Synthesis and Characterization of A₃Bi₂ (A = K, Rb, Cs) with Isolated Diatomic Dianion of Bismuth, [Bi₂]²⁻, and an Extra Delocalized Electron

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Homonuclear diatomic molecules are the simplest chemical species to manifest the power of atomic attraction, the chemical bond. Yet, despite their simplicity, there are still diatomic species in the yet-to-be-found category. The existence of such species, especially with multiple bonds, among the heavier elements brings always wonder and a degree of disbelief and the challenge to find the answers to the usual questions, why, how, and where else. Recently, we reported the synthesis of the diatomic double-bonded naked dianion $[Bi=Bi]^{2-}$ of the heaviest main-group element of the periodic system.[1] This diatomic molecule with distance of 2.8377(7) Å was characterized in the compound (K-crypt)₂Bi₂ crystallized from ethylenediamine and crypt (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) solution of the intermetallic precursor $K_5In_2Bi_4$. The structure of the precursor, chains of edge-sharing indium-centered tetrahedra of bismuth, and the presence of indium were initially thought to be essential for the formation of the molecule. Nevertheless, it was found later that the molecule can be made in much better yields from a more rational precursor without indium, K_3Bi_2. The structure, bonding, and properties of this precursor with unexpected diatomic bismuth molecules are the subject of this contribution.

Remarkably, large areas of such simple binary phase diagrams as alkali-metal−bismuth are structurally blank, and the stoichiometries of many proposed compounds are estimated only from thermal analysis. Thus, in the systems with K, Rb, or Cs known are only the Laves phases ABi₂ (MgCu₂-type) and the simple octet compounds with isolated bismuth atoms A₃Bi (Li₃Bi- or Na₃As-types). Proposed but structurally unknown are A₃Bi₂ and A₅Bi₄. Their existence, but not exact stoichiometries, has been confirmed by powder X-ray diffraction 40 years ago, and nothing further has been reported since.[2] The structures of liquid melts, on the other hand, have been studied more extensively lately.[3] A maximum in the electrical resistivity of such melts at bismuth fraction of 0.4 (corresponds to A₃Bi₂) suggests a compound formation, and neutron diffraction results have indicated short chains of bismuth atoms in the melts.

Initially, we studied the equimolar regions of the phase diagrams in order to explore for rational precursors for the solution molecule [Bi₂]²⁻, and the compounds K₃Bi₂, Rb₃Bi₂, and Cs₃Bi₂ were found in the products. Later, they were made in high yields from the corresponding stoichiometric mixtures heated at 650 °C for a day and slowly cooled to room temperature (5 °C/h).[4] The
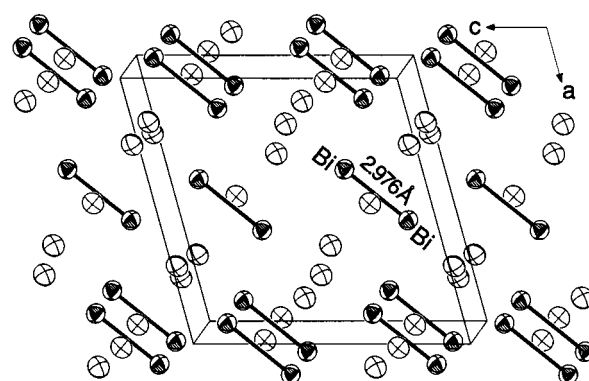

Figure 1. An ORTEP drawing (70% probability level for the thermal ellipsoids) of the structure of Cs₃Bi₂. The [Bi₂]²⁻ dimers are well separated by the cesium cations.

compounds are dark gray and brittle but shiny with metallic luster. They form large lumps of irregular crystals that are easy to separate from the usual second phase of powderish ABi₂. Single-crystal studies of Cs₃Bi₂ showed a very simple structure of isolated dimers of bismuth with long interdimer distances of 5.102(1) Å surrounded by alkali-metal cations (Figure 1).[5] Crystallographically there is only one bismuth atom, and a nearby 2-fold axis of the monoclinic cell generates the dimer. The dimers are all aligned along the direction of the long diagonal of the *a*, *c* face, the [ī01] direction (Figure 1).

Although structurally simple the A₃Bi₂ compounds are electronically puzzling, and it is somewhat difficult to reason their formation and existence. There are three possible ways to rationalize the stoichiometry: (a) the dimers are radicals of Bi₂³⁻; (b) the dimers are Bi₂⁴⁻ with an extra proton in the compound with formula A₃HBi₂; (c) the dimers are Bi₂²⁻ with an extra delocalized electron, that is, $3A^+ + Bi_2^{2-} + e^-$. Magnetic measurements were carried out and clearly indicated temperature-independent magnetization, which automatically excluded the first possibility.[6] Furthermore, the corrected molar susceptibility is positive and indicates Pauli-type paramagnetic behavior consistent with metallic conductivity. This is in agreement with only the third possibility, that is, Bi₂²⁻ dimers with an extra delocalized electron over the structure. Nevertheless, since the metallic paramagnetism is usually a very small positive number as in this

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(4) All operations were carried out in a N₂-filled glovebox with moisture level below 1 ppm. The mixtures of elements were loaded in niobium tubular containers that were later sealed by arc-welding under Ar. The containers were then placed in fused-silica jackets, and the latter were evacuated (below discharge) and sealed.

(5) A quarter-sphere of diffraction data (2θ_max = 50°) was collected at room temperature on CAD4 with Mo Kα radiation from a single crystal of Cs₃Bi₂ (irregular shape, 0.10 × 0.08 × 0.12 mm). Crystal data: monoclinic, C2/c, Z = 4, a = 10.077(1) Å, b = 10.3207(6) Å, and c = 10.145(1) Å, β = 105.21-(1)°, V = 1018.2(2) Å³, μ = 450 cm⁻¹, d_calc = 5.327 g/cm³, R1/wR2 = 4.14/8.30% for 673 observed reflections (I = 2σI) and 24 variables. Lattice parameters of the isostructural Rb₃Bi₂ and K₃Bi₂: a = 9.735(1) Å, b = 10.075-(1) Å, and c = 9.715(1) Å, β = 105.34(1)°, V = 918.9(3) Å³ and a = 9.381-(1) Å, b = 9.794(1) Å, and c = 9.284(1) Å, β = 104.99(1)°, V = 824.0(2) Å³, respectively. The structure solution and refinement (on F²) of the data (after applied empirical absorption corrections) were handled with the SHELXTL V5.1 package.

(6) The magnetization of 50 mg of K₃Bi₂ (sealed in quartz tubes) was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10−290 K. After corrections for the holder and for the ion-core diamagnetism the molar susceptibility was positive and temperature independent in the range (6.0−6.6) × 10⁻⁴ emu/mol. Similar values were obtained for the magnetization of Cs₃Bi₂. Simple two-probe electrical resistivity tests of large crystals of K₃Bi₂ and Cs₃Bi₂ (inside the glovebox) confirmed the metallic behavior at room temperature. Preliminary magnetic measurements of Cs₃Bi₂ at low field (100 Oe) and low temperatures show transition at around 9 K that is reminiscent of a superconducting transition (in Supporting Information). K₃Bi₂ shows similar transition at 7.5 K. (The same transitions are observed in samples made in tantalum containers.) More detailed measurements of the critical fields of the transitions are in progress, and the results of these elaborate studies of the superconductivity will be published separately.

case, the magnetic measurements alone cannot completely over-rule the second possibility, a diamagnetic compound with very small but negative molar susceptibility. Therefore, additional confirmation of the stoichiometry was needed, especially after a number of recent discoveries of hydrogen in supposedly hydrogen-free compounds.[7] Thus, neutron powder diffraction data (time-of-flight mode, $\lambda = 0.7-4.2$ Å, room temperature) were collected from a sample of K_3Bi_2 enclosed in an airtight vanadium container, and the refinement clearly indicated lack of hydrogen in the structure. This conclusion is quite unambiguous since the scattering power of hydrogen is similar to that of potassium and a half of that of bismuth. Therefore, this and the results from the magnetic measurements prove that these compounds can only be rationalized as metals that contain Bi_2^{2-} dimers, three alkali-metal cations, and an electron delocalized over the cations and the antibonding orbitals of the dimer. Such "metallic salts" with "extra" delocalized electrons are very rare but not unprecedented. Known are A_8Tr_{11} for A = K, Rb, Cs and Tr = In, Tl with isolated clusters of Tr_{11}^{7-} and one delocalized electron,[8,9] $K_{10}Tl_7$ with isolated Tl_7^{7-} and three delocalized electrons,[10] and the more complicated $K_{18}Tl_{20}Au_3$ with different species and one extra electron.[11]

Focusing our attention on the dimer itself, we find Bi−Bi distance of 2.976(2) Å. This is by far the shortest Bi−Bi distance in neat solids, that is, solids made by solid-state reactions from the elements. For comparison, the single-bond Bi−Bi distance in elemental Bi is 3.07 Å, and that in the more or less isolated single-bonded Bi_2^{4-} dimer in $Ca_{11}Bi_{10}$ is 3.15 Å.[12] Of course, we can compare the distance with single- and double-bond distances observed in molecular compounds, but this may not be very objective since the atoms of isolated molecules in the latter have only few directional interactions, while usually there are many nondirectional and delocalized strong interactions in neat solids. Thus, the bismuth atoms of the dimer in the molecular (K-crypt)$_2$Bi$_2$ interact only within the dimer since the cations are insulated by the crypt molecule. The atoms of the dimer in Cs$_3$-Bi$_2$, on the other hand, can and do interact also with the surrounding nine Cs-cations (Figure 3 in Supporting Information). Thus, when comparing distances it is more appropriate to compare them in compounds with similar interactions. For example, the

Bi−Bi distance in (K-crypt)$_2$Bi$_2$, 2.8377(7) Å, is more appropriately compared with that in other molecular compounds such as Ph_4Bi_2 and $(Me_3Si)_4Bi_2$ with single Bi−Bi bonds and distances of 2.990(2) and 3.035(3) Å, respectively,[13] and the double-bond distances of 2.8208(8) and 2.833(1) Å in [2,4,6-$\{(Me_3Si)_2CH\}_3H_2C_6]_2Bi_2$ and [$\{2,4,6-Me_3C_6H_2\}_2H_3C_6]_2Bi_2$, respectively.[14] Similarly, it is more appropriate to compare the distances in Cs$_3$Bi$_2$, elemental Bi and Ca$_{11}$Bi$_{10}$. The quite shorter distance in Cs$_3$Bi$_2$, therefore, indicates bond order higher than one.[15]

This distance, on the other hand, is clearly longer than what might be expected for a double bond in a neat solid ($\sim$2.90 Å). The elongation is caused by the extra electron delocalized over the cations and the antibonding states of the dimer, more appropriately written as $[Bi_2]^{(2+\delta)-}$. It should be mentioned here that unlike the paramagnetic O_2 the ground state of Bi_2^{2-} in (K-crypt)$_2$Bi$_2$ is singlet (shown by EPR) with paired electrons on an antibonding orbital.[1] A second antibonding orbital with almost identical energy is available, and it is that orbital that gets partially populated by the delocalized electron in Cs$_3$Bi$_2$, the δ-charge in $[Bi_2]^{(2+\delta)-}$. This results in the elongation of the bond and the observed temperature-independent metallic paramagnetism. The need for the extra cation arises most likely from packing requirements and "solvation" of the dianion by sufficient number of cations. For the formation of these compounds of bismuth it is perhaps important that unlike the lighter pnictogens (Pn) with infinite helical chains of $[Pn_n]^{n-}$ there are no such compounds of bismuth.[16] Attempts to "capture" the extra electron in A_3Bi_2 by either substitution of one bismuth atom by an atom of group 14 in analogy with the substitution of one In in K_8In_{11} by Hg to form the electronically balanced $K_8[In_{10}Hg]$,[17] or addition of a halogen in analogy with the formation of $K_8In_{11}Cl$,[18] are in progress but have been unsuccessful so far.

Remarkable is not only the existence of such almost-double-bonded bismuth dimer in the neat solids A_3Bi_2 but also that it can be "extracted" intact and as a completely double-bonded species into ethylenediamine solutions. (There are many diatomic molecules in neat solids but most of them are insoluble.[19]) During the dissolution process the extra electron is most likely either solvated similarly to when alkali metals are dissolved in crypt-containing ethylenediamine, or simply recombines with any traces of impurities that might be in the mixture. The solvation can be schematically represented as $[3K^+ + Bi_2^{2-} + e^-]_{solid} + en + crypt \rightarrow (K\text{-crypt})^+_{solv} + e^-_{solv} + [(K\text{-crypt})_2Bi_2]_{solid}$. The dimer in (K-crypt)$_2Bi_2$ crystallized from such solution is, of course, without the delocalized extra electron and also without the ionic interactions with alkali-metal cations. This brings the distance from 2.976 to 2.8377 Å. Oxidation of the solution by adventitious moisture, oxygen, or impurities in the solvent leads to oxidative coupling of the dimers to produce the known squares of $[Bi_4]^{2-}$.[20]

Supporting Information Available: A plot of the magnetic susceptibility of K_3Bi_2 versus the temperature, a plot of the magnetization of Cs_3Bi_2 at low temperatures and low field, a figure of the cesium cations around the bismuth dimers (PDF). An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Based on Pauling's formula $d_n = d_1 - Cx \log(n)$ where n is the bond order, d_1 and d_n are the lengths of bonds with bond order 1, respectively, and $C \approx 0.6$ (Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 239) we get $n = 1.43$ for $d_n = 2.976$ Å and $d_1 =$ the distance in elemental Bi, 3.07 Å.

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