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Bi_7^{3-}: The Missing Family Member, Finally Isolated and Characterized

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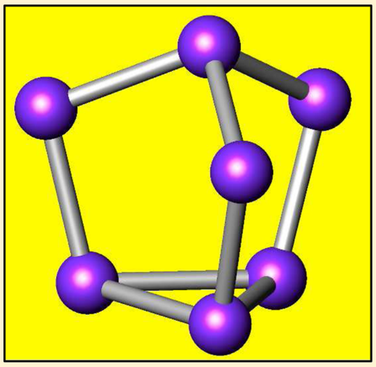
Ⓢ *Supporting Information*

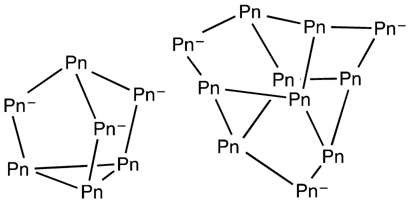
ABSTRACT: The synthesis and structure of Bi_7^{3-}, the only missing member of the family of heptanuclear pnictogen cluster anions Pn_7^{3-} (Pn = pnictogen, a group 15 element excluding the unique nitrogen), is reported. The new species is synthesized by oxidation of a solution of K_5Bi_4 by the solvent pyridine in the presence of $(C_6H_6)Cr(CO)_3$. The existence of the species in solution is confirmed by electrospray mass spectrometry, while its structure is elucidated by single-crystal X-ray diffraction in the compound $[K(2,2,2\text{-crypt})]_3Bi_7{\cdot}2py$ (monoclinic, $P2_1/n$, a = 13.8739(13) Å, b = 24.878(2) Å, c = 26.401(2) Å, β = 96.353(4)°, V = 9056.5(14) Å^3, Z = 4, and R1/wR2 = 0.0636/0.1390 for the observed data and 0.0901/0.1541 for all data).



■ INTRODUCTION

The pnictogens are well-known for their formation of polycyclic polyanions such as Pn_7^{3-} (Scheme 1, left),[1−6] Pn_{11}^{3-} (Scheme 1, right),[7−15] Pn_{14}^{4-},[16,17] Pn_{21}^{3-},[18] etc. (Pn = pnictogen, a group 15 element excluding the unique nitrogen). These species, some of them studied for almost a half-century, are made of formally neutral 3-bonded atoms Pn^0 and formally anionic 2-bonded atoms Pn^-, where the number of the latter defines the overall charge of the polyanion. Although not all of the polycyclic species are common for all members of the group, until recently, none of them was known for the heaviest element, Bi. Instead, Bi was known to form chain oligomers Bi_n^{n-} and squares Bi_4^{2-},[19−21] both with some multiple bonding, and also the chain tetramer Bi_4^{6-} with single bonds only.[22] Recently, the first 11-atom polycyclic species Bi_{11}^{3-} was reported by Dehnen and co-workers.[15] It has exactly the same shape as the lighter Pn_{11}^{3-} species, namely, a propeller-like formation with D_3 symmetry, where the three 2-bonded Pn^- vertices are at the propeller tips (Scheme 1, right).

Scheme 1. Shapes of the Known Pn_7^{3-} (left) and Pn_{11}^{3-} (right) Pnictogen Polycyclic Anions



We have been interested in building heteroatomic clusters by combining a main-group element, Bi in this case, and various ligated transition metals in zero oxidation state. A number of such mixed main-group/transition-metal clusters have been synthesized, e.g., $[Bi_3M(CO)_3]^{3-}$ for M = Cr and Mo, $[Bi_3Ni_4(CO)_6]^{3-}$, $[Bi_4Ni_4(CO)_6]^{2-}$, etc.[23,24] All of these species were synthesized by reacting solutions of K_5Bi_4 in ethylenediamine, a very reduction-resistant solvent, with an appropriate organometallic reagent. However, in recent exploratory studies of the effects of different solvents on those reactions, we encountered the species Bi_7^{3-} reported herein. Specifically, it forms when the same Bi precursor is reacted with $(C_6H_6)Cr(CO)_3$ in the more reduction-prone solvent pyridine, which, in turn, is reduced to a 4,4′-bipyridinium anion.[24] The existence of this species was initially proposed by Eduard Zintl more than 80 years ago,[25] but because it was never isolated and structurally characterized, it was thought to be absent from the family.[1−6,15]

■ RESULTS AND DISCUSSION

The intermetallic compound K_5Bi_4 contains isolated and planar-zigzag tetramers of $Bi_4^{(4+\delta)-}$.[19,26] We have shown before that dissolving this compound in ethylenediamine results in the formation of dimers Bi_2^{2-} and trimers Bi_3^{3-}. The latter has been isolated only as coordinated by ligated transition metals in deltahedral clusters such as $[(Bi_3^{3-})Cr_2(CO)_6]^{3-}$ and $[(Bi_3^{3-})Ni_4(CO)_6]^{3-}$.[24,27] It is safe to assume that these solutions also contain other chain and cyclic Bi_n^{m-} oligomers likely formed via redox processes. For example, Bi_4^{2-} squares and Bi_6^{4-} hexagons coordinated similarly by ligated transition-metal atoms have also been isolated from these solutions.[24] The same compound K_5Bi_4 dissolves also in pyridine in the presence of 2,2,2-crypt and produces a dark-brown solution. However, upon stirring for a few hours (4 and more), the solution changes color to

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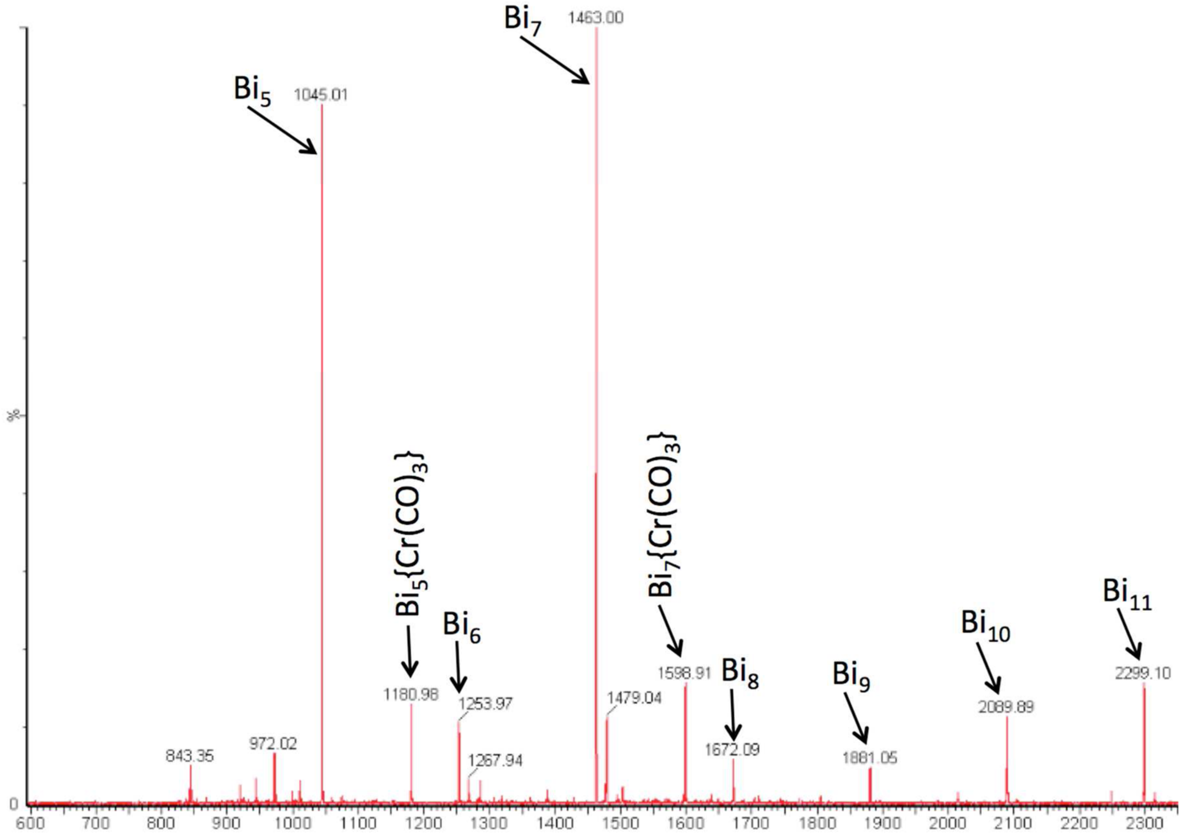

Figure 1. High-resolution ES-MS spectrum of a pyridine solution of K_5Bi_4 and $(C_6H_6)Cr(CO)_3$ after stirring for 3 h. Notice that the shown m/z range is very wide, 1700 mass units, and the signals appear as single sharp lines.

dark purple. This color is indicative of the presence of 4,4′-bipyridinium radical anions $(4,4'\text{-bipy})^{\bullet -}$, which form by reduction of a pyridine molecule and release of hydrogen gas by coupling with a second pyridine molecule,[24] i.e.

$$2\text{py} + e^- \rightarrow (4,4'\text{-bipy})^{\bullet -} + H_2$$

The reducing agents are obviously the dissolved polyatomic Bi anions, which, in turn, are oxidized from their very high negative charges.

The reported here Bi_7^{3-} was structurally characterized in the new compound $[K(\text{crypt})]_3Bi_7\cdot 2\text{py}$ (**1**). The latter was synthesized by dissolving K_5Bi_4 in pyridine in the presence of not only 2,2,2-crypt but also $(C_6H_6)Cr(CO)_3$. It crystallized after the mixture was stirred for 4 h followed by dilution with tetrahydrofuran (THF) and layering with toluene. The reaction can be written as

$$7\text{Bi}_n^{\,m-} + 2(7m - 3n)\text{py} \\ \rightarrow n\text{Bi}_7^{\,3-} + (7m - 3n)(4,4'\text{-bipy})^{\bullet -} + (7m - 3n)\text{H}_2$$

The importance of an oxidizing solvent is obvious because the same reaction in ethylenediamine produces the already reported $[Bi_3Cr_2(CO)_6]^{3-}$,[23] a trigonal bipyramid made of Bi_3^{3-} along one meridian and two equatorial and neutral $Cr(CO)_3$ fragments. We have seen the same effect of oxidation by the solvent before in the formation of $[Bi_4Ni_4(CO)_6]^{2-}$ (a deltahedral dodecahedron containing Bi_4^{2-}) from $[Bi_3Ni_4(CO)_6]^{3-}$ (a pentagonal bipyramid containing Bi_3^{3-}) upon dissolution of the latter in pyridine, which oxidizes the Bi from an average oxidation state of Bi^- to $Bi^{0.5-}$.[24]

What is interesting in the synthesis of **1** is the apparent necessity of $(C_6H_6)Cr(CO)_3$ to be present in the reaction mixture although no fragments of the compound are present in the product. The absence of the chromium compound leads to isolation of the very recently reported Bi_{11}^{3-} (crystallized as the reported structure of $[K(\text{crypt})]_3Bi_{11}\cdot 2\text{py}\cdot\text{tol}$), which had been unknown for a long time, although the same species were known for the other pnictogens. The role of the organometallic additive in the selective crystallization of Bi_7^{3-} over Bi_{11}^{3-} is not clear at this stage. One hint for some speculation comes from the electrospray mass spectrometry (ES-MS) spectrum of the reaction mixture [after removal of all pyridine and bipyridinium anions and redissolution of the solid in *N*,*N*-dimethylformamide (DMF)]. It shows the presence of both Bi_7 and Bi_{11} as monoanions (typically Zintl polyanions are detected as "oxidized" to monoanions by the electric field of the mass spectrometer) together with unknown species made of 5, 6, 8, 9, and 10 Bi atoms (Figure 1). What is noticeable, however, is that only the 5- and 7-atom formations are observed by mass spectrometry also with $Cr(CO)_3$, which is most likely coordinated to them, i.e., $[Bi_5Cr(CO)_3]$ and $[Bi_7Cr(CO)_3]$ anionic complexes (Figure 1). Bi_5^{5-} could potentially be the heavier analogue of the reported cyclic Sb_5^{5-},[28] a pnictogen analogue of the cyclopentadienyl anion $C_5H_5^-$ known to coordinate readily to transition metals. The 7-atom pnictogen species Pn_7^{3-} are also well-known to coordinate to transition metals, e.g., $[Pn_7M(CO)_3]^{3-}$ for Pn = P, As, Sb and M = Cr, Mo, W,[29−31] via one pseudosquare face containing two anionic and two neutral sites. At the same time, Pn_{11}^{3-} species are not known to have such capabilities (most likely because of the absence of any coordinating faces with enough negatively charged atoms). Thus, it can be speculated that the Bi_7^{3-} species are stabilized by the presence of $Cr(CO)_3$ in the solution, but they lose the transition-metal fragment upon crystallization. The nature of the stabilization is not clear, but it could simply be keeping the species intact for long enough time. It could also be, by changing the reduction potential of the Bi_7^{3-}/Bi_{11}^{3-} pair, enough to prevent further oxidation to Bi_{11}^{3-} by the pyridine solvent, i.e.

$$11Bi_7^{3-} + 24py \rightarrow 7Bi_{11}^{3-} + 12(4,4'\text{-bipy})^{\bullet -} + 12H_2$$
$$[\text{without } (C_6H_6)Cr(CO)_3]$$

but

$$11[Bi_7Cr(CO)_3]^{3-} + 24py \nrightarrow 7Bi_{11}^{3-} + 12(4,4'\text{-bipy})^{\bullet -} + 11Cr(CO)_3 + 12H_2$$

The new anion Bi_7^{3-} is the last member of the heptanuclear species in the pnictogen family and is structurally identical with the other congeners (Figure 2). It was structurally characterized in compound **1**. It is found positionally disordered among two orientations with 70 and 30% occupancies, and the metrics of only the major fraction will be discussed. The geometry is described as a nortricyclane-type cage made of four 3-connected and three 2-connected atoms. Three of the 3-connected atoms form a triangle (basal; atoms Bi5, Bi6, and Bi7 in Figure 2), while the fourth such atom (apical; atom Bi1) is positioned directly above the triangular base and is connected to it via the three 2-connected atoms (linking; atoms Bi2, Bi3, and Bi4). This shape defines three sets of distances: (A) apical−linking; (B) linking−basal; (C) basal−basal. In all previously known congeners, these distances increase in the order B < A < C. This order is exactly the same for Bi_7^{3-} with average distances of 2.931 Å for A, 2.897 Å for B, and 3.071 Å for C. Furthermore, even the ratios between these distances in the new species are very close to those previously known with B:A:C = 1:1.022:1.065 for P_7^{3-}, 1:1.025:1.069 for As_7^{3-}, 1:1.015:1.061 for Sb_7^{3-}, and 1:1.011:1.060 for Bi_7^{3-}. Some of the distances are also comparable to those in Bi_{11}^{3-}.[15] Thus, the distances between the 3-bonded Bi1 and 2-bonded Bi2, Bi3, and Bi4 in Bi_7^{3-}, 2.943(5), 2.938(4), and 2.913(5) Å, respectively, are within the range of observed distances between similar 3- and 2-bonded atoms in Bi_{11}^{3-}, 2.916−2.949 Å. However, while Bi_7^{3-} has a triangular formation, i.e., a base made of atoms Bi5, Bi6, and Bi7, there is no such strained formation in Bi_{11}^{3-}. Thus, the distances between the 3-bonded atoms of the base in Bi_7^{3-}, 3.030(4), 3.084(4), and 3.100(5) Å, are somewhat longer than the range of distances between the 3-bonded atoms in Bi_{11}^{3-}, 2.966−3.029 Å. The triangular base also affects the distances between the base and the 2-bonded connecting atoms Bi2, Bi3, and Bi4, 2.895(5), 2.882(4), and 2.915(5) Å, respectively, which are somewhat shorter than the range of distances between the 3- and 2-bonded atoms in Bi_{11}^{3-}, 2.916−2.949 Å. Exactly the same differences and similarities are observed for the remaining Pn_7^{3-} and Pn_{11}^{3-} species.

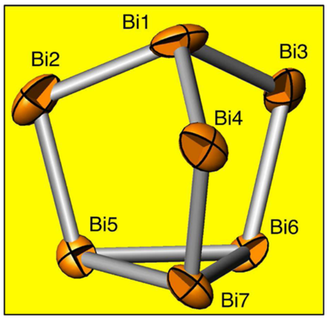

Figure 2. New species Bi_7^{3-} with four 3-bonded and three 2-bonded atoms.

Thus, what was thought to be species erroneously assigned as Bi_7^{3-} by Zintl based on his potentiometric titrations may not be that erroneous after all.[1,6,15,25] The experimental conditions at the time may have provided for some oxidation of what may have been initially Bi_4^{2-} species to Bi_7^{3-} mixed with even some other species that now we see in the mass spectra (see Figure 1).

EXPERIMENTAL SECTION

All reactions and materials were handled under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. K_5Bi_4 was synthesized from the elements (K, Sigma-Aldrich, 99.5%; Bi, Alfa Aesar, 99.998%) at high temperature as previously reported.[19] Pyridine (anhydrous, Acros, 99.0%), *N*,*N*-dimethylformamide (DMF; anhydrous, EMD Millipore, 99.8%), tetrahydrofuran (THF; anhydrous, EMD Millipore, 99.9+%), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt; Sigma-Aldrich, 98%), and benzene chromium tricarbonyl (Sigma-Aldrich, 98%) were used as received. Toluene (Alfa-Aesar, 99.8+%) was dried by passing over a copper-based catalyst and 4 Å molecular sieves and then stored in gastight ampules under nitrogen.

Synthesis of $(K[crypt])_3Bi_7 \cdot 2py$. K_5Bi_4 (104 mg, 0.101 mmol) and 2,2,2-crypt (193 mg, 0.512 mmol) were weighed in a test tube and dissolved in 2 mL of pyridine, yielding a dark-brown solution. After a few minutes, $(C_6H_6)Cr(CO)_3$ (22 mg, 0.102 mmol) was added to this solution and stirred for 4 h. The resulting dark-purple solution was centrifuged and filtered. The filtrate was diluted in a 1:1 ratio with THF and layered carefully with toluene to allow for crystallization. After a few days, black blocks (40% yield) were isolated from the deep-purple solution.

Sample Preparation for Mass Spectrometry. K_5Bi_4 (109 mg, 0.105 mmol) and 2,2,2-crypt (182 mg, 0.484 mmol) were weighed in a test tube and dissolved with 2 mL of pyridine, yielding a dark-brown solution. After a few minutes, $(C_6H_6)Cr(CO)_3$ (27 mg, 0.126 mmol) was added to this solution and stirred for 3 h. The solvent and any other volatiles were then removed under vacuum, and the resulting solid was washed with 40 mL of THF and then redissolved in DMF.

Mass Spectrometry. ES-MS spectra were collected on a Micromass Quattro-LC triple-quadrupole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 2.5 kV capillary voltage, and 30 V cone voltage.) Samples were introduced using a Harvard syringe pump at 10 μL/min via direct infusion.

Structure Determination. Single-crystal diffraction data were obtained on a Bruker APEX-II diffractometer equipped with a curved graphite monochromator and a CCD area detector using Mo Kα radiation at 120 K. The crystal was mounted on a Mitegen micromount loop after selection from Paratone-N oil and positioned under a nitrogen cold stream. The structure was solved using *SHELXT*[31] and refined on F^2 against all reflections using *SHELXL2014*.[32] Crystal data: monoclinic, $P2_1/n$, a = 13.8739(13) Å, b = 24.878(2) Å, c= 26.401(2) Å, β = 96.353(4)°, V = 9056.5(14) Å^3, Z = 4, R1/wR2 = 0.0636/0.1390 for observed data and R1/wR2 = 0.0901/0.1541 for all data.

ASSOCIATED CONTENT

Ⓢ Supporting Information

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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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to the memory of Professor John D. Corbett.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on October 14, 2014, with an error in the last equation of the paper. The corrected version was reposted on October 15, 2014.