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Synthesis and Crystal Structure of a “FeBi” Cluster Compound with Noncovalent Low-Valent Bi···π_{Arene} Interactions

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Supporting Information

ABSTRACT: We describe the synthesis and structural characterization of the unprecedented $[Bi_4Fe_3(CO)_9]$ cluster, the low-valent Bi atoms of which are involved in the types of previously not identified intermolecular Bi···π_{arene} and ΔBi···π_{arene} interactions. Different coordination modes of arene rings bound to Bi atoms were determined.

Over the past few decades, substantial progress has been made in the supramolecular chemistry of heavier group 15 elements (pnictogens; Pn = As, Sb, Bi) with emphasis mainly placed on the weak Pn^{III}···arene π interactions. Although experimental findings have revealed structural versatility of the Pn−π complexes and subsequent theoretical analyses have shed light on the nature of the secondary bonding interactions between the *trivalent* Pn atom and an aromatic ring, this area of research remains topical up to now.[1] As stated in the work of Johnson and co-workers published a short time ago about the Pn···π interaction as a complementary component in supramolecular assembly design,[2] “A better understanding of the nature of the pnictogen···π interaction is necessary for improved supramolecular design and an important consideration in Group 15 coordination chemistry”. Our research interest focuses on the manifestation of noncovalent π interactions in the chemistry of bismuth, specifically in that of low-oxidation-state bismuth metal compounds.

Since the first publication[3] in 1968 about bismuth−arene (Bi−Ar) π complexation involving bismuth trihalides and neutral aromatic mono- and polycyclic hydrocarbons, the number of reports about the Bi^{III}−Ar complexes has grown tremendously. Determination of the first crystal structures dates back to 1986 when Schmidbaur and co-workers successfully subjected two π complexes, $BiCl_3\cdot(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)$ and $(BiCl_3)_2\cdot(\eta^6\text{-}C_6Me_6)$, to X-ray diffraction analyses.[4] For the latter, a unique type of so-called “double-sided arene coordination” was established. One more illustration of a π complex of bismuth(III), $[BiN(C_6H_2Me_2CH_2O)_3]_2\cdot(\eta^6\text{-}PhMe)$, invoking “inverse sandwich” interactions was presented by Turner et al. in 2006.[5] A number of bismuth alkoxide complexes with π−arene interactions were also reported.[6]

In contrast to the abundant examples of bismuth(III) complexes containing arene molecules as π ligands,[1−7] only a few Bi^{II}−Ar complexes have been described so far. These are represented by molecular assemblies consisting of mono- or polycyclic hydrocarbons π complexed to *divalent* Bi atoms that constitute the dibismuthane $[Bi_2(\mu\text{-}O_2CCF_3)_4]$ units alternating through double-sided arene coordination.[8−10] A heterometallic $[BiRh(\mu\text{-}O_2CCF_3)_4\cdot(\eta^6{}_{(Bi)},\eta^2{}_{(Rh)}\text{-}C_{16}H_{10})]_\infty$ complex with metal-site-controlled pyrene coordination was also characterized.[10]

A heteronuclear bismuth−tungsten cluster with composition $[W_2(CO)_8(\mu_2\text{-}\eta^2\text{-}Bi_2)\{\mu\text{-}BiMeW(CO)_5\}]\cdot Bz$[11] (**BiW**·Bz; Bz is benzene) was reported in 1985 and is the sole compound synthesized up to now, according to our quantum-chemical analysis, where a Bi atom being in the formal oxidation state of zero is involved in weak π interaction with the Bz ring.

In this Communication, we report a new “FeBi” carbonyl cluster, $[Bi_4Fe_3(CO)_9]$ (**1**), the electronic structure of which offers unique types of intermolecular low-valent Bi···π_{arene} and ΔBi···π_{arene} interactions [Δ corresponds to a triangular base in **1**]. Our finding contributes thus to the existing knowledge about the Bi^{III}− and Bi^{II}−Ar complexes and expands it toward the low-valent $Bi^{I,0}$−Ar complexes. Note that the structural and physical chemical aspects of the compounds of bismuth(III) and bismuth(II) ligated by aromatic hydrocarbons were highlighted by two excellent reviews of Schmidbaur and Breunig and co-workers.[12]

The salt metathesis reaction between 0.85 mmol (2 equiv) of $BiBr_3$ and 1.28 mmol (3 equiv) of $Na_2[Fe(CO)_4]$ in THF at the applied conditions (−78 °C → room temperature) led to a color change of the resultant mixture from light green to dark brown. After all volatiles were removed under vacuum and a residue was extracted with toluene (PhMe) at room temperature, a further workup of the PhMe solution enabled isolation of the black block crystals of a $[Bi_4Fe_3(CO)_9]\cdot 2(PhMe)$ compound [hereafter referred to as **1**·2(PhMe)]. For more details on the syntheses of the latter, see the Supporting Information (SI).

$$4BiBr_3 + 6Na_2[Fe(CO)_4] \xrightarrow[-12NaBr \\ -3Fe(CO)_5]{\text{THF / PhMe}} [Bi_4Fe_3(CO)_9]\cdot 2(PhMe)$$

Cluster **1** crystallizes in the monoclinic space group $P2_1/c$ with two toluene molecules in the asymmetric unit (Table S1 in the

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SI). Figure 1 shows **1** in the π crystallization environment of the PhMe molecules in the solid-state structure of **1**·2(PhMe).

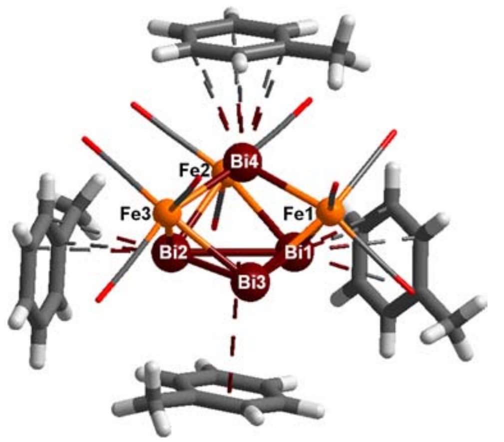

Figure 1. Perspective view of **1** that is surrounded by four PhMe molecules involved in the Bi···π_{PhMe} interactions in the crystal structure of **1**·2(PhMe). Two of the PhMe molecules are symmetry equivalents of the others. Selected bond lengths [pm]: Bi1−Bi2 319.93(3), Bi1−Bi3 316.91(3), Bi1−Bi4 323.36(3), Bi2−Bi3 318.65(3), Bi2−Bi4 322.92(3), Bi3−Bi4 321.08(3), Bi1−Fe1 276.04(8), Bi1−Fe2 275.95(8), Bi2−Fe2 275.09(8), Bi2−Fe3 274.82(8), Bi3−Fe1 275.61(8), Bi3−Fe3 276.34(8), Bi4−Fe1 263.11(8), Bi4−Fe2 263.17(7), Bi4−Fe3 262.58(8), Bi1···$(\text{PhMe})_{\text{centroid}}$ 341.2, Bi2···$(\text{PhMe})_{\text{centroid}}$ 350.0, Bi4···$(\text{PhMe})_{\text{centroid}}$ 323.9, ΔBi1,2,3···$(\text{PhMe})_{\text{centroid}}$ 391.9. The hapticities of the PhMe rings are η^4 [Bi1···C_{PhMe}], η^3 [Bi2···C_{PhMe}], and η^6 [Bi4···C_{PhMe}]. Color code: Bi, maroon; Fe, orange; O, red; C, gray; H, off-white.

1, the molecular ion peak of which was detected by electrospary ionization mass spectrometry (Figure S1 in the SI), is not only a family member of the previously reported low-nuclear "FeBi" carbonyl compounds[13] but also constitutes the family of the high-nuclear "FeBi" clusters ($\{Bi_4Fe_4\}$, **I**;[14] $\{Bi_4Fe_5\}$, **II**;[15] $\{Bi_4Fe_8\}$, **III**[16]), formally displaying a Bi_4 core, three of the four triangular faces of which are μ_3 capped with the iron tricarbonyl moieties $Fe(CO)_3$. The number of cluster valence electrons for **1** is 54; that is, it has 27 cluster valence molecular orbitals. According to Wade's electron-counting rules, **1** possesses a skeletal electron count (SEC) of 18 (SEC = 4 × 3 from Bi + 3 × 2 from $Fe(CO)_3$). Hence, with 9 skeletal electron pairs, the shape of **1** corresponds to a *nido*-polyhedral cluster ($n + 2$, where $n = 7$), and the seven-vertex Bi_4Fe_3 skeleton of **1** with a bare ΔBi1,2,3 base can be regarded as deduced from a Bi_4Fe_4 rhombic disphenoid constituted of **III** upon removal of a μ_3-Fe atom.

Although the shape of the metal skeleton in **1** is reminiscent of that in the dianionic cluster $[Bi_4Fe_4(CO)_{13}]^{2-}$[14] (**I**) and that in the neutral cluster $[Bi_4Fe_3(CO)_9\{Fe(CO)_2Cp''\}_2]$[15] (**II**), the following striking dissimilarities between **1** and **I**/**II** can be found: (i) each of the four Bi atom apexes in **1** refrains from involvement in the additional μ_1 coordination to the hypothetical iron fragment [e.g., $Fe(CO)_4$]. (ii) In contrast to the hitherto reported 20-SEC clusters **I** and **II** and to the 24-SEC cluster $[Bi_4Fe_8(CO)_{28}]^{4-}$ (**III**),[16] our cluster **1** has the same number of skeletal electrons (18-SEC) as the previously synthesized and structurally described clusters, $[Bi_4Pd_4(PPh_2Me)_8]^{2+}$ (**IV**)[17] and $[Bi_4Ni_4(CO)_6]^{2-}$ (**V**).[18] Thus, it is evident that $[Bi_4Fe_3(CO)_9]$ (**1**) may have an electronic structure entirely different from that of a $[Bi_4Fe_3(CO)_9]^{2-}$ fragment ($\mathbf{1}^{2-}$) constituted of **I** or **II**.

By looking at the geometry of a formally viewed Bi_4 tetrahedron in **1**, one finds that it is slightly distorted [$d_{\text{Bi-Bi}}$ = 316.91(3)−323.36(3) pm] from the ideal T_d symmetry and this complies with the previous observations done for tetrahedral Bi_4 entities in the other heterometallic clusters. For comparison, only marginal deviations between the Bi−Bi distances were observed in the largest cluster of the iron−bismuth family, **III** [$d_{\text{Bi-Bi}}$ = 342.76(9)−343.84(8) pm],[16] and in the $[Bi_4Co_4(CO)_{12}]$ cluster, **VI** [$d_{\text{Bi-Bi}}$ = 335.1(1) and 336.4(1) pm;[19] $d_{\text{Bi-Bi}}$ = 331.59(15)−337.58(10) pm[15]]. By contrast, strong deviations were established in clusters **I**, **II**, and **IV**, with the Bi−Bi distances in the ranges $d_{\text{Bi-Bi}}$ = 314.0(2)−347.3(2),[14] 308.93(11)−352.98(9),[15] and 320.1(2)−350.93(14) pm,[17] respectively. The interatomic Bi−Bi distances in the Bi_4 tetrahedra in **1** and in **I**−**IV** and **VI** are much shorter than the sum of the bismuth van der Waals (vdW) radii ($\Delta\sum r_{\text{vdW}}$ = 480[12] and 414 pm[20]). However, they are astonishingly comparable with the Bi−Bi contacts (307.1 and 352.9 pm at T = 298 K and 306.4 and 351.6 pm at T = 78 K) defined between two nearest neighbors in the pure bismuth metal.[21]

Another striking difference between the crystal structures of **1** and clusters **I** and **II** is that, in contrast to the latter two, the former is surrounded by four uncharged monocyclic arene molecules, three of which are π-coordinated to the Bi1, Bi2, and Bi4 apexes with interatomic Bi···C_{PhMe} distances of 355.6−379.7, 347.8−402.5, and 344.7−360.9 pm, respectively, and the fourth one to the triangular ΔBi1,2,3 base of **1** (Figure 1). The coordination modes of the PhMe rings involve the following hapticities: η^4 for Bi1···C_{PhMe} = 355.6, 355.7, 368.3, 369.6, 379.4, and 379.7 pm; η^3 for Bi2···C_{PhMe} = 347.8, 361.3, 364.2, 387.1, 392.3, and 402.5 pm; η^6 for Bi4···C_{PhMe} = 344.7, 347.2, 347.6, 355.5, 356.3, and 360.9 pm. The distances between the Bi atoms and the geometrical centers of the PhMe rings are d[Bi1···$(\text{PhMe})_{\text{centroid}}$] = 341.2 pm, d[Bi2···$(\text{PhMe})_{\text{centroid}}$] = 350.0 pm, and d[Bi4··· $(\text{PhMe})_{\text{centroid}}$] = 323.9 pm. Thus, the Bi4···PhMe interaction occurs within the distance that is shortened compared to the ones determined for the Bi1···PhMe and Bi2···PhMe interactions. This is due to the fact that the Bi4 atom in $\mathbf{1}_{\text{comput}}$ is somewhat oxidized [natural electron configuration (NEC), $6s^{1.62}6p^{2.15}$; total electron count (TEC), 81.8] with respect to the formally *zerovalent* Bi1 and Bi2 atoms ($6s^{1.81}6p^{2.47}$; 82.3) from the ΔBi1,2,3 base, according to density functional calculations at the BP86 level (Table S2 in the SI). Furthermore, the absolute chemical shifts computed for the Bi centers in $\mathbf{1}_{\text{comput}}$ suggest that the μ_3-Bi4 atom with δ = +4468 pm situated above the ΔBi1,2,3 triangular base is strongly shielded with respect to the Bi1, Bi2, and Bi3 atoms with δ = +8045 pm each (Table S3 in the SI). The distinctions between the NECs and between the TECs of the Bi4 atom and the Bi1, Bi2, and Bi3 atoms as well as those between the absolute chemical shifts of the latter (δ = +7051 pm for Bi4 and +7108 pm for Bi1,2,3) in $\mathbf{1}_{\text{comput}}^{2-}$ are far less pronounced owing to the 2− net charge of this cluster (Tables S2 and S3 in the SI), which makes the key difference to our cluster $\mathbf{1}_{\text{comput}}$. In this regard, the interaction between the more Lewis acidic Bi4 metal ion and the weak Lewis base, PhMe, in $\mathbf{1}_{\text{comput}}$ can be viewed as a sort of cation−π interaction. The π binding involving Bi1 and Bi4 is comparably ensured by attractive dispersion and electrostatic forces (Figure S2 and Table S4 in the SI). For a discussion about computational methodology applied herein, see the SI.

The PhMe ligands in the crystal of **1**·2(PhMe) are, furthermore, involved in "inverse sandwich" π complexations, and this is shown in Figure 2. Otherwise, the $\{Bi_4Fe_3\}$ skeleton

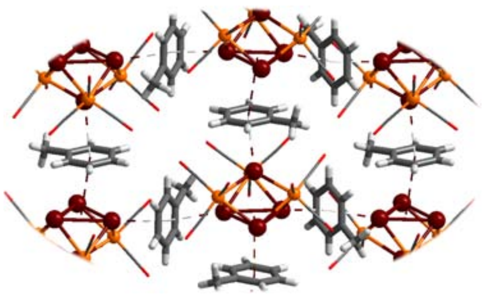

Figure 2. View into the extended 2D coordination network in the crystal of **1**·2(PhMe). The hapticities of the PhMe rings are not shown for clarity. Color code: Bi, maroon; Fe, orange; O, red; C, gray; H, off-white.

entities are linked together by intermolecular $\text{Bi}\cdots\pi_{\text{arene}}\cdots\text{Bi}$ and $\text{Bi}\cdots\pi_{\text{arene}}\cdots\Delta\text{Bi}$ interactions to form a two-dimensional (2D) coordination network. It is worth emphasizing, however, that there is possibly no other chance of packing for the chainlike arrangement with bridging toluene ligands between Bi1 and Bi2 and one further toluene molecule bound to Bi4. As with other structures of the complexes $(\text{BiCl}_3)_2\cdot(\eta^6\text{-C}_6\text{Me}_6)$,[4] $[\text{BiN}(\text{C}_6\text{H}_2\text{Me}_2\text{CH}_2\text{O})_3]_2\cdot(\eta^6\text{-PhMe})$,[5] and $[\text{Bi}_2(\mu\text{-O}_2\text{CCF}_3)_4\cdot(\eta^6\text{-Ar})]_\infty$,[8,9] the crystal structure of the π complex described herein includes arene molecules with double-sided coordination. Besides, our experimental finding and the cluster complexes $[\text{BiRh}(\mu\text{-O}_2\text{CCF}_3)_4\cdot(\eta^6{}_{(\text{Bi})},\eta^2{}_{(\text{Rh})}\text{-C}_{16}\text{H}_{10})]_\infty$[10] and **BiW**·Bz[11] represent rare examples of heterometallic compounds where Bi atoms are π-complexed by neutral aromatic hydrocarbons.

It is important to note that the 2D network in the crystal structure of **1**·2(PhMe) offers an exclusive type of intermolecular interactions between triangular ΔBi1,2,3 bases and the PhMe rings within distances of 391.9 pm. To the best of our knowledge, such unique $\Delta\text{Bi}\cdots\text{Ar}$ interface contacts are observed for the first time. We believe that the emergence of these intriguing interactions in bismuth chemistry may stimulate subsequent experimental and theoretical studies of adsorption of aromatic hydrocarbons on Bi(111), Bi(110), and Bi(100) surfaces[22] in view of the great interest for the "cluster-surface" analogy[23] involving the bismuth metal.

In summary, a novel "FeBi" cluster (**1**) was prepared by employing a "transition metal analog of a Grignard reagent"[24] as a reducing agent for the Bi^{III} source. The solid-state structure of **1**·2(PhMe) is dominated by weak, noncovalent π interactions[25] caused by the specific electronic features of **1**. The π binding sites of PhMe in **1**·2(PhMe) may be available for ligand substitution by the stronger Lewis bases. Further experimental and theoretical works are now in progress.

■ ASSOCIATED CONTENT

Supporting Information

Syntheses and structural data of **1**·2(PhMe) (CCDC 922530) and details of quantum-chemical calculations. 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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