Structure and Bonding of Pd@$[Bi_{10}]^{4+}$ in the Subbromide $Bi_{14}PdBr_{16}$**

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Dedicated to Prof. Hubert Langbein
on the occasion of his 60th birthday

The number of compounds that contain polycations is tiny compared with the huge variety that contain polyanions. Most of the hitherto known polycations are formed by the heavy and electron-rich elements of the p block of the periodic table,[1] particularly selenium,[2] tellurium,[2] and bismuth.[3] Besides homonuclear polycations such as $[Te_8]^{2+}$[4] and $[Bi_9]^{5+}$,[5] mixed species of these elements are also accessible, as the example $[Bi_4Te_4]^{4+}$[6] illustrates. Here we present the first heteronuclear polycation of bismuth and a transition element, which combines theoretically predicted features with some unexpected findings.

The title compound $Bi_{14}PdBr_{16}$ is a comparatively halogen-rich member of a series of ternary bismuth subhalides[7] that ranges from the intermetallic compounds Bi_nM (M = Ru, Rh, Ir, Ni, Pd, Pt; $n \geq 1$) to the binary bismuth subhalides, for example, BiI,[8] BiBr,[9] Bi_6Br_7,[9] and Bi_6Cl_7[5]. Within this sequence the character of the species changes as a result of the progressive expansion of regions of electronic localization. The weakly oxidized subhalides, such as $Bi_{12}Rh_3Br_2$[10] or $Bi_{5.6}Ni_5I$[11] are three-dimensional metallic frameworks with an inclusion of halide anions. Further increase of the halogen content leads to a significant reduction in the degree of metallic conductivity. Accordingly, the subiodides $Bi_{13}Pt_3I_7$[12] and $Bi_{12}Ni_4I_3$[13] consist of alternating metallic and semiconducting layers (two-dimensional metals), while only metallic rods remain embedded within isolating matrices in the structures of $Bi_9Ir_2I_3$[14] and $Bi_{6.86}Ni_2Br_5$[7] (one-dimensional metals). Passing through the intermediate steps of the semiconducting columnar structures, such as Bi_4RuX_2 (X = Br, I)[15] and their oligomeric fragments, for example, $Bi_{24}Ru_3Br_{20}$[16], the "halogen-rich" end-members of the series, that is, ionic cluster salts such as $Bi_{14}Si_2MI_{12}$ (M = Rh, Ir)[17] or $Bi_{6+x}MX_{12+y}$ (M = Rh, Ir, Pt; X = Cl, Br),[18] as well as the molecular cluster compound Bi_7RhBr_8[19], are reached.

The transition-metal content of the new subbromide $Bi_{14}PdBr_{16}$ is the lowest of the entire series. Subdividing the formula of $Bi_{14}PdBr_{16}$ into 14 BiBr·$PdBr_2$ illustrates the proximity to the monobromide BiBr.[9] However, determina-

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tion of the structure by single-crystal X-ray diffraction reveals that $Bi_{14}PdBr_{16}$ possesses no constitutional relationship with either BiBr or $PdBr_2$. Instead it is a complex salt that consists of cluster cations $[PdBi_{10}]^{4+}$ and anionic octahedra chains ${}_{\infty}^{1}[Bi_4Br_{16}{}^{4-}]$ (Figure 1).

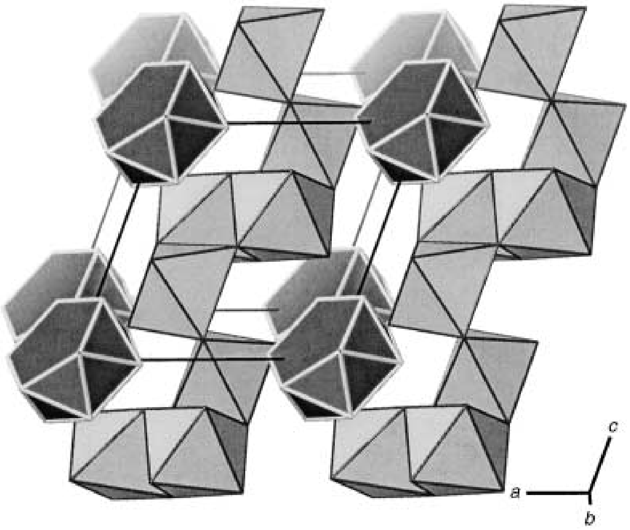

Figure 1. Crystal structure of $Bi_{14}PdBr_{16}$ containing $[PdBi_{10}]^{4+}$ Archimedean antiprisms and ${}_{\infty}^{1}[(BiBr_{2/1}Br_{4/2}{}^{-})_4]$ zigzag chains.

The eye-catching building block in the triclinic crystal structure is the cationic cluster $[PdBi_{10}]^{4+}$, a pentagonal antiprism of ten Bi atoms with a Pd atom at their center (Figure 2). The only crystallographic symmetry of the $[PdBi_{10}]^{4+}$ polycation is the center of inversion; nonetheless the D_{5d} symmetry of the pentagonal antiprism is almost perfectly observed: The maximum deviation from a plane of the Bi atoms in a pentagon is less than 2 pm, the bond angles in the ring are 108 ± 0.6°, and the rotation angle between the two rings is about 42°. Furthermore, the interatomic distances within the five-membered ring (313–319 pm) and between the two pentagons (311–318 pm) are equivalent. The Pd–Bi bonds range from 297 to 302 pm in length, with an average of 300 pm, and the Bi-Pd-Bi angle for neighboring Bi atoms is about 63.4°, and is independent of whether the Bi atoms belong to one or other pentagons. Thus, the $[PdBi_{10}]^{4+}$ polycation is a semiregular or Archimedean polyhedron.

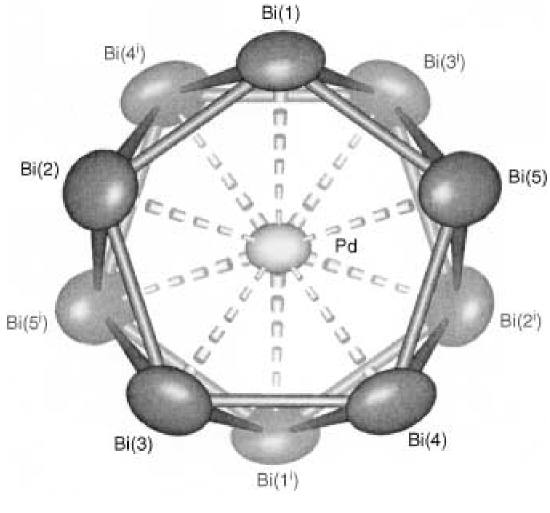

Figure 2. $[PdBi_{10}]^{4+}$ cluster in the crystal structure of $Bi_{14}PdBr_{16}$ (the ellipsoids represent 90% probability). Selected bond lengths [pm] and angles [°]: Pd-Bi(1) 301.9(2), Pd-Bi(2) 296.9(1), Pd-Bi(3) 298.7(2), Pd-Bi(4) 301.4(2), Pd-Bi(5) 301.0(1), Bi(1)-Bi(2) 315.3(2), Bi(2)-Bi(3) 317.4(2), Bi(3)-Bi(4) 313.5(1), Bi(4)-Bi(5) 318.8(2), Bi(5)-Bi(1) 312.8(1), Bi(1)-Bi(3^i) 314.2(2), Bi(1)-Bi(4^i) 318.1(2); Bi(1)-Pd-Bi(2) 63.53(4), Bi(1)-Pd-Bi(3^i) 63.09(4), Bi(1)-Bi(2)-Bi(3) 108.03(4). Symmetry code: (i) $-x, -y, -z$.

Electronic neutrality is maintained by polymeric bromobismuthate(III) anions, ${}_{\infty}^{1}[BiBr_4{}^{-}]$. Despite their simple composition, the constitution of the anions is rather complex: Six Br atoms surround each of the Bi atoms Bi(6) and Bi(7) in a distorted octahedral coordination (Figure 3). The $[Bi^{III}Br_6]$ octahedra are paired by sharing common edges while the octahedra pairs are linked by common corners to form the infinite zigzag chain ${}_{\infty}^{1}[(BiBr_{2/1}Br_{4/2}{}^{-})_4]$. The separation of the polycations from the anionic chains is evident: The Bi–Br bond lengths in the bromobismuthate(III) chain range from 272 to 325 pm, with an average of 291 pm; the shortest separation between a Bi atom of the $[PdBi_{10}]^{4+}$ polycation and a Br atom is 345 pm.

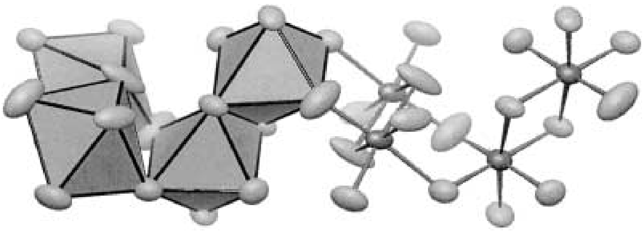

Figure 3. Concatenation of $[BiBr_6]$ octahedra in the anionic bromobismuthate(III) polymer ${}_{\infty}^{1}[(BiBr_{2/1}Br_{4/2}{}^{-})_4]$ (the ellipsoids represent 90% probability).

Until now all bismuth polycations have proved to have an optimized electron count,[20] while the halogenobismuthate(III) anions provide a seemingly infinite number of possibilities in adjusting their constitution, conformation, and charge in order to meet the dominant spatial, electronic, and electrostatic requirements of the diverse polycations.[7] Thus any discussion about the chemical bonding in $Bi_{14}PdBr_{16}$ must focus on the $[PdBi_{10}]^{4+}$ cluster.

Only a few ten-coordinated polyhedra with high symmetry exist. Among them, only the pentagonal prism and antiprism provide symmetry equivalence of all vertices. If the interligand distance, as well as the separation between the ligands and the central atom remain constant, the rotation of the two pentagons from the eclipsed to the staggered conformation is the only remaining conformational degree of freedom that can be used to optimize the interactions between the rings.

In order to gain a deeper understanding of the bonding character, quantum mechanical calculations for the solid (relativistic density functional theory (DFT) and extended Hückel (EH) calculations) and the isolated cluster cation (EH) were performed. Independent of the method used in the calculations, the band structure of $Bi_{14}PdBr_{16}$ displays only moderate dispersions for all bands, which is indicative of highly localized electrons and predominantly ionic interactions (Figure 4). The calculated band gap of approximately 1 eV corresponds with the black color of the powder.

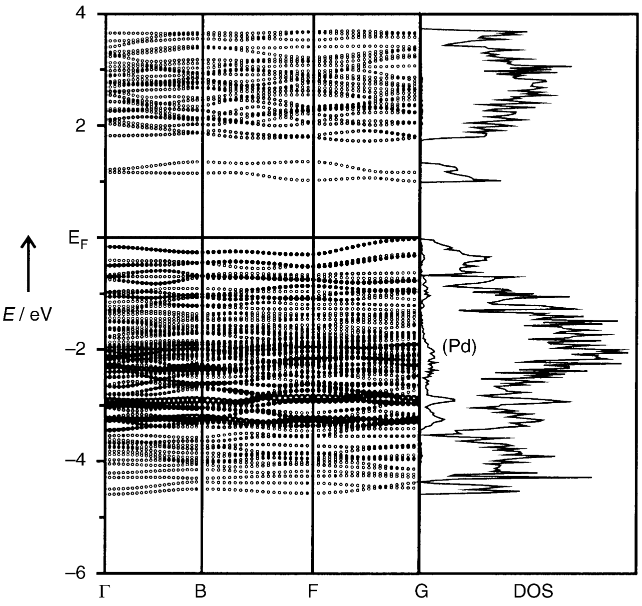

Figure 4. Electronic band structure and density of states (DOS) of $Bi_{14}PdBr_{16}$ from relativistic DFT calculations.

The crystal orbital overlap population (COOP) derived from the EH band-structure calculations demonstrates only a slight orbital overlap, especially between Bi and Pd (Figure 5), which is in agreement with the small dispersion of the Pd bands in the DFT band structure ("fat bands" in Figure 4). Although some states near the Fermi level are antibonding, the sum of the COOP(Bi–Pd) up to the Fermi level is still a small positive number, that is, the Bi–Pd interactions are weakly bonding. The weakness of the interaction between the central transition-metal atom and the surrounding Bi atoms represents an essential difference to the known, filled bismuth clusters, such as $[MBi_6X_{12}]$[17,18] or $[RhBi_7Br_8]$.[19]

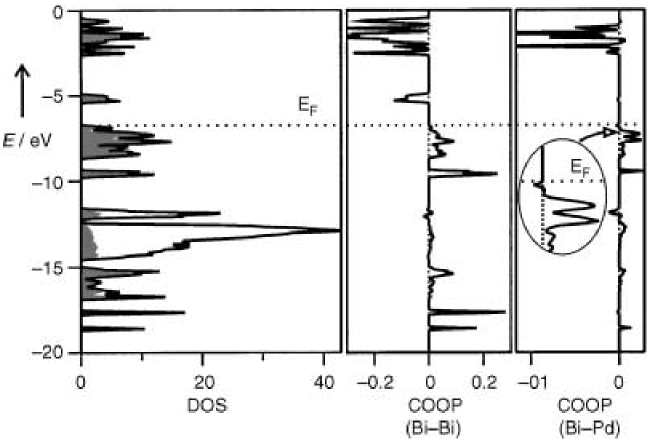

Figure 5. Total DOS and projected DOS of the Bi and Pd atoms (highlighted) in $Bi_{14}PdBr_{16}$, as well as overlap populations (COOP) for Bi–Bi and Bi–Pd interactions, as derived from EH calculations.

For the Bi–Bi interactions in the polycation, the Fermi level neatly separates the bonding from the antibonding states, that is to say the cluster shell has the optimum number of electrons. The almost identical COOP for the Bi–Bi interactions, both within the five-membered rings and between them, confirms a uniform bonding in the equilateral triangles of the pentagonal antiprism. Consequently, and in contrast to well-known bis(η^5-cyclopentadienyl) complexes of transition metals such as ferrocene, the inter-ring interaction is not predominantly steric but covalent. The $[PdBi_{10}]^{4+}$ polycation is a filled cluster, not a complex. Recently it has been predicted from ab initio (DFT-B3LYP) calculations that the hypothetical empty $[Bi_{10}]^{4+}$ polycation should have the shape of a D_{5d} pentagonal antiprism with Bi–Bi interactions of 324 pm within the rings, and 322 pm between them.[20] Actually the bonding situation, and even the shapes of the HOMO and LUMO, are nearly the same for the $[Bi_{10}]^{4+}$ shell of the $[PdBi_{10}]^{4+}$ cluster as for the empty $[Bi_{10}]^{4+}$ polycation. Disregarding the 6s electrons, which do not contribute because of their stabilization by relativistic effects, the $[Bi_{10}]^{4+}$ polyhedron with $10\times3-4=26$ electrons in the skeleton fulfills the expectations for an *arachno*-cluster of 10 atoms ($2\times n + 6=26$ electrons for bonding within the cluster).

All of these details imply that the positive charge of the $[PdBi_{10}]^{4+}$ cation is located on the Bi shell and the Pd atom is essentially uncharged. The closed-shell behavior ($4d^{10}5s^0$) of the Pd atom is even more evident in the corresponding MO scheme (Figure 6): The 4d orbitals of the Pd atom, filled with 10 electrons, are almost unaffected by the inclusion in the $[Bi_{10}]^{4+}$ antiprism, while the 5s orbital of the Pd atom undergoes a repulsion, which shifts it to energies high above the Fermi level. Regarding the weak interaction between the closed Pd^0 shell and the electron-precise *arachno*-cluster $[Bi_{10}]^{4+}$, the appropriate formulation for the $[PdBi_{10}]^{4+}$ polycation is $Pd@[Bi_{10}]^{4+}$, an endohedral inclusion compound comparable to $He@C_{60}$,[21] or in some aspects to the recently discovered $W@Au_{12}$ and $Mo@Au_{12}$ molecules.[22]

In this light, experimental observations have further meaning: All attempts to synthesize bismuth palladium subbromides directly from the elements have failed because of the precipitation of $PdBr_2$ and the formation of $[Bi_9]^{5+}$ polycations (crystallizing as Bi_6Br_7). However, the high-temperature reaction of the intermetallic phase Bi_2Pd with additional bismuth and bromine yields gray lustrous platelets of $Bi_{14}PdBr_{16}$. Thus, we argue that the synthetic clue is to hide the palladium center from the oxidizing halogen atoms by initially "wrapping" it in bismuth atoms through the preformation of the intermetallic phase, and to use it at the same time as a template for the arrangement of the entropically less favorable $[Bi_{10}]^{4+}$ polycation.

Experimental Section

Synthesis: Prior to its use in synthesis, Bi shot (99.9%, Riedel-de Haën) was reduced with hydrogen at 490 K to remove any oxide

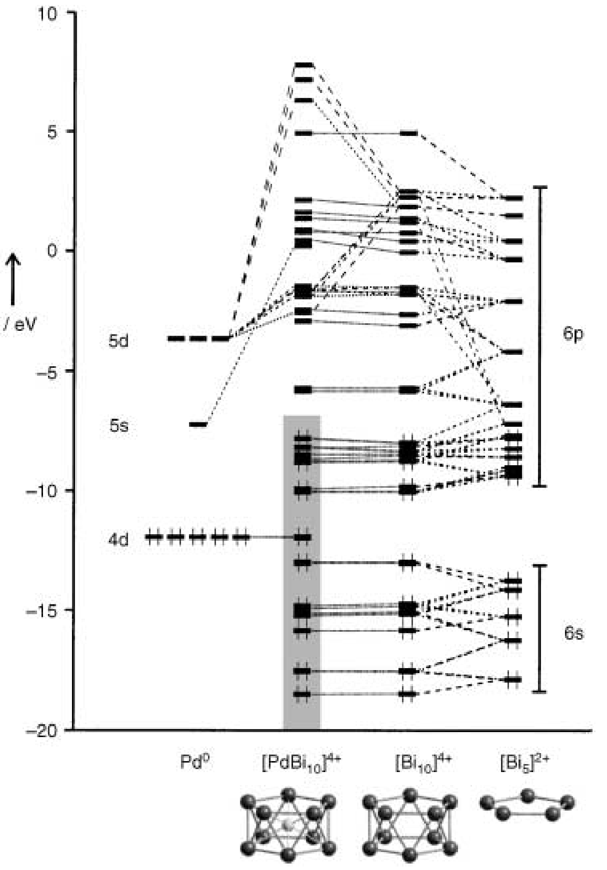

Figure 6. Evolution of the MO diagram of [PdBi$_{10}$]$^{4+}$ (point group C_i) based on EH calculations (filled MOs are highlighted).

from the surface. Then, Bi and Pd powder (99.99%, Degussa) were reacted in an evacuated quartz ampoule to give the intermetallic phase Bi$_2$Pd (m.p. 758 K).[23] To synthesise Bi$_{14}$PdBr$_{16}$, the starting materials Bi$_2$Pd (5 mmol), Bi (18 mmol), and Br$_2$ (20 mmol, 99.5%, Riedel-de Haën) were heated to 1270 K in an evacuated quartz ampoule. After two days the sample was cooled to 670 K over a period of a further four days. Any residual BiBr$_3$ was sublimed from the solid product while the temperature was reduced from 600 K to room temperature. Gray lustrous platelets of Bi$_{14}$PdBr$_{16}$ can be removed easily from unavoidable by-products, such as Bi$_6$Br$_7$ (black needles); pure Bi$_{14}$PdBr$_{16}$ can be left in the air without any visible decomposition. The energy-dispersive X-ray (EDX) analysis of a single crystal that had previously been checked by precession photography for a crystallographic match with Bi$_{14}$PdBr$_{16}$ gave the atomic ratio Bi:Pd:Br = 47:7:46; EDX is only a semiquantitative technique, which in this case overestimates the Pd content somewhat.

Crystal-structure determination of Bi$_{14}$PdBr$_{16}$: four-circle diffractometer CAD4 (Enraf Nonius), Mo$_{K\alpha}$ radiation, $\lambda = 71.073$ pm, ω/θ-scan, $2\theta_{max} = 60°$, $T = 293(2)$ K; crystal dimensions $0.45 \times 0.15 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), lattice parameters from 75 reflections of a powder diffraction diagram (Stadi P, Cu$_{K\alpha}$ radiation, 293(2) K): $a = 1084.8(7)$, $b = 1103.0(6)$, $c = 1115.7(4)$ pm, $\alpha = 118.15(3)$, $\beta = 108.82(3)$, $\gamma = 91.94(3)°$, $V = 1086.1 \times 10^6$ pm^3, $Z = 1$, $\rho_{calcd} = 6.591$ g cm^{-1}, μ(Mo$_{K\alpha}$) = 716 cm^{-1}, numerical absorption correction (X-RED), crystal description optimized using 17 ψ-scans (X-SHAPE), transmission factors 0.136 to 0.003, structure solution with direct methods (SHELXS), full-matrix least-squares refinement on F_o^2 (SHELXL[24]), 11183 reflections, 6070 unique, 142 parameters, anisotropic displacement parameters, $R1(3478\,F_o > 4\sigma(F_o)) = 0.035$, $wR2 = 0.043$, residual electron density +2.17 to -1.96×10^{-6} pm^{-3}. Graphical representation: DIAMOND. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412895.

Theoretical calculations: DFT calculations were performed with the WIEN97[25] code using the linearized augmented plane wave (LAPW) method. The muffin-tin radii were chosen to be 2.6 au for Pd, 2.6 au for Bi, and 2.4 au for Br. RKMAX and GMAX were taken to be 10 and 12 au^{-1}, respectively. The local-density functional LDA[26] was used as the exchange-correlation functional. The Brillouin-zone integration was performed using a tetrahedron method[27] using 64 inequivalent k points corresponding to 150 k points throughout the whole Brillouin zone within the SCF cycles. 90 inequivalent k points (250 k points in the Brillouin zone) were used for the calculation of the density of states (DOS). The extended Hückel calculations were performed using the YAeHMOP program[28] with the following parameters: orbital energies H_{ij} [eV] (coefficient ζ1); Bi: 6s −15.19 (2.56), 6p −7.790 (2.07); Br: 4s −22.08 (2.59), 4p −13.10 (2.13); Pd 5s −7.32 (2.19), 5p −3.75 (2.15), 4d −12.02 (5.98); double ζ-functions for Pd: 0.5535, 2.6130, 0.6701.

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