A Naked Diatomic Molecule of Bismuth, [Bi$_2$]$^{2-}$, with a Short Bi−Bi Bond: Synthesis and Structure

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Received July 12, 1999

We have made a naked diatomic dianion of bismuth with a short Bi−Bi bond of 2.8377(7) Å that suggests possible multiple bonding. While diatomic molecules with multiple bonds are known among the lighter elements and are abundant in nature (O$_2$ and N$_2$ account for 99% of the atmosphere, C$_2$$^{2-}$ in CaC$_2$), they are rare or nonexistent among the heavier main-group elements (only S$_2$, Se$_2$, and P$_2$ at high temperatures). Substituted diatomic species with multiple homoatomic bonds, on the other hand, have become quite common. Numerous examples of RP=PR, RAs=AsR, R$_2$Si=SiR$_2$, and R$_2$Ge=GeR$_2$ are known.[1] In addition to these, a few examples of the heaviest pnictogens, Sb and Bi,[2] and group 14 congeners, Sn and Pb,[3] have been made more recently although the multiplicity of the bonds in the latter two is questionable. A triply bonded gallium molecule was also reported,[4] but the multiplicity of its bond has been also disputed ever since.[5] An important feature common for all of these substituted species is the extremely bulky organic substituents that stabilize the species but at the same time makes them inaccessible for reactions. The multiple bonds are the result of the abnormally low coordination that is sterically forced by the organic groups. There is also a number of substituted diatomic species with single bonds.[1,6,7] Singly bonded naked molecules are also known but all in insoluble neat solids. Examples are CaP, CaAs, Ca$_{11}$Sb$_{10}$, and Ca$_{11}$Bi$_{10}$ with P$_2$$^{4-}$, As$_2$$^{4-}$, Sb$_2$$^{4-}$, and Bi$_2$$^{4-}$, respectively, and Ca$_5Si_3$, Ca$_5Ge_3$, Ba$_5Sn_3$, and Ba$_5Pb_3$ which contain Si$_2$$^{6-}$, Ge$_2$$^{6-}$, Sn$_2$$^{6-}$, and Pb$_2$$^{6-}$, respectively.[8] All of these are isoelectronic with the well-known soluble O$_2$$^{2-}$, S$_2$$^{2-}$, and the neutral diatomic molecules of the halogens. This collection, until now, lacked a naked diatomic molecule with a double bond. We report here the synthesis and structure of the soluble (K-crypt)$_2$Bi$_2$ (1)[9] which contains Bi$_2$$^{2-}$ with a very short bond distance

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(9) Crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

comparable to the distances in the two known RBi=BiR compounds with a double Bi=Bi bond.[2a,b]

Compound 1 was initially detected as a small fraction, ~10%, of a multiphase product crystallized from ethylenediamine solution of a precursor compound K$_5$In$_2$Bi$_4$, the latter made by heating a stoichiometric mixture of the elements.[10] The green-blue solution of the precursor in ethylenediamine and crypt is filtered, and the filtrate is carefully layered with toluene.[11] The reaction vessel was left undisturbed for a week in the initial synthesis. During that time crystals grow on the walls as a result of the toluene's diffusion into the ethylenediamine. The synthesis is reproducible and was successfully carried out repeatedly. The product usually contains two other phases as well, (K-crypt)$_2$(InBi$_3$) (2) with tetrahedra of [InBi$_3$]$^{2-}$ (~80%) and (K-crypt)$_6$(In$_4$Bi$_5$)$_2$ (3) with monocapped square antiprisms of [In$_4$Bi$_5$]$^{3-}$ (~10%). The structures of 2 and 3 were also determined from single-crystal X-ray diffraction[12] and were found to be isostructural with previously reported compounds. Compound 2 is isostructural and isoelectronic with (K-crypt)$_2$(Sn$_2$Bi$_2$) and (K-crypt)$_2$(Pb$_2$Sb$_2$),[13a,b] while compound 3 is isostructural but not isoelectronic with (K-crypt)$_6$(Sn$_9$)$_2$ and (K-crypt)$_6$(Pb$_9$)$_2$.[13c,14] The initial goal was to investigate whether it was possible to make deltahedral hetero-atomic clusters of elements differing by two or more groups, i.e., In and Bi from groups 13 and 15, respectively. Thus, the existence of compound 3 proves that this is possible.

The yield of 1 was later improved greatly by increasing the amount of toluene and prolonging the time for its diffusion into the ethylenediamine. Apparently, the solubility of 1 in ethylenediamine is very high, and quantitative extraction (crystallization) is achieved by lowering that solubility with additional toluene and longer time for the diffusion. The product of such process carried out for over a month contains nearly 80% of 1 and the size of the crystals is in the order of 3 to 4 mm.

The crystals of 1 are hexagonal red-brown plates (greenish when thin). Several of them were selected and sealed in glass capillaries, and the structure was determined from X-ray diffraction data collected from one of them.[15] The compound crystallizes in a very high-symmetry space group, rhombohedral R3̄, perhaps

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(10) Bobev, S.; Sevov, S. C., unpublished results. The precursor was initially synthesized by a reaction designed to explore for clusters of [In$_5$Bi$_4$]$^{5-}$ that are isoelectronic with the known Pb$_9$$^{4-}$ found in K$_4$Pb$_9$ (Queneau, V.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 1358). Thus, a mixture of the elements with stoichiometry K$_5$In$_5$Bi$_4$ was heated in a welded niobium container sealed in evacuated quartz ampule at 600 °C for a week. Later K$_5$In$_2$Bi$_4$ was made starting from the correct stoichiometry.

(11) Redistilled ethylenediamine packaged under nitrogen (99.5+%, Aldrich) and crypt (Kryptofix 222, 98%, Acros) were used as received, and the toluene (99.5+%, Fisher) was dried and kept over sodium. All operations of the dissolution and crystallization were performed in a helium-filled glovebox.

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(14) The number of bonding electrons in the clusters (Sn$_9$)$^{3-}$ and (Pb$_9$)$^{3-}$ is $9 \times 2 + 3 = 21$, and therefore the clusters are paramagnetic, while this number for (In$_4$Bi$_5$)$^{3-}$ is $4 \times 1 + 5 \times 3 + 3 = 22$ and indicates diamagnetic species. (Sn$_2$Bi$_2$)$^{2-}$ and (Pb$_2$Sb$_2$)$^{2-}$, on the other hand, have $2 \times 2 + 2 \times 3 + 2 = 12$ bonding electrons, the same as for (InBi$_3$)$^{2-}$, i.e., $1 \times 1 + 3 \times 3 + 2 = 12$.

(15) A sixth of a sphere of X-ray diffraction data ($2\theta_{max} = 50°$) was collected at room temperature on CAD4 with Mo Kα radiation from a single crystal of (K-crypt)$_2$Bi$_2$ (plate, red-brown, $0.60 \times 0.48 \times 0.05$ mm). Crystal data: rhombohedral, $R\bar{3}$, $Z = 3$, $a = 12.220(1)$ Å, $c = 28.927(3)$ Å, $V = 3740.9(5)$ Å^3, $\mu = 72.68$ cm^{-1}, $d_{calc} = 1.66$ g·cm^{-3}, R1/wR2 = 2.83/6.82% for the observed 1298 reflections ($I \geq 2 \sigma_I$) and R1/wR2 = 3.41/7.12% for all 1437 reflections and 134 variables. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located from difference Fourier maps and were fully refined with isotropic thermal parameters. The structure solution and refinement (on F^2) were handled with the SHELXTL V5.1 package. The data were corrected for absorption using a lamina model with the aid of seven ψ-scans at different θ-angles (min/max transmission = 0.1699/0.7360). Qualitative microprobe elemental analysis (energy-dispersive X-ray analysis for elements heavier than oxygen) performed on the same crystal showed Bi and K only.
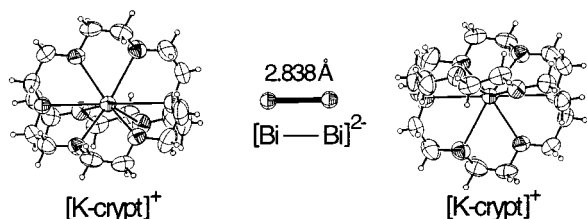
Figure 1. An ORTEP drawing (50% probability level for the thermal ellipsoids) of Bi_2^{2-} and the two neighboring K-crypt cations along the bond direction (see text). The carbon and hydrogen atoms are shown as crossed ellipsoids and open circles, respectively. The bismuth, potassium, nitrogen, and oxygen atoms are drawn as ellipsoids with shaded segments.

due to the simplicity of the molecules it contains, Bi_2^{2-}. The naked dianions (Figure 1) are oriented along the 3-fold axis. Each molecule is surrounded by eight $[K\text{-crypt}]^+$ cations, two are along the molecular axis (shown in Figure 1) and the other six are around the molecule in two sets of three on both sides of the equatorial plane. The closest neighbors to the bismuth atoms are aliphatic hydrogen atoms at distances of 3.47 Å and longer. The corresponding carbon atoms are at distances larger than 3.9 Å. These distances are longer than the sums of the corresponding van der Waals radii ($r_{vdw} = 1.20$ and 1.70 Å for H and C, respectively, estimated $r_{vdw} \approx 2.02$ Å for Bi), and therefore the molecule is indeed isolated and nonbonded.

The Bi–Bi distance is 2.8377(7) Å. It compares very well with observed double-bond distances between bismuth atoms in substituted diatomic species, 2.8208(8) Å in $[2,4,6\text{-}\{(Me_3\text{-}Si)_2CH\}_3H_2C_6]_2Bi_2$ and 2.833(1) Å in $[\{2,4,6\text{-}Me_3C_6H_2\}_2H_3C_6]_2\text{-}Bi_2$.[2a,b] The distance in Bi_2^{2-} is slightly longer, most likely due to the electrostatic repulsion of the negative charges. This is very similar to C_2^{2-} in CaC_2 with a C–C distance of 1.19 Å,[16a] and the C–C distance of 1.18 Å in the corresponding H-substituted acetylene.[16b] It has already been shown that these distances correspond to a double bond for bismuth.[1a,2a,b,5a,17] The Bi–Bi distance of 2.8377 Å in **1** corresponds to a Pauling bond order of 2.01.[18] For comparison, the Bi–Bi distances in dimers with single bonds are 2.990(2) and 3.035(3) Å in the substituted Ph_4Bi_2 and $(Me_3Si)_4Bi_2$, respectively,[6] and 3.15 Å in the naked Bi_2^{4-} anions found in $Ca_{11}Bi_{10}$.[19]

There are different possibilities for the electronic structure of the Bi_2^{2-} species. The molecule is a 12-electron system, isoelectronic with known species such as B_2H_6, C_2H_4, N_2H_2, and O_2. Although isoelectronic the latter four show different bonding modes, i.e., diborane is double-bridged, ethylene and diazene are with one σ and one π bonds, while oxygen is with a double bond but with one σ- and two π-type overlaps where two unpaired electrons occupy the two π^* MOs, making it paramagnetic. Since there are no substituents on Bi_2^{2-} it is likely to be O_2-like. Ab initio calculations were performed on the species (with electron correlation and relativistic effective-core potentials, B3LYP functional with $(4s4p1d)/[2s2p1d]$[20,21]). The optimized distances from these calculations, 2.954 Å for the triplet and 2.958 Å for the singlet states, are in substantial disagreement with the experimental 2.8377 Å. This is most likely due to the assumption that the species are isolated in gas phase with no counterbalancing

cations. The calculations also suggested triplet ground state. To test the latter we measured the magnetization of the solid compound and the EPR of the solid and solution of the redisolved compound at different temperatures.[22] These measurements showed diamagnetic behavior and therefore a singlet ground state for the molecule. There are a few possible reasons for the "failure" of the calculations. One is that the bond distance was not optimized accurately to begin with. Second, it has been pointed out that "theoretical investigations of anions is traditionally among the most demanding fields in quantum-mechanical ab initio calculations" due to: (1) the much larger correlation energy of anions compared to neutral molecules, and (2) the much more diffuse electron density of anions.[23] Third, bismuth is very heavy and its relativistic effects are difficult to handle in calculations. As a consequence, "much more sophisticated treatments of the correlation energy combined with one-particle basis sets augmented by diffuse and high angular momentum functions are required for an appropriate description of the extra electrons in anions",[23] or in other words, the calculations should be done at much higher level in order to asses the real electronic state of the Bi_2^{2-} species.

It is important to note also that our attempts to make **1** from precursors containing only K and Bi (nominal composition "K_2Bi_2", treated similarly as the synthesis of $K_5In_2Bi_4$[10]) were unsuccessful. The product contains only the known $(K\text{-crypt})_2Bi_4$ with squares of Bi_4^{2-}.[24] The latter can be thought as made of two Bi_2^{2-} by oxidative ring formation, $2Bi_2^{2-} - 2e^- \rightarrow Bi_4^{2-}$. The reason for the different outcomes from the different precursors is not clear, although it can be speculated that the structure of $K_5In_2Bi_4$ and the formal charges of the bismuth atoms in it are important for the formation of Bi_2^{2-}. The precursor $K_5In_2Bi_4$ contains chains of edge-sharing tetrahedra of bismuth centered by indium, and the chains are separated by the potassium cations. There are one-, two-, and three-bonded bismuth atoms with formal charges of $2-$, $1-$, and 0, respectively. The "K_2Bi_2" precursor, on the other hand, contains elemental potassium and the compound KBi_2. The latter is isostructural with the so-called Laves phase $MgCu_2$, a structure typical for alloys with a network of heavily interconnected Bi-atoms with uniform formal charges of 0.5-. This means that the atoms are not reduced enough for the formation of Bi_2^{2-} where the charge per atom is $1-$. The availability of low-coordinated bismuth atoms with very negative charges in $K_5In_2Bi_4$ clearly makes the difference. Furthermore, the other two phases that cocrystallize with **1** are with less reduced bismuth, formally $Bi^{(2/4)-}$ in **2** and $Bi^{(3/9)-}$ in **3**. Also, they "extract" the indium atoms from the chains and provide the highly charged bismuth atoms for the formation of the dimers. Experiments to use alkali-metal rich precursors such as K_3Bi containing isolated Bi^{3-} species are in progres, and may prove more appropriate and rational for the synthesis of Bi_2^{2-}.

Supporting Information Available: A space-filling figure showing the six K-crypt cations around the waist of the Bi_2^{2-} molecule and a drawing of a part of the chain of the structure of the precursor $K_5In_2Bi_4$ (PDF). An X-ray crystallographic file, in CIF format. This material is avaiable free of charge via the Internet at http://pubs.acs.org.

JA992422I

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