Fakultät für Chemie, Universität Duisburg-Essen
Universitätsstrasse 5–7, 45141 Essen (Germany)

[**] C.B.B. thanks the TUM Graduate School for support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404343.

polymer obtained by the reaction of $[Ge_9]^{4-}$ with $[Zn_2(\text{Mesnacnac})_2]$ that contains a $[Zn{-}Zn]^{2+}$ unit,[17] we investigated the reactivity of polybismuthide-containing solutions with Zn^I organyls. We have shown recently that under similar experimental conditions the reaction of $[Ge_9]^{4-}$ with Zn^I compounds leads to the polymeric $^1_\infty[Zn(Ge_9)]^{2-}$ anion,[17] whereas the reaction of $[Ge_9]^{4-}$ with the Zn^{II} compound $Zn(C_6H_5)_2$ leads to $[(C_6H_5)Zn(\eta^4\text{-}Ge_9)]^{3-}$.[19] Thus the employment of Zn^I compounds had a dramatic influence on the product formation which has been attributed to a disproportionation reaction of the Zn^I compound.[17] Therefore we modified the known reaction of solutions of K_5Bi_4 with $Zn(C_6H_5)_2$, which occurred with formation of $[Zn@(Zn_8Bi_4)@Bi_7]^{5-}$,[20] and replaced $[Zn(C_6H_5)_2]$ by Zn^I compounds as reactants. The reaction of $[Zn_2(\text{Mesnacnac})_2]$ with K_3Bi_2 and K_5Bi_4 in liquid ammonia in the presence of [18]crown-6 and [2.2.2]crypt, respectively, led to $K_4[ZnBi_2](NH_3)_{12}$ (**1**) containing the linear $[Bi{-}Zn{-}Bi]^{4-}$ unit (**1a**; Scheme 2). The unit cell of a single crystal of compound **1** contains four isolated linear [Bi−Zn−Bi] units (**1a**), 16 K cations, and 48 ammonia molecules, and thus the charge of **1a** is −4. **1a** is the first three-atom 16 VE compound that contains the two possible allotropic forms of CO_2 and SiS_2. The anion **1a** is also the first metal-atom-containing CO_2 analogue obtained in solution.

$$2\,K_3Bi_2 + L_2Zn_2 \longrightarrow (K^+)_4[ZnBi_2]^{4-} + [Bi_2]^{2-} + 2\,K^+ + Zn^{2+} + 2L^-$$

Scheme 2. Possible reaction for the formation of the $[ZnBi_2]^{4-}$ anion from K_3Bi_2 in the presence of the $[Zn{-}Zn]^{2+}$ complex in liquid ammonia.

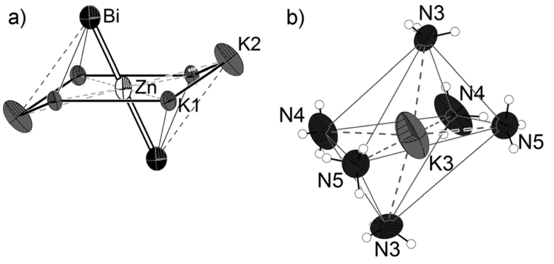


Figure 1. a) The $[ZnBi_2]^{4-}$ unit (**1a**) with its K environment. b) The $[K(NH_3)_6]^+$ complex. Ellipsoids of the atoms are set at 50% probability at 100 K. Selected distances [Å] and angles [°]: Zn1–Bi1 2.5528(5), Zn1–K1 3.591(2)–3.608(2), Zn1–K2 3.6121(2), Bi1–K1 3.940(2), 3.943(2), Bi1–K2 4.0704(5), 4.0703(5), K1–K1 3.740(3), K1–K2 3.598(2), 3.601(2), K3–N3 2.97(1), K3–N4 2.92(1), K3–N5 2.898(13); Bi1-Zn1-Bi1 180.

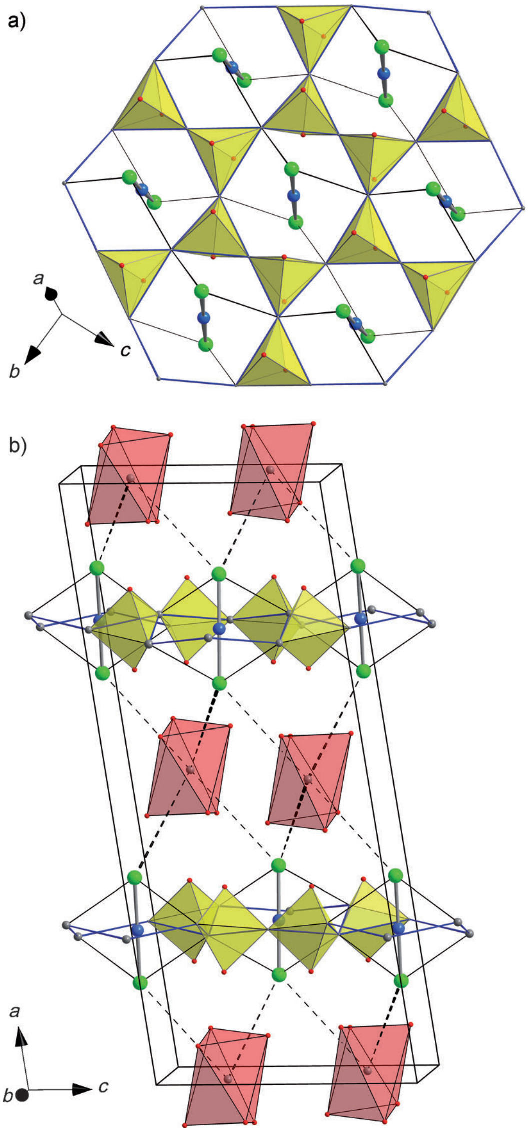


Figure 2. a) One layer of $[ZnBi_2]^{4-}$ units with its K and N environment emphasizing the K Kagomé net-like layers in **1**. b) The layers are separated by distorted $[K(NH_3)_6]^+$ octahedra. Zn blue, Bi green, K gray, N red.

The K1 and K2 atoms form Kagomé net-like layers of three- and six-membered K-rings with a mean K−K distance of 3.67 Å (Figure 2). The K−K distances in compound **1** appear rather short but compare well to the shortest distance those in the neat solid K_4ZnP_2 with $d(K{-}K) = 3.73$ Å.[13] The K_6 rings are not planar but exhibit a chair-type conformation. In the center of the K_6 hexagon the Zn1 atom is positioned with the orientation of the linear $ZnBi_2$ unit almost, but not fully, perpendicular to the mean plane of the K1 atoms and with a tilt angle of 65.63(1)° with respect to the mean plane. Consequently there are three shorter K−Bi distances with $d(Bi1{-}K1) = 3.940(2)$ (twice) and $d(Bi1{-}K2) = 4.0704(5)$ Å (Figure 1a). The K−Bi distances are considerably longer than in the neat solid K_5Bi_4, in which the K−Bi distances range from 3.53 to 3.80 Å,[21] whereas the K−Zn distances (3.591(2) to 3.6121(2) Å) fall in the range of those found in neat solids such as K_4ZnP_2 and $KZnF_3$ with $d(Zn{-}K) = 3.58$[22] and 3.51 Å,[23] respectively.

The triangles of K atoms (2 × K1 and K2) of the Kagomé net-like layers are capped above and below the plane by the N atom of a solvate ammonia molecule (N1 and N2) with a mean distance of $d(K{-}N) = 2.90$ Å. The mean planes of the K atom layers lie parallel to the crystallographic *bc* plane and are separated from each other by layers of distorted $[K(NH_3)_6]^+$ octahedra (Figure 2b). Mean K−N distances in the $[K(NH_3)_6]^+$ complexes are $d(K3{-}N) = 2.91$ Å (Figure 1b) and are thus in the expected range found in compounds with NH_3 molecules coordinating to K cations.[18]

The two equivalent Zn–Bi bonds in **1a** of 2.553(1) Å are considerably shorter than the sum of Pauling's single bond covalent radii of Zn and Bi (2.77 Å),[24] and the angle Bi–Zn–Bi is 180° by symmetry (Figure 1a). As a consequence, the structure of the linear polyanion **1a** adopts perfect local $D_{\infty h}$ symmetry. Most intriguingly, the Zn–Bi bond length is significantly shorter than that in the ternary Zintl phase Ba_2ZnBi_2 (2.86 Å) with the SiS_2-analogous polymer with exclusively single-bonded atoms (Scheme 1),[8] which strongly supports the multiple bond character between the atoms in **1a**.[25]

To gain a better insight into the bonding of the linear $[Bi{-}Zn{-}Bi]^{4-}$ unit (**1a**), we investigated the molecular orbital diagram and applied different population analyses at the BP/SVP and PBE0/TZVPP levels. For charge compensation of **1a**, the conductor-like screening model (COSMO) or polarized continuum model (PCM) approaches were used, yielding negative energies for all occupied molecular orbitals.

As depicted in Figure 3, the lowest-lying molecular orbitals 28 and 29 show mainly Bi s-orbital contributions, whereas the next higher five orbitals 30 to 34 are more or less unperturbed filled Zn d-orbitals. The molecular orbitals $35\sigma_g$ and $36\sigma_u$ are consistent with the Zn–Bi σ-bonding and σ-antibonding orbitals, respectively. Most intriguing are orbitals $37\pi_u$ and $38\pi_u$ that unequivocally describe the π bonds between the metals atoms Bi and Zn, followed by the lone pair orbitals $39\pi_g$ and $40\pi_g$. Thus the highest-occupied orbitals directly correspond to the MOs of CO_2. A gap of circa 2.5 eV separates the HOMOs from the LUMO 41. The π-orbital contribution hints at resonance structure **III** (Scheme 3).

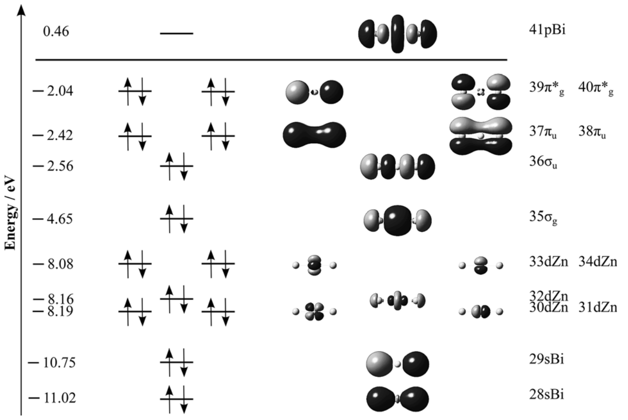
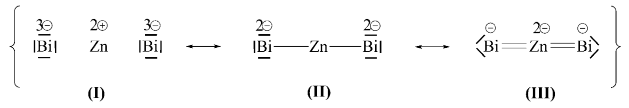


Figure 3. Molecular orbital diagram for the linear $[Bi{-}Zn{-}Bi]^{4-}$ unit calculated at the BP/SVP/PCM level (acetonitrile, $\varepsilon = 36.64$[26]).

Natural population analysis (NPA) and population analysis based on occupation numbers (PABOON) at the BP/SVP level indicate negative partial charges for the Bi atoms (NPA/PABOON: −2.38/−2.32) and positive partial charges for the Zn atom (NPA/PABOON: +0.75/+0.64) in $[Bi{-}Zn{-}Bi]^{4-}$. Comparable results are obtained at the PBE0/TZVPP level. Mulliken and, even more, Loewdin population analyses show a strong dependence on the method/basis set combination and are therefore regarded as less reliable. Considering the possible resonance structures for **1a** (Scheme 3), the partial charges obtained from different population analyses show a tendency for resonance structure **II**. Furthermore, the Wiberg bond indices[27] for the Bi–Zn bond with 0.92 (BP/SVP/PCM) and 0.89 (PBE0/TZVPP/PCM) account for a two-bonded central Zn atom and two single-bonded terminal Bi atoms in **1a** (for details, see Table S2 in the Supporting Information). Considering the molecular orbital analysis and the partial charges we conclude that the bond situation is best described with resonance structures **II** and **III**.



Scheme 3. Possible resonance structures of **1a**.

In the course of completing this manuscript,[15] a high-temperature synthesis from the elements of the neat solid K_4ZnBi_2 containing a slightly bent $[ZnBi_2]^{4-}$ unit (177.3°) but with the same short Zn–Bi bond has been reported.[28] However, as in case of a typical Zintl phase the anion is surrounded by 17 K atoms and considerable shorter K–Bi (3.517 Å–3.682 Å) and K–Zn (3.470 Å–3.588 Å) bonds compared to 6 more loosely bound K atoms in the solvate structure **1** reported herein.

In summary, we presented the synthesis of the compound $K_4[ZnBi_2](NH_3)_{12}$ (**1**) with the linear heteroatomic polyanion $[Bi{-}Zn{-}Bi]^{4-}$ by the reaction of $[Zn_2(Mesnacnac)_2]$ with K_3Bi_2 and K_5Bi_4 in liquid ammonia. From solutions of the neat solid K_3Bi_2[29] and [2.2.2]crypt in liquid ammonia we recently obtained the compound $[K([2.2.2]crypt)]_2[Bi_2](NH_3)_4$ with isolated $[Bi{=}Bi]^{2-}$ polyanions.[18] In the presence of $[Zn_2(Mesnacnac)_2]$, formally the insertion of a Zn atom, most likely originating from the disproportionation reaction of the $[Zn{-}Zn]^{2+}$ unit in liquid ammonia,[17] into the Bi–Bi bond of the Bi_2 unit occurs, yielding the $[ZnBi_2]^{4-}$ anion. The electrons for the reduction may originate from the K_3Bi_2 phase, which exhibits one extra electron per formula unit K_3Bi_2 (Scheme 1).

Strong experimental indicators for a multiple bond character are bond energies, stretching frequencies, and bond lengths if they can be compared to the singly bonded atoms of the same type, whereas calculated quantum-chemical properties are often debatable. The 16 VE species $[ZnBi_2]^{4-}$ represents a rare case in which bond lengths for both isomeric forms, the discrete ionic $[ZnBi_2]^{4-}$ unit (**1a**) and the polymeric $^{1}_{\infty}[(ZnBi_{4/2})^{4-}]$ species (**2a**),[8] are accessible through single-crystal structure determination. Bond shortening in monomeric **1a** by 9% with respect to polymeric **2a** is in the same range as the contraction of two carbon atoms by increasing the C–C multiple bond character.

Experimental Section

General: All manipulations and reactions were performed under a purified argon atmosphere, using standard Schlenk-line and glovebox techniques. The Zintl phases of the nominal composition K_5Bi_4 and K_3Bi_2 were prepared from mixtures of the elements in sealed tantalum containers, which were encapsulated in evacuated fused silica tubes. K_5Bi_4: 430 mg (11.0 mmol) K, 1672 mg (8.00 mmol) Bi. K_3Bi_2: 516 mg (13.2 mmol) K, 1672 mg (8.00 mmol) Bi. These mixtures were heated to 600 °C with a rate of $2\,°C\,min^{-1}$, held at this temperature for 7 days and then slowly cooled to room temperature with a rate of $0.1\,°C\,min^{-1}$. K_5Bi_4 contained small amounts of K_3Bi_2 (see below). $[Zn_2(Mesnacnac)_2]$ was synthesized according to the literature method.[30] [2.2.2]crypt was dried in vacuo. [18]crown-6 was sublimed under dynamic vacuum at 80 °C. Liquid ammonia was dried and stored over sodium metal.

$K_4[ZnBi_2](NH_3)_{12}$ (**1**): a) The Zintl phase with the nominal composition of K_5Bi_4 (75 µmol, 77 mg), [2.2.2]crypt (300 µmol, 113 mg), and $[Zn_2(Mesnacnac)_2]$ (75 µmol, 60 mg) were dissolved in liquid ammonia (ca. 2 mL) at −78 °C. The obtained dark-purple solution was stored at −70 °C. After six months, black block-shaped crystals were isolated with approximately 20 % yield (based on the Zn complex) and characterized by single-crystal X-ray diffraction.

b) The Zintl phase with the nominal composition of K_3Bi_2 (75 µmol, 40 mg), [18]crown-6 (150 µmol, 40 mg), and $[Zn_2(Mesnacnac)_2]$ (75 µmol, 60 mg) were dissolved in liquid ammonia (ca. 2 mL) at −78 °C. The obtained dark-purple solution was stored at −70 °C. After five months, black block-shaped crystals were isolated in circa 20 % yield (based on the Zn complex) and characterized by single-crystal X-ray diffraction.

Further characterization by IR and Raman spectroscopy could not yet be carried out because the product was obtained as tiny crystals that easily lose ammonia and were embedded in the residual bulk material.

Single-crystal structure determination of **1**: The air- and moisture-sensitive crystals of **1** were transferred from the reaction mixture that was cooled with dry-ice/isopropanol into perfluoropolyalkyl ether oil cooled with a stream from liquid nitrogen. The single crystal was fixed on a glass capillary and positioned in a 100 K cold N_2 stream using the crystal cap system. Data collection at 100(2) K: Oxford-Diffraction Xcalibur3 diffractometer (MoK_α radiation). The structure was solved by Direct Methods and refined by full-matrix least-squares calculations against F^2 (SHELXL-97).[31] CCDC 972871 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound **1** crystallized as black block-shaped crystals with the size of $0.1\times0.1\times0.1\,mm^3$; unit cell parameters: $a=28.5688(13)$, $b=7.2241(4)$, $c=12.3033(6)$ Å, $\beta=97.830(4)°$, $V=2155.5(2)$ Å^3; monoclinic, space group $C2/c$ (No. 15), $Z=4$, $\rho_{calc}=2.23\,g\,cm^{-3}$, $\mu=15.57\,mm^{-1}$, $\theta_{max}=27.50°$, 5510 measured reflections, 2894 independent reflections, $R_{int}=0.0767$, $R_1=0.0477$, and $wR_2=0.1234$ for reflections with $I>2\sigma(I)$, $R_1=0.0752$, and $wR_2=0.1299$ for all data.

Powder X-ray diffraction: Phase analyses of the Zintl phases of the nominal compositions "K_3Bi_2" and "K_5Bi_4" were performed using a Stoe STADI P diffractometer (Ge(111) monochromator; $CuK_{\alpha1}$ radiation) equipped with a linear position-sensitive detector (Mythen), and measured in Debye–Scherrer mode. Whereas K_3Bi_2 appears as a single phase, the diffractogramm of K_5Bi_4 showed additional reflections of K_3Bi_2 (see the Supporting Information, Figure S2 and S3 of reference [18]). Data analysis was carried out using the Stoe WinXPOW software package.[32]

The calculations were performed with the quantum-chemical programs TURBOMOLE 6.3[33] and Gaussian09 rev. B.01[34]. The structure was optimized with the DFT functional BP86[35,36] and the hybrid DFT functional PBE0[36–39] using the def2-TZVPP[40] and def2-SVP basis sets, respectively. An effective core potential (ECP) was used for Bi (ecp-46).[41] The COSMO solvation model[42] (for TURBOMOLE) with standard parameters and a dielectric constant of $\varepsilon=36.64$ (acetonitrile at $T=293.2$ K)[26] and PCM (for Gaussian09) with the option "solvent = acetonitrile" were used for charge compensation. For comparison, results obtained with a dielectric constant of $\varepsilon=16.61$ (ammonia[43]) for COSMO are given in the Supporting Information, Table S2. The symmetry was constrained to the point group D_{6h}. A frequency analysis showed no imaginary frequencies, proving a local minimum on the potential energy surface. Additionally, electric charges were calculated by NPA,[44] PABOON,[45,46] Mulliken,[47] and Loewdin.[48] Wiberg Bond Indices were calculated with NBO 3.1 as implemented in Gaussian09.[27,49]

The Supporting Information contains illustrations of the displacement parameters of Zn1 and K2 (Figure S1), the orientation of the $ZnBi_2$ units (Figure S2), and also a table of selected crystallographic and refinement data for compound **1**. Tables S2 and S3 contains the results for the population analysis applying COSMO for acetonitrile and ammonia, respectively, and Table S4 has calculated bond lengths.

Received: April 16, 2014

Keywords: bismuth · carbon dioxide · solid-state structures · zinc · Zintl ions

[1] See, for example, a recent review on this topic: M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662–8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537.

[2] a) P. P. Power, *J. Chem. Soc. Dalton Trans.* **1998**, 2939–2951; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504; c) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; d) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923.

[3] M. Friesen, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1097–1100.

[4] a) V. Iota, C. S. Yoo, H. Cynn, *Science* **1999**, *283*, 1510–1513; b) S. Serra, C. Corazon, G. L. Chiarotti, S. Scandolo, E. Tossatti, *Science* **1999**, *284*, 788–790; c) C.-S. Yoo, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7949–7966.

[5] M. A. Zwijnenburg, R. G. Bell, F. Corà, *J. Solid State Chem.* **2008**, *181*, 2480–2487.

[6] H. Schnöckel, R. Köppe, *J. Am. Chem. Soc.* **1989**, *111*, 4583–4586.

[7] L. A. Mück, V. Lattanzi, S. Thorwirth, M. C. McCarthy, J. Gauss, *Angew. Chem.* **2012**, *124*, 3755–3758; *Angew. Chem. Int. Ed.* **2012**, *51*, 3695–3698.

[8] B. Saparov, S. Bobev, *Inorg. Chem.* **2010**, *49*, 5173–5179.

[9] a) H. J. Meyer, *Z. Anorg. Allg. Chem.* **1991**, *593*, 185–192; b) J. Goubeau, W. Anselment, *Z. Anorg. Allg. Chem.* **1961**, *310*, 248–260; c) M. Wörle, H. Meyer zu Altenschildesche, R. Nesper, *J. Alloys Compd.* **1998**, *264*, 107–114; d) M. Häberlen, J. Glaser, H. J. Meyer, *J. Solid State Chem.* **2005**, *178*, 1478–1487; e) N. G. Vannerberg, *Acta Chem. Scand.* **1962**, *16*, 2263; f) O. Reckeweg, H.-J. Meyer, *Angew. Chem.* **1998**, *110*, 3619–3621; *Angew. Chem. Int. Ed.* **1998**, *37*, 3407–3410; g) H. J. Meyer, *Z. Anorg. Allg. Chem.* **1991**, *594*, 113–118.

[10] T. M. Klapötke, *Angew. Chem.* **1994**, *106*, 1651–1652; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1575–1576.

[11] M. Somer, M. Hartweg, K. Peters, T. Popp, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1991**, *595*, 217–223.

[12] a) M. Somer, W. Carrillo-Cabrera, K. Peters, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **2000**, *626*, 897–904; b) H. G. von Schnering, M. Somer, M. Hartweg, K. Peters, *Angew. Chem.* **1990**, *102*, 63–64; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 65–67.

[13] See, for example: $[ZnN_2]^{4-}$ in Ca_2ZnN_2, $[MP_2]^{4-}$ ($M=$ Zn, Cd, Hg), $[ZnAs_2]^{4-}$ in K_4ZnAs_2, $[AuPn_2]^{5-}$ ($Pn=$ P, As), $[CuPn_2]^{5-}$ ($Pn=$ As, Sb): a) M. Y. Chern, F. J. DiSalvo, *J. Solid State Chem.* **1990**, *88*, 528–533; b) B. Eisenmann, M. Somer, *Z. Naturforsch. B* **1989**, *44*, 1228–1232; c) Y. Prots, U. Aydemir, S. S. Öztürk, M. Somer, *Z. Kristallogr. New Cryst. Struct.* **2007**, *222*, 163–164; d) B. Eisenmann, J. Klein, M. Somer, *J. Alloys Compd.* **1992**, *178*,

431–439; e) G. Savelsberg, H. Schäfer, *Z. Naturforsch. B* **1979**, *34*, 771–773.

[14] S.-J. Kim, F. Kraus, T. F. Fässler, *J. Am. Chem. Soc.* **2009**, *131*, 1469–1478.

[15] C. B. Benda, Dissertation, Technische Universität München, Verlag Dr. Hut **2013**, ISBN: 978-3-8439-1443-7.

[16] a) S. Gondzik, S. Schulz, D. Bläser, C. Wölper, R. Haack, G. Jansen, *Chem. Commun.* **2014**, *50*, 927–929; b) S. Gondzik, S. Schulz, D. Bläser, C. Wölper, *Chem. Commun.* **2014**, *50*, 1189–1191.

[17] C. B. Benda, R. Schäper, S. Schulz, T. F. Fässler, *Eur. J. Inorg. Chem.* **2013**, 5964–5968.

[18] C. B. Benda, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2014**, *640*, 40–45.

[19] J. M. Goicoechea, S. C. Sevov, *Organometallics* **2006**, *25*, 4530–4536.

[20] J. M. Goicoechea, S. C. Sevov, *Angew. Chem.* **2006**, *118*, 5271–5274; *Angew. Chem. Int. Ed.* **2006**, *45*, 5147–5150.

[21] F. Gascoin, S. C. Sevov, *Inorg. Chem.* **2001**, *40*, 5177–5181.

[22] B. Eisenmann, M. Somer, *Z. Naturforsch. B* **1989**, *44*, 1228–1232.

[23] M. M. Lukina, G. P. Klientova, *Sov. Phys. Crystallogr.* **1969**, *14*, 314–315.

[24] L. Pauling, *J. Am. Chem. Soc.* **1947**, *69*, 542–553.

[25] The Zn–Bi bond is also considerably shorter compared to that in the heteroatomic clusters $[Zn@Zn_8Bi_4@Bi_7]^{5-}$ and $[Zn@Zn_5Sn_3Bi_3@Bi_5]^{4-}$, with Zn–Bi bond lengths ranging from d(Zn–Bi) = 2.60 to 2.97 Å; see: a) F. Lips, S. Dehnen, *Angew. Chem.* **2009**, *121*, 6557–6560; *Angew. Chem. Int. Ed.* **2009**, *48*, 6435–6438; b) Ref. [20].

[26] D. R. Lide, *Handbook of Chemistry and Physics*, *Vol. 89*, CRC, Boca Raton, FL, **2008–2009**, pp. 6–156.

[27] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.

[28] Q. Qin, L. Zhou, Y. Wang, R. Sang, L. Xu, *Dalton Trans.* **2014**, *43*, 5990–5993.

[29] F. Gascoin, S. C. Sevov, *J. Am. Chem. Soc.* **2000**, *122*, 10251–10252.

[30] S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics* **2009**, *28*, 1590–1592.

[31] SHELXTL, Bruker Analytical X-ray instruments: Madison, WI **1998**.

[32] STOE/WinXPOW, Version 2.08, STOE & Cie GmbH, Darmstadt **2003**.

[33] TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[34] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[35] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[36] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[37] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[38] J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982–9985.

[39] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.

[40] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[41] H. Stoll, B. Metz, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563–2569.

[42] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805.

[43] D. R. Lide, *Handbook of Chemistry and Physics*, *Vol. 89*, CRC, Boca Raton, FL, **2008–2009**, pp. 6–155.

[44] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[45] C. Ehrhardt, R. Ahlrichs, *Theor. Chim. Acta* **1985**, *68*, 231–245.

[46] R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33–45.

[47] R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833–1840.

[48] P. O. Löwdin, *Adv. Quantum Chem.* **1970**, *5*, 185–199.

[49] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO Version 3.1.