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$[ZnBi_4]^{3-}$ Pentagon in K_6ZnBi_5: Aromatic All-Metal Heterocycle

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Supporting Information

ABSTRACT: The first aromatic all-metal heterocycle, $[ZnBi_4]^{3-}$, found in the metallic salt, K_6ZnBi_5, has been synthesized and structurally characterized. The exactly planar $[ZnBi_4]^{3-}$ pentagon with six π electrons coupled with multiply bonded Zn−Bi and Bi−Bi bonds, multicentered π-conjugated bonding, and negative nucleus-independent chemical shift values reveals its aromatic character. The metallic nature of K_6ZnBi_5 has been established by Pauli-type temperature-independent paramagnetism and theoretical analysis of the band structure and total/partial density of states.

Zintl clusters have been receiving extensive and enduring interest because of their fascinating and diversified structures, intriguing chemical bonding, unique reactivity, and applications in materials science.[1] They are usually rationalized by the Zintl−Klemm concept,[2] the $8 - N$ rule, and Wade−Mingos' rules.[3] The concept of aromaticity describing planar organic rings possessing $4n + 2$ π electrons and having specific stability, seems foreign for all-metal systems such as Zintl clusters as a consequence of the fact that the structurally characterized examples known as the aromatic homoatomic rings Tt_5^{6-} (Tt = Si, Sn, Pb)[4−6] and $(RGa)_3^{2-}$[7] are extremely rare. Their aromaticity has also been examined by NMR spectra.[6] Of note is that the antiaromatic pentagonal $[Pb_5]^{4-}$ has also been reported.[8] Aromatic metallic rings have been observed in gas phases as well-known as Al_4^-,[9] XAl_3^- (X = Si, Ge, Sn, Pb),[10] and Pn_5^- (Pn = P, As, Sb, Bi).[11] These aromatic all-metal rings exhibiting traditional organic aromatic behavior are of special importance in gaining deeper insight into aromaticity. However, to the best of our knowledge, structurally well-defined all-metal heterocycles have not thus far been reported. Herein, we present the first structurally characterized example of aromatic all-metal heterocycles, $[ZnBi_4]^{3-}$, found in the Zintl phase K_6ZnBi_5 (**1**), which is isoelectronic and isostructural with the aromatic anionic tetrazole heterocycle $[HCN_4]^-$. Of note is that a number of transition metal (M)−bismuth ternary Zintl phases such as $Ba_{11}Cd_8Bi_{14}$,[12] $Ca_9Zn_4Bi_9$,[13] $BaZnBi_2$,[14] $SrZnBi_2$,[15] $Yb_9Zn_4Bi_9$,[16] $LnZn_xBi_2$ (Ln = Ce, La, Pr),[17a] AE_2ZnBi_2 (AE = Eu, Sr),[17b] and $LiZnBi$[18] have been known, but all of them possess extended structures except for the Zintl anion $[Zn_9Bi_{11}]^{5-}$[19] obtained from a solution that represented a new type of cage structure.

1 was obtained as silver-gray crystals from the stoichiometric proportion of the elements (see the Supporting Information, where this part is detailed) and characterized by X-ray crystallography.[20] The purity of **1** has been confirmed by powder X-ray diffraction, as shown in Figure S1 in the SI. Such a unique K−Zn−Bi system produced the unprecedented discrete cyclic cluster **1** rather than extended phases previously obtained from the AE−Zn−Bi (AE = Ba, Ca, Sr, Yb, Ce, La) system.[13−17] It can be rationalized by the fact that more monovalent K^+ ions than divalent AE^{2+} required for charge balance prefer the formation of discrete cluster anions instead of extended ones. Of note is that the Li−Zn−Bi system yielded the extended LiZnBi[18] probably as a consequence of the small size of Li^+. Such a scissoring role of alkali metals in the formation of discrete cluster anions has also been observed in other solid synthesis systems.[21] X-ray structural analysis of **1** reveals that it is made of alkali metals and the $[ZnBi_5]$ (**1a**) cluster anion. **1a** has crystallographic C_{2v} symmetry induced by the 2-fold axis running through Zn and Bi_3, as shown in Figures 1a and S2 in the SI. It features an unprecedented, exactly planar $ZnBi_4$ (**1b**) pentagon with a terminal Bi atom that completes the triangular coordination of the sp^2-hybridized heterometal zinc. There are four crystallographically independent K atoms as countercations stabilizing **1a**, as demonstrated in Figure 2. Three of them (K1, K2, and K3) interact with both ring and terminal Bi atoms. Of special note is K4, which is located between the **1b** pentagons to form a one-dimensional $KZnBi_4$ sandwich chain, as demonstrated in Figure 1b, which is somewhat similar to the sandwitch $Li[Sin_5]^{6-}$,[4a] suggestive of the existence of a similar π-conjugated system in **1b** to be detailed later.

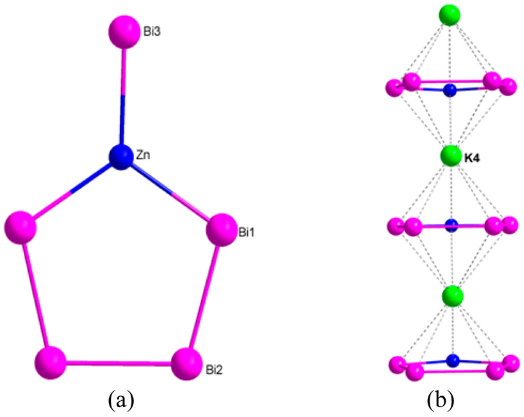

Figure 1. (a) Planar pentagonal structure of **1a**. (b) Infinite sandwich chain of $K[ZnBi_4]$.

Unlike the straightforward geometric structure, the electronic structure of **1a** is quite difficult to rationalize. **1a** can be

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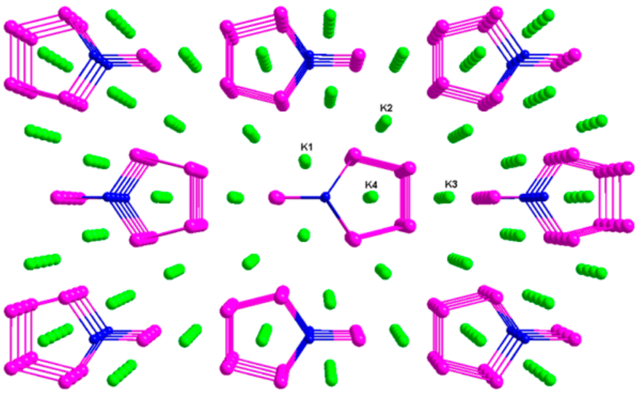

Figure 2. Crystal structure of **1**.

conveniently viewed as resulting from the in situ cycloaddition of ZnBi and Bi_4 driven by the resulting aromaticity to be detailed later. The formal fragment $Bi^{2-}Zn^{2-}$ in $[BiZnBi_4]^{5-}$ is isolobal with the HC fragment of the aromatic anionic tetrazole $[HCN_4]^-$, which is isoelectronic and isostructural with $[BiZnBi_4]^{5-}$. This is supported by the fact that the flat trans-zigzag tetramer Bi_4^{4-} with a delocalized electron observed in the metallic salt K_5Bi_4 has been well established by Gascoin and Sevov.[22] Further evidence comes from the observation that the transformation to the flat cis-tetramer Bi_4 in **1a** required by the cycloaddition does not change the electronic structure of Bi_4, as indicated by their almost identical bond lengths and angles [*cis*-Bi_4 in **1a**, Bi1−Bi2, 2.990(1) Å, Bi2−Bi2′, 3.065(2) Å, Bi1−Bi2−Bi2′, 104.14(3)°; *trans*-Bi_4^{4-} in K_5Bi_4, Bi1−Bi2, 2.998(2) Å, Bi2−Bi2′, 3.046(3) Å, Bi1−Bi−Bi2′, 106.30(8)°]. It has been well established that K_5Bi_4 appeared as a metallic salt as in the case of K_3Bi_2 ($3K^+ + Bi_2^{2-} + e^-$)[23] with one delocalized electron, that is, $5K^+ + Bi_4^{4-} + e^-$.[22] To examine whether **1** exists as a metallic salt as well, which were usually encountered in potassium polybismuthides such as K_5Bi_4 and K_3Bi_2, we measured the molar susceptibility of **1** over the temperature range 2−300 K. As shown in Figure S3 in the SI, the corrected, positive molar susceptibility and Pauli-type paramagnetic behavior revealed by temperature-independent magnetization clearly indicate that **1** belongs to a very rare class of "metal salt" built of cluster anions with well-defined charge and one or more delocalized free electrons, making them metallic. Such metallic salts were previously known as A_8Tr_{11} (Tr = Ga, In, Tl) with isolated clusters of Tr_{11}^{7-} and a delocalized electron[24] and $K_{10}Tl_7$ with isolated clusters of Tl_7^{7-} and three delocalized electrons.[25] The formation of the above-mentioned metal salts results from balanced requirements between a stable closed-shell electronic structure and the local electroneutrality induced by compact/uniform packing of anions/cations. This is especially the case for alkali metals, more of which than required for a closed-shell structure are needed to achieve a neutral local environment with balanced Fermi energies. As a consequence, **1** has a cluster charge of 5− with an extra delocalized electron over the structure: $6K^+ + [ZnBi_5]^{5-} + e^-$. The cycloaddition of BiZn and Bi_4 is presumably driven by the resulting aromaticity. Because the terminal Bi3 atom needs two electrons to satisfy the "octet" rule, the **1b** pentagon has a charge of 3−. This is consistent with the cycloaddition of Bi_4^{4-} and the Zn atom: the sp^2-hybridized Zn has two electrons to form Zn−Bi1 (or its equivalent) and Zn−Bi3 σ bonds. The remaining empty sp^2 σ and p_z π orbitals of Zn in and perpendicular to the pentagon are available to accept σ and π electrons from *cis*-Bi_4, respectively. Consequently, the discrete *trans*-Bi_4^{4-} in K_5Bi_4 becomes *cis*-Bi_4^{3-} in the **1b** pentagon as a consequence of accepting one σ electron from Zn with the six π electrons retained. Therefore, the planar $[ZnBi_4]^{3-}$ pentagon, which is isoelectronic and isostructural with Bi_5^-, has a total of six π electrons conforming to the structural criterion and $4n + 2$ electron-counting rule for aromaticity, which is believed to account for the occurrence of the cycloaddition Bi_4^{4-} and Zn and finally the formation of **1**.

The aromatic character of the $[ZnBi_4]^{3-}$ pentagon has also been structurally supported by the significantly shorter bond lengths than the corresponding single bonds. The Bi1−Bi2 and Bi2−Bi2′ bond lengths are 2.990(1) and 3.065(2) Å, respectively, with bond orders of 1.36 and 1.02 based on the Pauling formula: $\log(n) = (d_1 - d_n)/0.6$, where d_1 and d_n are the single bond (3.07 Å) for Bi in elemental bismuth and observed distance. The bond elongation of Bi2−Bi2′ presumably results from the fact that the delocalized electron resides for part of the time on the lowest unoccupied molecular orbital (LUMO) of **1a**, which features the Bi2−Bi2′ π^*-antibonding interaction to be detailed later, as in the case of Bi_4^{4-}.[22] This is further supported by the fact that the corresponding value [3.206(1) Å] in $[Bi_4]^{6-}$ with two more electrons is markedly greater.[26] Normal Bi=Bi double bonds in molecular compounds without electronic delocalization and back-donation are 2.8206, 2.833, and 2.8377 Å in $(Tbt)_2Bi_2$, $(2,6\text{-}Mes_2H_3C_6)Bi_2$,[27] and the naked Bi_2^{2-} in $(K\text{-}crypt)_2Bi_2$.[28] The additional structural evidence comes from the markedly shorter Zn−Bi1 distance of 2.736(2) Å than the reported Zn−Bi single bonds [ave 2.847(9) Å][13−16,18] with a Pauling bond order of 1.53 ($d_1 = 2.847$). The similar short Zn−Bi distances causing Zn−Bi π bonding have also been observed in $LnZn_xBi_2$[17a] [2.655(7)−2.780(7) Å] and AE_2ZnBi_2[17b] [2.714(1)−2.7297(7) Å] with tricoordinated Zn. Of note is the even shorter Zn−Bi3 bond [2.659(4) Å], indicative of the significant double bonding as a consequence of the extended π-conjugated system to be detailed below. To further evaluate the aromatic character of the heterometallic pentagon of **1a**, the absolute magnetic shieldings, nucleus-independent chemical shifts (NICSs), at selected points were computed as a function of the electron density, as described by Schleyer et al. in 1996,[29] which were widely recognized as an essential criterion of aromaticity. The theoretical calculation is based on the experimental data without optimization and density functional theory method B3LYP with Lanl2dz basis sets from *Gaussian03*.[30] In order to ensure negative orbital energies of occupied orbitals, a polarizable continuum model[31] is employed. Using the method of Giao-B3lyp from *Gaussian03*, the computed NICS value is −8.3, somewhat similar to that of benzene (−11.5), indicative of the aromaticity of the pentagonal ring of **1a**.

Detailed π-bonding pictures of **1a** can be obtained from visualization of the natural bond order calculation, as shown in Figure S4 in the SI. The Bi1−Bi2 and 4-centered Bi_4 π bonds can be clearly observed in HOMO−5 and HOMO−8, respectively. HOMO−3 is mainly composed of the Bi1−Zn−Bi1′−Bi3 4-centered π bond, accounting for the short Zn−Bi1 and Zn−Bi3 bonds described above. The resonance structures of $[ZnBi_4]^{3-}$ similar to those of $[HCN_4]^-$ are displayed in Figure S5 in the SI. Highest occupied molecular orbital (HOMO) is made of a small amount of Bi2−Bi2′ π-bond and nonbonding orbitals of the other Bi atoms. As expected, the LUMO is mainly made of the Bi2−Bi2 antibonding π^* orbital (64%), responsible for the Bi2−Bi2′ bond elongation described above.

To examine the metallic nature of **1** as described above, theoretical analysis of the band structure and total/partial density of states (DOS/PDOS) of **1** has been carried out by Vienna ab initio simulation package[32] using the projector augmented wave[33] method. As shown in Figures S6 and S7 in the SI, both the band structure and DOS/PDOS clearly reveal the metallic nature of **1**, consistent with Pauli-type temperature-independent paramagnetism. The K 3p and 4s orbitals participate in the band below −3.3 eV and above −2.8 eV, indicating incomplete charge transfer to the cluster anions, responsible for the bond lengths longer than those in the related molecular compounds. Except for the orbitals of K, strong Zn−Bi hybridizations occurring below −3.3 eV are mainly formed by Zn 4s and Bi 6p states. The bands from −1.6 eV to the Fermi level are mainly composed of Zn 3p and Bi 6p orbitals, which are believed to account for the delocalized π bonds of the pentagonal **1a**, and the bands between −2.7 and −1.6 eV are mainly contributed by Zn 3s and 4p and Bi 6p orbitals.

In conclusion, the first aromatic all-metal heterocycle, $[ZnBi_4]^{3-}$, found in the metallic salt **1** has been synthesized and structurally characterized. The exactly planar $[ZnBi_4]^{3-}$ pentagon with six π electrons, which conforms to the structural criterion and $4n + 2$ electron-counting rule for aromaticity, coupled with the multiply bonded Zn−Bi and Bi−Bi bonds, multicentered π-conjugated bonding, and negative NICS values reveals its aromatic character. The metallic nature of **1** has been established by Pauli-type temperature-independent paramagnetism and theoretical analyses of the band structure and DOS/PDOS.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, powder X-ray diffraction, computational description, susceptibility, π-bonding pictures, total/partial density of states, band structure, and crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) Crystallographic data of **1**: a = 15.280(13) Å, b = 5.498(4) Å, c =11.582(11) Å, V = 972.95(14) Å^3, Z = 2, ρ = 4.591 g cm^{-3}, T = 293(2) K, space group *Pmmn* (No. 59), 5989 reflections measured, 975 independent reflections (R_{int} = 0.1679), final R1 = 0.0528 [$I > 2\sigma(I)$], final wR(F^2) = 0.1209 [$I > 2\sigma(I)$], and goodness of fit on F^2 = 1.003.

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