Stabilization of Ozone-like $[Bi_3]^{3-}$ in the Heteroatomic *closo*-Clusters $[Bi_3Cr_2(CO)_6]^{3-}$ and $[Bi_3Mo_2(CO)_6]^{3-}$

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The existence of ions $[Pn_3]^{3-}$ for Pn (*Pn*ictide) = As, Sb, or Bi in liquid ammonia was proposed initially by Zintl seventy years ago.[1] Later, some of these Zintl ions were observed in molten salts, but had not been isolated and structurally characterized before.[2] Our interest in such species started with the discovery of the naked double-bonded molecule $[Bi{=}Bi]^{2-}$ in (K-crypt)$_2$-Bi$_2$ (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) crystallized from an ethylenediamine solution of the compound K_3Bi_2.[3] The latter, itself, contains the $[Bi_2]^{2-}$ dimer but has also an extra electron that is delocalized over the structure to make the compound metallic.[4] A second precursor compound, K_5Bi_4 with zigzag tetramers of $[Bi_4]^{4-}$ and also with a delocalized "extra" electron, was found in this system as well.[5] It also readily dissolves in ethylenediamine and crypt, and the same compound (K-crypt)$_2$Bi$_2$ containing the bismuth dimers $[Bi_2]^{2-}$ can be crystallized from the solution. More oxidized species, squares of $[Bi_4]^{2-}$ in (K-crypt)$_2$Bi$_4$, are also known.[6] These observations imply possible coexistence of a variety of bismuth species in these solutions. We have not been able to crystallize any other "naked" species yet, but we have been successful in stabilizing the trimer $[Bi_3]^{3-}$ by coordinating it to two transition-metal (M) tricarbonyl species, Cr(CO)$_3$ and Mo(CO)$_3$. We report here the synthesis and structure of the heteroatomic clusters $[Bi_3Cr_2(CO)_6]^{3-}$ and $[Bi_3Mo_2(CO)_6]^{3-}$ with the shape of trigonal bipyramids made of bent $[Bi_3]^{3-}$ and two equatorial M(CO)$_3$ groups.

Transition-metal tricarbonyl fragments of M(CO)$_3$ have been used before in combinations with existing Zintl anions such as $[E_9]^{4-}$ in [K-crypt]$_4$[E$_9$Cr(CO)$_3$] for E = Sn and Pb[7] and $[Pn_7]^{3-}$ in [K-crypt]$_3$[Pn$_7$M(CO)$_3$] for Pn = P, As, and Sb and M = Cr, Mo, and W,[8] and have proven very effective in forming such heteroatomic species. At the same time, it is surprising that despite the extensive studies of Zintl ions made of the lighter pnictides P, As, and Sb,[9] there is very little done with the heaviest homologue bismuth. On the other hand, a number of bismuth−transition metal compounds made by a different approach, i.e., without the use of Zintl ions, have been reported recently.[10]

The new compounds K(K-crypt)$_5$[Bi$_3$M$_2$(CO)$_6$]$_2$·3en, where M = Cr (**1**) or Mo (**2**) and en = ethylenediamine, were synthesized by reacting ethylenediamine solutions of K_5Bi_4 and crypt either with solid (mesitylene)Cr(CO)$_3$ or (cycloheptatriene)Mo(CO)$_3$, respectively, or with their toluene solutions. The color changes quickly from blue-green for the ethylenediamine solution of the precursor (absorption at 434 and 604 nm) to brown-red for the product (absorption at 360 and 500 nm measured for **2**). Crystals of **1** and **2**, both with the same brown-red color, crystallize in a week (about 40% yield for both **1** and **2**, based on the amount of dissolved precursor) as a result of the slow diffusion of carefully layered toluene.[11] The same slow diffusion but in the absence of a transition-metal complex yields (K-crypt)$_2$Bi$_2$ with the $[Bi_2]^{2-}$ dimers,[3] while evaporation of that solution reportedly produces the more oxidized squares of $[Bi_4]^{2-}$.[6]

The structures of **1** and **2** were determined by single-crystal X-ray diffraction.[12] The two compounds are isostructural but the structure of **1** was refined in a subcell half the size of the unit cell of compound **2**, i.e., the real supercell was missed for **1** (most likely due to its much weaker diffraction and the use of a less-sensitive diffractometer), and a few atoms were refined disordered among split positions in **1**. The compounds contain pairs of trigonal bipyramidal clusters of $[Bi_3M_2(CO)_6]^{3-}$ (Figure 1), where the M(CO)$_3$ fragments are equatorial. The shape and the electron count of the cluster are consistent with a *closo*-deltahedron, i.e., 12 delocalized bonding electrons for a *closo*-cluster ($2n + 2$, where n = number of vertexes) and 6 electrons for lone pairs (three naked vertexes) are available from the three Bi atoms and the charge. The cluster is isoelectronic and isostructural with the known trigonal bipyramidal $[E_5]^{2-}$, where E = Ge, Sn, Pb,[13] and $[Bi_5]^{3+}$.[14] The two clusters in Figure 1 are crystallographically different in **2**, labeled **A** and **B**, but are refined as one unique cluster in **1**. The distances in the clusters follow the general pattern observed for other trigonal bipyramidal clusters, i.e., the equatorial distances are considerably longer than the apical ones. Thus, the equatorial M−M distances, 3.097(3) Å for the chromium cluster and 3.220(3) and 3.253(3) Å for the molybdenum clusters **A** and **B**, respectively, are too long for M−M interactions. The lack of interactions is evidenced by the IR spectrum of **2**, which shows only three carbonyl bands.[15] The equatorial Bi−M distances are also very long, with average distances of 3.035 Å in **1** and 3.128 and 3.156 Å for clusters **A** and **B** in **2**, respectively. The average apical Bi−M distances, 2.706 Å in **1** and 2.852 and 2.848 Å for

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(11) The precursor K_5Bi_4 was made from a stoichiometric mixture of the elements (Alfa-Aesar) heated at 500 °C for 1 day in sealed (by arc-welding) niobium containers that were jacketed in evacuated fused-silica ampules. Approximately 0.8 mmol of K_5Bi_4 is dissolved in 1 mL of ethylenediamine (redistilled and packaged under nitrogen, 99.5+%, Aldrich) and 0.8 mmol of Kryptofix 222 (98%, Acros) in a test tube. Complete dissolution usually occurs in less than 30 min (blue-green solution). 0.55 mmol of (mesitylene)Cr(CO)$_3$ (Aldrich) or (cycloheptatriene)Mo(CO)$_3$ (Strem) is then added either directly or as solutions in 0.2 mL of toluene (dried and kept over sodium, 99.5%, Fisher), and the resulting brown-red solutions are layered in the test tube with another 3 mL of toluene. Brown-red bars of **1** and irregular crystals of **2** grow on the walls and the bottom. The mother liquor is decanted after a week and the crystals are dried.

(12) X-ray diffraction data were collected with graphite-monochromated Mo Kα radiation, and the structures were solved by direct methods in $P\bar{1}$ and refined on F^2 (after applying empirical absorption corrections for **1** and SADABS for **2**) using the SHELXTL 5.1 package. Compound **1**: A hemisphere of data ($2\theta_{max} = 50°$) was collected at room temperature on a CAD4 diffractometer from a single crystal of **1** (brown-red bar, 0.52 × 0.15 × 0.10 mm). Crystal data: $a = 12.679(3)$ Å, $b = 17.724(2)$ Å, and $c = 18.254(2)$ Å, $\alpha = 71.31(1)°$, $\beta = 81.37(3)°$, and $\gamma = 78.82(2)°$, $V = 3795(1)$ Å^3, $Z = 1$, $\mu = 74.70$ cm^{-1}, $d_{calc} = 1.772$ g/cm^3, $R1/wR2 = 7.65/16.65\%$ for 5927 observed reflections ($I \geq 2\sigma_I$) and 847 variables. Compound **2**: A full sphere of data ($2\theta_{max} = 53°$) was collected at −100 °C on a BRUKER APEX diffractometer with a CCD area detector from a single crystal of **2** (irregular, 0.42 × 0.27 × 0.15 mm). Crystal data: $a = 12.635(4)$ Å, $b = 21.115(6)$ Å, and $c = 29.197(8)$ Å, $\alpha = 91.602(6)°$, $\beta = 102.387(6)°$, and $\gamma = 91.953(6)°$, $V = 7599(4)$ Å^3, $Z = 2$, $\mu = 74.79$ cm^{-1}, $d_{calc} = 1.867$ g/cm^3, $R1/wR2 = 13.03/31.48\%$ for 19907 observed reflections ($I \geq 2\sigma_I$) and 1640 variables.

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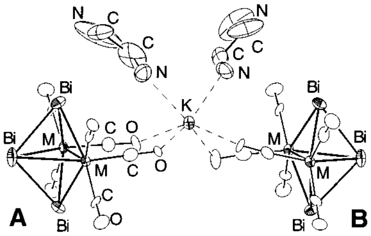

Figure 1. ORTEP drawing (shown for **2** with 50% probability thermal ellipsoids) of the pair of trigonal bipyramidal clusters $[Bi_3M_2(CO)_6]^{3-}$ (labeled **A** and **B** in **2**, refined as one cluster in **1**). Distances in **1** [Å]: Bi−Bi 2.956(1), 2.954(1), Bi_{ap}−Cr 2.694(2), 2.696(2), 2.711(2), 2.725(2), Bi_{eq}−Cr 3.045(2), 3.025(2), Cr−Cr 3.097(3) (Bi_{eq} and Bi_{ap} are equatorial and apical atoms, respectively). Distances in cluster **A** of **2** [Å]: Bi−Bi 2.992(1), 3.005(1), Bi_{ap}−Mo 2.838(2), 2.854(2), 2.863(2), 2.855(2), Bi_{eq}−Mo 3.123(2), 3.133(2), Mo−Mo 3.220(3). Distances in cluster **B** of **2** [Å]: Bi−Bi 2.987(2), 2.987(1), Bi_{ap}−Mo 2.844(2), 2.834(2), 2.868(2), 2.844(2), Bi_{eq}−Mo 3.134(2), 3.184(2), Mo−Mo 3.253(3). The clusters are "connected" by a noncryptated potassium cation coordinated to oxygen of four carbonyl groups (two per cluster) and two ethylenediamine molecules.

clusters **A** and **B** in **2**, respectively, are quite shorter. Also, they differ significantly for the two transition metals while the Bi−Bi distances differ only slightly, 2.955 Å in **1** and 2.987 and 2.999 Å for **A** and **B** in **2**, respectively.

The species $[Bi_3M_2(CO)_6]^{3-}$ can be viewed also in a "noncluster" way, i.e., without delocalized bonding. Thus, they can be described as made of bent $[Bi_3]^{3-}$ molecules coordinated to two neutral $M(CO)_3$ moieties. The trimer $[Bi_3]^{3-}$ is isoelectronic and isostructural with ozone, O_3, where the average bond order is 1.5 per bond, i.e., $[\mathrm{Bi{-}Bi{=}Bi}]^{3-} \leftrightarrow [\mathrm{Bi{=}Bi{-}Bi}]^{3-}$ or $[\mathrm{Bi \overset{\cdots}{-} Bi \overset{\cdots}{-} Bi}]^{3-}$. Hence, the Bi−Bi distances are relatively short and fall between the single bond distance of 3.02 Å (according to Pauling's sum of single-bond radii)[16] and the double bond distance of 2.8377(7) Å observed for the naked diatomic molecule $[\mathrm{Bi{=}Bi}]^{2-}$.[3] They are also noticeably shorter than the average distance of 3.157 Å in the triangular bismuth unit found in $[\{Bi_3Fe_3(CO)_9\}BiFe(CO)_4]^{2-}$,[17] and the apical distances in the isoelectronic trigonal bipyramidal $[Bi_5]^{3+}$, 3.013(5) Å.[14] On the other hand, these distances are somewhat longer than the average distance of 2.939 Å in the $[Bi_4]^{2-}$ square which has a bond order of 1.25.[6] The reason for the elongation is clearly the coordination of the transition-metal moieties to the π-system of the trimer and the resulting electron back-donation and partial population of the π^*-antibonding orbitals of $[Bi_3]^{3-}$, just like for coordinated alkenes.

The elongation of the Bi−Bi bonds can be rationalized also by considering that the electrons carried by an isolated $[Bi_3]^{3-}$ are delocalized over the whole deltahedral cluster and do not belong just to the trimer any longer. Furthermore, simple molecular orbital calculations on the isolated trimer $[Bi_3]^{3-}$ show that none of these electrons is antibonding, and therefore sharing them with other atoms leads, logically, to bond elongation.

The [Bi−Bi═Bi] angle in $[Bi_3Cr_2(CO)_6]^{3-}$, 93.02(3)°, is virtually equal to the [C−Bi═Bi] angle of 92.5° in $\{2,6\text{-}Mes_2H_3C_6{-}Bi{=}Bi{-}C_6H_3\text{-}2,6\text{-}Mes_2\}$.[18] These angles in clusters **A** and **B** of $[Bi_3Mo_2(CO)_6]^{3-}$ are also close to orthogonal, 97.17(5) and 96.29(5)°, respectively. This indicates that the central bismuth atom in both $[Bi_3]^{3-}$ and [C−Bi═Bi] is not s−p hybridized, but rather the bonding is achieved by orbitals of almost pure p-character. Reduced hybridization and smaller bonding angles are quite typical for the heavy elements. For example, the angles in the series $\{2,6\text{-}Mes_2H_3C_6{-}Pn{=}Pn\text{-}C_6H_3\text{-}2,6\text{-}Mes_2\}$ are 103.6 (av), 98.5, 94.1, and 92.5° for Pn = P, As, Sb, and Bi, respectively.[18,19] The angle in $[Bi_3]^{3-}$ can be compared with the angles in similarly bent P_3 and As_3 units coordinated to transition metals in $K[(Cp^*)_2ZrP_3]$ with a planar ZrP_3 core and $[(CpMo)_2(As_3)(AsS)]$ with a trigonal bipyramidal Mo_2As_3 core, respectively. The two compounds can be considered as $K\{[(Cp^*)_2Zr]^{2+}[P_3]^{3-}\}$ and $\{[(As{=}S)(CpMo)_2]^{3+}[As_3]^{3-}\}$, respectively, with $[Pn_3]^{3-}$ species, although they were not viewed as such in the original publications.[20] The $\mathrm{Pn \overset{\cdots}{-} Pn \overset{\cdots}{-} Pn}$ angles follow the same trend, 119.4° for $[P_3]^{3-}$, 107.3° for $[As_3]^{3-}$, and the observed here angles close to 90° for $[Bi_3]^{3-}$. The distances within the $[Pn_3]^{3-}$ trimers, 2.10 Å for $[P_3]^{3-}$, 2.374 Å for $[As_3]^{3-}$, and those of $[Bi_3]^{3-}$ observed in **1** and **2**, are all shorter than the corresponding Pauling's single-bond distances,[16] and manifest their multiple nature. Also, theoretical calculations for $[Sb_3]^{3-}$ have shown that the bent, ozone-like species are more stable than the triangular ones.[21]

There are five cryptated and one free potassium cations per two clusters of $[Bi_3M_2(CO)_6]^{3-}$ as well as three solvent molecules of ethylenediamine. The two clusters "point" toward each other with their carbonyl groups and are linked by the noncryptated potassium cation (Figure 1). The latter is "coordinated" to oxygen from four carbonyl groups (two from each cluster, one per transition metal) with quite short K−O distances in the range 2.67(1)−2.74(1) Å. The coordination sphere is completed by two ethylenediamine molecules with K−N distances of ca. 2.85 Å. This and one cryptated potassium cations in the structure of **1** are refined disordered among two half-occupied positions related by an inversion center.

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Supporting Information Available: Two figures showing the cations around the dimer of clusters (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] The IR spectrum of **2** (measured in a KBr pellet) exhibits three CO bands: a singlet at 1884.2 and a doublet at 1742.0 and 1728.4 cm^{-1}. Compared to the corresponding bands in the precursor (cycloheptatriene)$Mo(CO)_3$, a singlet at 1990 and a doublet at 1911 and 1884 cm^{-1}, these are shifted toward lower energy by about 150 cm^{-1} as expected for three negative charges. Also, the pattern is consistent with the C_s symmetry around the Mo center (close to C_{3v}).

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