

Maximilian Knies and Michael Ruck*

Bismuth-rich bimetallic clusters $(\text{CuBi}_8)^{3+}$ and $[\text{MBi}_{10}]^{4+}$ ($M = \text{Pd}, \text{Pt}$) from ionothermal synthesis

<https://doi.org/10.1515/znb-2021-0159>

Received October 12, 2021; accepted October 25, 2021;

published online November 8, 2021

Abstract: The reaction of Bi, BiBr₃, and CuBr in the Lewis-acidic ionic liquid [BMIm]Br·4AlBr₃ (BMIm = 1-*n*-butyl-3-limidazolium) at 180 °C yielded air-sensitive, shiny black crystals of $(\text{CuBi}_8)[\text{AlBr}_4]_2[\text{Al}_2\text{Br}_7]$. Crystals of $[\text{MBi}_{10}][\text{AlCl}_4]_4$ ($M = \text{Pd}, \text{Pt}$) were obtained by reacting Bi, BiCl₃, and MCl₂ under similar conditions. The structures have been determined by X-ray diffraction on single-crystals and were found to be very similar to that of the known analogues with other halogens, although not isostructural. In crystals of the complex salts, polyhedral bimetallic clusters $(\text{CuBi}_8)^{3+}$ or $[\text{MBi}_{10}]^{4+}$ are embedded in matrices of halogenidoaluminate anions. The heteroatomic *nido*-cluster $(\text{CuBi}_8)^{3+}$ consists of a $(\text{Bi}_8)^{2+}$ square antiprism η^4 -coordinating a copper(I) cation. In the cluster cation $[\text{MBi}_{10}]^{4+}$, the metal atoms M center a pentagonal antiprism of bismuth atoms.

Keywords: bimetallic clusters; bismuth; cluster compounds; copper; palladium; platinum.

Dedicated to Professor Christian Näther on the occasion of his 60th birthday.

1 Introduction

Homonuclear polycations containing bismuth in low oxidation states have been known since the discovery of $(\text{Bi}_9)^{5+}$ in Bi₆Cl₇ [1]. Over the last decades, other clusters of different sizes and charges have been discovered [2–21] or predicted [22]. Bismuth polycations can also act as ligands or hosts for electron-rich transition metals ($M = \text{Au}, \text{Cu}, \text{Pd}, \text{Pt}, \text{Rh}, \text{Ru}$) [23–34]. These intermetalloid clusters crystallize

from both high-temperature melts and ionic liquids (ILs) [35], typically stabilized by weakly coordinating anions, such as $[\text{AlX}_4]^-$ ($X = \text{Cl}, \text{Br}$).

The recently discovered polyhedral cation $(\text{CuBi}_8)^{3+}$ exhibits a novel bonding mode between copper and bismuth atoms [24], two elements that normally avoid direct bonding to each other. Only a few intermetallic compounds are known, in which they appear in close proximity to each other, e. g., BaBiCu [36] or YbBiCu [37]. Binary compounds, such as CuBi [38, 39] or Cu₁₁Bi₇ [38, 40], all synthesized under high pressure of 4–6 GPa, are only metastable. The latter show a clear preference for homonuclear bonding, leading to structural segregation of the two elements. Heating induces decomposition into the elements, in the case of CuBi already below 200 °C [39]. The only example of a non-bridged Cu–Bi single bond was found in the molecule $(\text{Me}_3\text{Si})_2\text{Bi}-\text{Cu}(\text{PMe}_3)_3$ [41]. Here, the different ligands polarize the two metal atoms, which have almost equal electronegativity. However, the compound is highly susceptible to decomposition by light, moisture, and temperatures above –20 °C. In contrast, $(\text{CuBi}_8)[\text{AlCl}_4]_2[\text{Al}_2\text{Cl}_7]$ proved to be a thermodynamically stable compound, although it is sensitive to moisture. The cluster cation $(\text{CuBi}_8)^{3+}$ (Figure 1A) can be considered either as a $(\text{Bi}_8)^{2+}$ square antiprism η^4 -coordinating a copper(I) cation, or as a heteroatomic *nido*-cluster [24] according to modified Wade rules [42]. Here we present the analogous bromide $(\text{CuBi}_8)[\text{AlBr}_4]_2[\text{Al}_2\text{Br}_7]$.

An isolated Bi_{10}^{4+} polycation has not yet been observed, but it appears as a host for noble metal atoms such as palladium(0) [25, 31, 32, 34], platinum(0) [25], or gold(I) [34]. The $[\text{PdBi}_{10}]^{4+}$ cluster is shown in Figure 1B. Furthermore, the empty Bi_{10}^{4+} polycation has been found in the center of the $[\text{Au}_2\text{Bi}_{10}](\text{SbBi}_3\text{Br}_9)_2$ molecule (Figure 1C), where it η^5 -coordinates two gold atoms forming the heteroicosahedron $[\text{Au}_2\text{Bi}_{10}]^{6+}$, a bimetallic *closo*-cluster [28, 33]. The details of the chemical bonding in the $[\text{MBi}_{10}]^{4+}$ clusters ($M = \text{Pd}, \text{Pt}$) are still the subject of controversial discussions. The results of quantum chemical calculations suggest a host-guest scenario with only weak interactions, [34] so that the $[\text{MBi}_{10}]^{4+}$ clusters are analogous to filled fullerene type cages, e. g. $[\text{He}@\text{C}_{60}]$ [43] or $[\text{M}@\text{C}_{60}]$ ($M = \text{Ba}, \text{Ce}, \text{Gd}, \text{La}, \text{Nd}, \text{Pr}, \text{Y}$) [44], or to polyanions with endohedral atoms, e. g. $[\text{MPb}_{12}]^{2-}$ ($M = \text{Pd}, \text{Pt}$) [45, 46]. In contrast, a recent real-space

*Corresponding author: Michael Ruck, Fakultät Chemie und Lebensmittelchemie, Technische Universität Dresden, 01062 Dresden, Germany; and Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany, E-mail: michael.ruck@tu-dresden.de

Maximilian Knies, Fakultät Chemie und Lebensmittelchemie, Technische Universität Dresden, 01062 Dresden, Germany

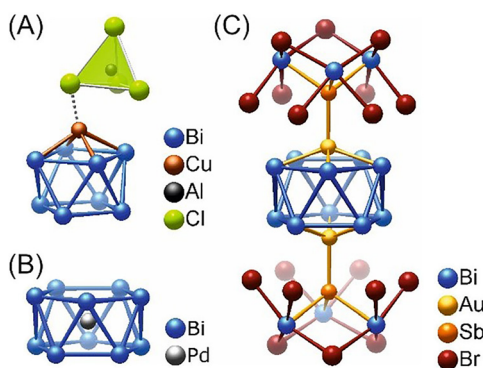


Figure 1: Bimetallic bismuth-rich clusters: (A) $(\text{CuBi}_8)^{3+}$ coordinated by an $[\text{AlCl}_4]^-$ group. (B) The $[\text{PdBi}_{10}]^{4+}$ cluster. (C) $[\text{Au}_2\text{Bi}_{10}]^{6+}$ as the central unit in the $[\text{Au}_2\text{Bi}_{10}](\text{SbBi}_3\text{Br}_9)_2$ molecule.

bonding analysis indicated substantial bonding between the noble metal and its bismuth shell [47]. Here we present two new salts $[\text{MBi}_{10}][\text{AlCl}_4]_4$ ($M = \text{Pd}, \text{Pt}$) containing such cluster cations.

2 Results and discussion

2.1 Synthesis

The reactions of stoichiometric amounts of Bi, BiX_3 ($X = \text{Cl}, \text{Br}$) and either CuBr , PtCl_2 or PdCl_2 in Lewis-acidic ionic liquids $[\text{BMIm}]\text{X}\cdot 4\text{AlX}_3$ ($\text{BMIm} = 1\text{-}n\text{-butyl-3-methylimidazolium}$) at 180°C resulted in air-sensitive, shiny black crystals of $(\text{CuBi}_8)[\text{AlBr}_4]_2[\text{Al}_2\text{Br}_7]$ (**1**), $[\text{PtBi}_{10}][\text{AlCl}_4]_4$ (**2**) and $[\text{PdBi}_{10}][\text{AlCl}_4]_4$ (**3**) respectively. **1** crystallizes as planks, while **2** and **3** form needles. The products were obtained in estimated yields of 70–80%. In all cases, $(\text{Bi}_5)[\text{AlX}_4]_3$ was observed as a side product together with residuals of AlX_3 (Figures S1–S3). To avoid the co-precipitation of $(\text{Bi}_5)[\text{AlX}_4]_3$ appeared to be almost impossible owing to the dynamic equilibria between the different bismuth polycations in the IL solution. Yet, the side products can easily be distinguished visually: $(\text{Bi}_5)[\text{AlX}_4]_3$ forms red cubes and AlX_3 colorless hexagonal plates. Energy dispersive X-ray (EDX) spectroscopy confirmed the 8:1 ratio of bismuth and copper for **1** and 10:1 of bismuth and the noble metal M for **2** and **3**.

2.2 Crystal structures

2.2.1 Crystal structure of $(\text{CuBi}_8)[\text{AlBr}_4]_2[\text{Al}_2\text{Br}_7]$

$[\eta^4\text{-Octabismuth(2+)-copper(I)}]\text{-bis[tetrabromidoaluminate]-heptabromidodialuminate}$ (**1**) crystallizes in the monoclinic

space group $P2_1/n$ (no. 14) with four formula units per unit cell and lattice parameters $a = 1830.9(1)$ pm, $b = 1048.4(1)$ pm, $c = 1946.7(1)$ pm, and $\beta = 95.87(1)^\circ$ at $170(1)$ K. Atomic parameters and interatomic distances are listed in Tables S1 and S2 of the Supporting Information. The crystal structure of **1** (Figure 2) contains three different complex ions, $(\text{CuBi}_8)^{3+}$ clusters, $[\text{AlBr}_4]^-$ tetrahedra, and vertex-sharing $[\text{Al}_2\text{Br}_7]^-$ di-tetrahedra.

In the $(\text{CuBi}_8)^{3+}$ cation, the copper(I) ion is η^4 -coordinated by a square face of the antiprismatic $(\text{Bi}_8)^{2+}$ polycation. Although its crystallographic symmetry is only C_1 , the deviations from C_{4v} are fairly small. The average Cu–Bi distance of 268.2(3) pm in **1** is little different from that in the chloride analogue $(\text{CuBi}_8)[\text{AlCl}_4]_2[\text{Al}_2\text{Cl}_7]$ (267.3(4) pm) [24] but is 6 pm shorter than in $[(\text{Me}_3\text{Si})_2\text{Bi}-\text{Cu}(\text{PMe}_3)_3]$ [41]. The average Bi–Bi distances (Table 1) are virtually the same as those in $(\text{CuBi}_8)[\text{AlCl}_4]_2[\text{Al}_2\text{Cl}_7]$. Compared to an isolated $(\text{Bi}_8)^{2+}$ cluster [3], the Bi–Bi distances in the coordinating square face are elongated. The extension of the *arachno*-cluster $(\text{Bi}_8)^{2+}$ by one copper vertex results in the heteroatomic *nido*-cluster $(\text{CuBi}_8)^{3+}$ (22 skeletal electrons) [24, 42]. One of the bromine vertices of an $[\text{AlBr}_4]^-$ anion is coordinated to the copper cation opposite to the bismuth cluster with a Cu–Br distance of 238.8(2) pm, which is 11 pm longer than the Cu–Cl distance in the analogous chloride. This lengthening approximately corresponds to the difference of the ionic radii of the halide ions ($r_{\text{Cl}} = 181$ pm; $r_{\text{Br}} = 196$ pm) [48]. Compared to the ternary compound $\text{Cu}[\text{AlBr}_4]$ [49], the Cu–Br distance is about 9 pm shorter, indicating a significant interaction between the copper(I)

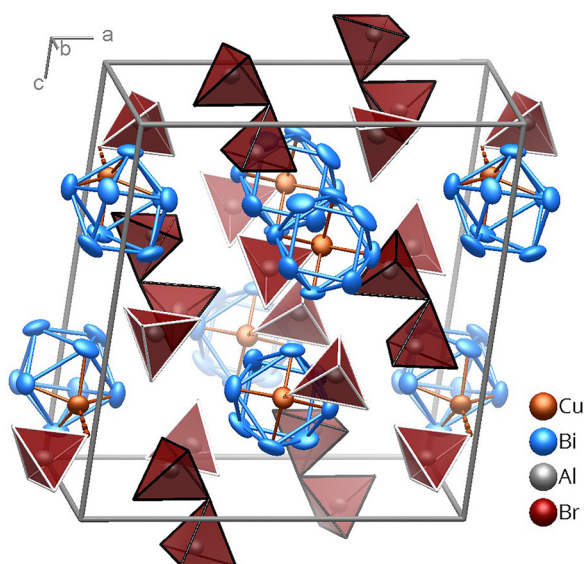


Figure 2: Crystal structure of **1** at 170 (1) K. $[\text{AlBr}_4]^-$ tetrahedra are shown with light edges, $[\text{Al}_2\text{Br}_7]^-$ groups with dark edges. The ellipsoids comprise 99% of the probability density of the atoms.

Table 1: Comparison of Bi–Bi distances in $(\text{CuBi}_8)[\text{AlX}_4]_2[\text{Al}_2\text{X}_7]$ compounds with $X = \text{Br}, \text{Cl}$. Values for $X = \text{Cl}$ are taken from [24].

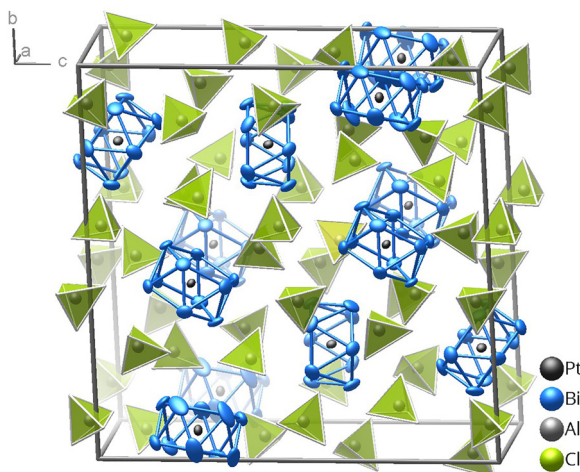
Bi–Bi distance/pm	$X = \text{Cl}$	$X = \text{Br}$
Coordinating square face	329 (2)	330 (3)
Non-coordinating square face	308 (1)	309 (1)
Inter-square connections	310 (2)	311 (2)

atom and the bromide ions and extending the $(\text{CuBi}_8)^{3+}$ cluster to a $\{(\text{CuBi}_8)[\text{AlBr}_4]\}^{2+}$ ion pair.

The average Al–Br distances in the $[\text{AlBr}_4]^-$ tetrahedra are 230 (3) pm, matching those in $\text{Cu}[\text{AlBr}_4]$ [49] or $(\text{Bi}_5)[\text{AlBr}_4]_3$ [11]. The bromine atom that is also coordinated to the copper(I) atom is 236.4 (4) pm away from the aluminum atom. Similarly, the bridging bromine atom in the $[\text{Al}_2\text{Br}_7]^-$ di-tetrahedra, exhibits elongated Al–Br distances of 241.9 (3) pm. Such differences in the bond lengths of terminal and bridging halogen atoms were also observed, e.g., in KAl_2Br_7 [50] or Al_2Br_6 [51] and were predicted as well as observed for adducts of the lighter chloridoaluminates $[\text{Al}_n\text{Cl}_{3n+1}]^-$ [52, 53]. Despite the obvious similarities in space group symmetry and lattice parameters between the chloride and bromide compounds, their structures differ significantly. Although the centers of the $[\text{AlX}_4]$ tetrahedra and the centers of the $(\text{CuBi}_8)^{3+}$ clusters occupy very similar positions in the unit cell, the orientation of the cluster cations and their connection to the $[\text{AlX}_4]$ tetrahedra are different. A comparison between the reduced structures of the two compounds can be found in Figure S4 and Table S3. Finally, we would like to mention that in our previous work [24] we also found evidence for a compound $(\text{CuBi}_8)[\text{AlCl}_4]_3$. Its crystal structure can be described in the monoclinic space group $P2_1/c$ with four formula units per unit cell and lattice parameters $a = 1580.9(1)$ pm, $b = 1444.9(1)$ pm, $c = 1292.5(1)$ pm, and $\beta = 90.71(1)^\circ$ at 170(1) K. However, the structure suffers from orientation disorder of all polyhedral groups. The inclusion of low-symmetry $[\text{Al}_2\text{X}_7]^-$ anions in the crystals obviously suppresses orientation disorder.

2.2.2 Crystal structure of $[\text{PtBi}_{10}][\text{AlCl}_4]_4$

[Platinumdecabismuth(4+)]-tetrakis(tetrachloridoaluminate) (**2**) crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with eight formula units per unit cell and lattice parameters $a = 1103.3(1)$ pm, $b = 2621.5(1)$ pm, $c = 2625.8(1)$ pm, $\alpha = 90.90(1)^\circ$, $\beta = 90.71(1)^\circ$, and $\gamma = 91.10(1)^\circ$ at 100(2) K. Atomic parameters and interatomic distances are listed in Tables S4 and S5 of the Supporting Information. The pseudo-tetragonal unit cell contains $[\text{PtBi}_{10}]^{4+}$ clusters and $[\text{AlCl}_4]^-$ tetrahedra (Figure 3).

**Figure 3:** Crystal structure of **2** at 100(2) K. The ellipsoids comprise 99% of the probability density of the atoms.

The $[\text{PtBi}_{10}]^{4+}$ cation can be divided into a formally uncharged platinum atom and a pentagonal antiprismatic $(\text{Bi}_{10})^{4+}$ shell. The latter is an *arachno*-cluster (26 skeletal electrons) according to modified Wade rules [42]. The average Pt–Bi distance of 298(2) pm (range: 293.7(2)–301.9(2) pm), of the intra-ring Bi–Bi bond length of 314(2) pm (range: 311.3(2)–319.6(2) pm) and of the inter-ring Bi–Bi distance of 310(2) pm (range: 305.9(2)–315.0(2) pm) in **2** match those observed in the bromide analogue [25]. Such tenfold coordination of a platinum atom in a solid compound has so far only been observed for this type of filled cluster. An anionic homologue $[\text{PtPb}_{10}]^-$ has only been detected in the gas phase through decomposition of $[\text{PtPb}_{12}]^{2-}$ but could not be isolated as a salt in the solid state yet [46].

The tetrahedral $[\text{AlCl}_4]^-$ ions show Al–Cl distances of 210(2) pm to 217.1(9) pm which slightly exceed those in $\text{Na}[\text{AlCl}_4]$ [54] but fit to the values in $(\text{Bi}_8)[\text{AlCl}_4]_2$ [3] and on average those in $(\text{Bi}_5)[\text{AlCl}_4]_3$ [6]. Large and elongated anisotropic displacement parameters of most chloride ions suggest a high degree of rotational freedom for the highly symmetric anions. This phenomenon is known for polycationic compounds containing such anions [3] and is most likely caused by the absence of strong interactions between cationic and anionic groups (shortest Bi–Cl distance 323(1) pm). For the lattice parameters of **2**, there are only minor deviations from the tetragonal metric, with c being only 0.2% larger than b and all angles deviating at most 1° from the right angle. Indeed, the bromine analogue of **2** crystallizes in the tetragonal space group $P\bar{4}$ [25]. Its lattice parameters a and b are about $\sqrt{2}$ larger than b and c in **2**. The structural similarity is even more evident when the two unit cells are superimposed (Figure S5). The drastic reduction in symmetry in **2** is associated with a slight tilting of the

Table 2: Lattice parameters of compounds [PdBi₁₀][AlX₄]₄ (X = Cl, Br [25]) at room temperature.

X	Cl	Br
a/pm	2637 (2)	3817.9 (1)
b/pm	2639 (2)	3827.9 (1)
c/pm	1113 (1)	1134.9 (1)
α/°	90.01 (1)	90
β/°	90.03 (1)	90
γ/°	90.33 (1)	90
V/(10 ⁶ pm ³)	7745 (5)	16543 (1)

[PtBi₁₀]⁴⁺ clusters in different directions and position shifts of the tetrahedra. These effects probably arise from directional interactions between cationic and anionic groups in the chlorine compound **2**.

Poor crystal quality prevented a comprehensive structure elucidation of [PdBi₁₀][AlCl₄]₄ (**3**). The chemical composition, the lattice parameters, and the diffraction pattern suggest that it crystallizes isostructural to **2**. The lattice parameters and their relation to the known bromine homologue (Table 2) match the observations made for the platinum compounds.

3 Conclusions

Modifications of the halogenidoaluminate used in ionothermal syntheses led to the crystallization of three new compounds containing bismuth clusters with electron-rich late transition metal atoms. Although their crystal structures contain the same kinds of building units, they differ in details of the packing from those of their already known lighter or heavier homologues, which also affect the space group symmetry. The synthesis of (CuBi₈)[AlBr₄]₂[Al₂Br₇] did not yield a secondary phase containing only tetrahedral [AlBr₄][−] anions, as was the case with its chloride analogue. Orientational disorder is typically observed in those compounds that consist of isolated polyhedral groups. The incorporation of [Al₂X₇][−] groups, which do not have a spherical envelope, strongly reduces or prevents such disorder.

4 Experimental

4.1 Synthesis and chemical analysis

All compounds were handled in an argon-filled glove box (M. Braun; p(O₂)/p⁰ < 1 ppm., p(H₂O)/p⁰ < 1 ppm). The reactions were carried out in silica ampoules with a length of 120 mm and a diameter of 14 mm.

(CuBi₈)[AlBr₄]₂[Al₂Br₇] (**1**) was synthesized in the ionic liquid [BMIm]Br·4AlBr₃, which acted as solvent and reactant. The ampoule was loaded with a mixture of 14.3 mg CuBr (0.1 mmol, 98%, Sigma Aldrich), 152.6 mg Bi (0.73 mmol, 99.9%, abcr, treated twice with H₂ at 220 °C), 30.5 mg BiBr₃ (0.07 mmol, 98%, Alfa Aesar, sublimed three times), 188.2 mg [BMIm]Br (0.86 mmol, 98%, Alfa Aesar, dried under vacuum at 100 °C), and 916.0 mg AlBr₃ (3.43 mmol, sublimed two times) and heated at 180 °C for 60 h. The ionic liquid turned black at this temperature. Before cooling the mixture to room temperature at ΔT/t = −6 K h^{−1}, the ampoule was tilted to enable the separation of already precipitated by-products. Black crystals of **1** were obtained alongside with red (Bi₅)[AlCl₄]₃ and colorless AlCl₃ (Figure S1). The crystals of the target compound were mechanically separated from both byproducts based on their shape and color.

[MBi₁₀][AlCl₄]₄ with M = Pd (**3**) or Pt (**2**) was synthesized in the ionic liquid [BMIm]Cl·4AlCl₃. The ampoule was loaded with 14.2 mg PdCl₂ (0.08 mmol, 99.9%, Alfa Aesar) or 21.3 mg PtCl₂ (0.08 mmol, 73.27% Pt, Alfa Aesar), 153.3 mg Bi (0.73 mmol, 99.9%, abcr, treated twice with H₂ at 220 °C), 21.0 mg BiCl₃ (0.07 mmol, 98%, Alfa Aesar, sublimed three times), 150.0 mg [BMIm]Cl (0.86 mmol, 98%, Sigma Aldrich, dried under vacuum at 100 °C), and 450.0 mg AlCl₃ (3.38 mmol, sublimed three times). The evacuated and sealed ampoule was heated at 180 °C for 48 h. The ionic liquid turned black at this temperature. Before cooling the mixture to room temperature at ΔT/t = −6 K h^{−1}, the ampoule was tilted to enable the separation of already precipitated by-products. Black crystals of **2** and **3** were obtained alongside red (Bi₅)[AlCl₄]₃ and colorless AlCl₃ (Figures S2 and S3). No further treatment was applied to the crystals of the target compounds, as the small amounts of residual IL on the crystal surface did not impede the following investigations.

Energy dispersive X-ray spectroscopy (EDS) measurements were conducted using a SU8020 (Hitachi) SEM equipped with a Silicon Drift Detector (SDD) X-Max^N (Oxford) and confirmed the ratio of bismuth to transition metal of 8: 1 for **1** and 10: 1 for **2** and **3**. The sensitivity of the compounds to moisture led to discrepancies in the Al and X contents, as observed in other cases. Calcd./exp. Cu: Bi: Al: Cl (at.-%) in (CuBi₈)[AlBr₄]₂[Al₂Br₇]: 3.6: 28.6: 14.3: 53.6/3(1): 28(2): 23(2): 46(2). Calcd./exp. Pt: Bi: Al: Cl (at.-%) in [PtBi₁₀][AlCl₄]₄: 3.2: 32.3: 12.9: 51.6/3(1): 35(6): 18(1): 44(4). Calcd./exp. Pd: Bi: Al: Cl (at.-%) in [PdBi₁₀][AlCl₄]₄: 3.2: 32.3: 12.9: 51.6/3(1): 32(2): 17(1): 48(2).

4.2 X-ray crystal structure determination

X-ray diffraction on single-crystals was performed using a four-circle Kappa APEX II CCD diffractometer (Bruker) with a graphite(002)-monochromator and a CCD-detector at T = 170(1) K for **1** and 100(2) K for **2**. Mo-K_α radiation (λ = 71.073 pm) was used. After integration [55], a numerical absorption correction based on an optimized crystal description was applied [56]. The initial structure solution was performed with JANA2006 [57] and further refinement against F_o² processed in SHELXL [58–60]. (CuBi₈)[AlBr₄]₂[Al₂Br₇]: monoclinic; space group P2₁/n (no. 14); T = 170(1) K; a = 1830.9(1) pm, b = 1048.4(1) pm, c = 1946.7(1) pm, β = 95.87(1)°, V = 3717.0(2) × 10⁶ pm³; Z = 4; ρ_{calcd.} = 5.44 g cm^{−3}; μ(Mo-K_α) = 54.5 mm^{−1}; 2θ_{max} = 49.5°, −21 ≤ h ≤ 21, −12 ≤ k ≤ 12, −22 ≤ l ≤ 22; 59,817 measured, 6359 unique reflections, R_{int} = 0.094, R_σ = 0.065; 281 parameters, R₁[4595 F_o > 4σ(F_o)] = 0.029, wR₂(all F_o²) = 0.036, GooF = 0.96, min./max.

residual electron density: $-1.39/1.51 \text{ e} \times 10^{-6} \text{ pm}^{-3}$. For atomic parameters see Table S2 of the Supporting Information.

$[\text{PtBi}_{10}][\text{AlCl}_4]_4$: triclinic; space group $P 1$ (no. 2); $T = 100(2) \text{ K}$; $a = 1103.3(1) \text{ pm}$, $b = 2621.5(1) \text{ pm}$, $c = 2625.8(1) \text{ pm}$, $V = 7585.8(5) \times 10^6 \text{ pm}^3$; $Z = 8$; $\rho_{\text{calcd.}} = 5.18 \text{ g cm}^{-3}$; $\mu(\text{Mo-K}\alpha) = 51.1 \text{ mm}^{-1}$; $2\theta_{\text{max}} = 50.8^\circ$, $-13 \leq h \leq 12$, $-31 \leq k \leq 31$, $-31 \leq l \leq 31$; 129,883 measured, 27,839 unique reflections, $R_{\text{int}} = 0.152$, $R_\sigma = 0.175$; 1027 parameters, $R_1[14,595 F_o > 4\sigma(F_o)] = 0.045$, $wR_2(\text{all } F_o^2) = 0.072$, $\text{Goof} = 0.76$, min./max. residual electron density: $-2.53/4.18 \text{ e} \times 10^{-6} \text{ pm}^{-3}$. For atomic parameters see Table S4 of the Supporting Information.

Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository numbers CSD-2102127 for $(\text{CuBi}_8)[\text{AlBr}_4]_2$, $[\text{Al}_2\text{Br}_7]$ and CSD-2102128 for $[\text{PtBi}_{10}][\text{AlCl}_4]_4$.

5 Supporting information

Additional representations of the crystal structures for a comparison of the title compounds to their homologues as well as powder diffractograms and atomic coordinates including displacement parameters are provided as supplementary material available online.

Acknowledgments: We acknowledge technical support by M. Münch and A. Brünner (TU Dresden).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This research was funded by the Deutsche Forschungsgemeinschaft (DFG) within the Priority Program SPP 1708.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- Hershaft A., Corbett J. D. *J. Chem. Phys.* 1962, 36, 551–552.
- Krebs B., Hücke M., Brendel C. J. *Angew. Chem.* 1982, 94, 453–454; *Angew. Chem. Int. Ed. Engl.* 1982, 21, 445–446.
- Beck J., Brendel C. J., Bengtsson-Kloo L., Krebs B., Mummert M., Stankowski A., Ulvenlund S. *Chem. Ber.* 1996, 129, 1219–1226.
- Kalpen H., Hönle W., Somer M., Schwarz U., Peters K., von Schnering H. G., Blachnik R. *Z. Anorg. Allg. Chem.* 1998, 624, 1137–1147.
- Lindsjö M., Kloo L., Fischer A. *Eur. J. Inorg. Chem.* 2005, 2005, 670–675.
- Ahmed E., Köhler D., Ruck M. *Z. Anorg. Allg. Chem.* 2009, 635, 297–300.
- Wosylus A., Dubenskyy V., Schwarz U., Ruck M. *Z. Anorg. Allg. Chem.* 2009, 635, 1030–1035.
- Wahl B., Ruck M. *Z. Anorg. Allg. Chem.* 2010, 636, 337–342.
- Groom R., Jacobs A., Cepeda M., Drummey R., Lattner S. E. *Chem. Mater.* 2017, 29, 3314–3323.
- Beck J., Hilbert T. *Eur. J. Inorg. Chem.* 2004, 2004, 2019–2026.
- Ruck M., Steden F. *Z. Anorg. Allg. Chem.* 2007, 633, 1556–1562.
- Wahl B., Ruck M. *Z. Anorg. Allg. Chem.* 2008, 634, 2873–2879.
- Corbett J. D. *Inorg. Chem.* 1968, 7, 198–208.
- Burns R. C., Gillespie R. J., Luk W.-C. *Inorg. Chem.* 1978, 17, 3596–3604.
- Krebs B., Mummert M., Brendel C. *J. Less Common. Met.* 1986, 116, 159–168.
- Heerman L., D'Olieslager W. *J. Electrochem. Soc.* 1991, 138, 1372.
- Ulvenlund S., Wheatley A., Bengtsson L. A. *J. Chem. Soc. Chem. Commun.* 1995, 59–60; <https://doi.org/10.1039/c39950000059>.
- Ulvenlund S., Ståhl K., Bengtsson-Kloo L. *Inorg. Chem.* 1996, 35, 223–230.
- Ichikawa K., Yamanaka T., Takamuku A., Glaser R. *Inorg. Chem.* 1997, 36, 5284–5290.
- Ruck M., Locher F. *Coord. Chem. Rev.* 2015, 285, 1–10.
- Knies M., Kaiser M., Lê Anh M., Efimova A., Doert T., Ruck M. *Inorganics* 2019, 7, 45.
- Kuznetsov A. N., Kloo L., Lindsjö M., Rosdahl J., Stoll H. *Chem. Eur. J.* 2001, 7, 2821–2828.
- Müller U., Isaeva A., Richter J., Knies M., Ruck M. *Eur. J. Inorg. Chem.* 2016, 2016, 3580–3584.
- Knies M., Kaiser M., Isaeva A., Müller U., Doert T., Ruck M. *Chem. Eur. J.* 2018, 24, 127–132.
- Groh M. F., Wolff A., Wahl B., Rasche B., Gebauer P., Ruck M. *Z. Anorg. Allg. Chem.* 2017, 643, 69–80.
- Groh M. F., Isaeva A., Frey C., Ruck M. *Z. Anorg. Allg. Chem.* 2013, 639, 2401–2405.
- Groh M. F., Isaeva A., Ruck M. *Chem. Eur. J.* 2012, 18, 10886–10891.
- Wahl B., Ruck M. *Z. Anorg. Allg. Chem.* 2008, 634, 2267–2275.
- Ruck M. *Z. Anorg. Allg. Chem.* 1997, 623, 1591–1598.
- Groh M. F., Müller U., Isaeva A., Ruck M. *Z. Anorg. Allg. Chem.* 2017, 643, 1482–1490.
- Ruck M., Dubenskyy V., Söhnel T. *Angew. Chem.* 2003, 115, 3086–3090; *Angew. Chem. Int. Ed.* 2003, 42, 2978–2982.
- Dubenskyy V., Ruck M. *Z. Anorg. Allg. Chem.* 2004, 630, 2458–2462.
- Wahl B., Kloo L., Ruck M. *Angew. Chem.* 2008, 120, 3996–3999; *Angew. Chem. Int. Ed.* 2008, 47, 3932–3935.
- Wahl B., Erbe M., Gerisch A., Kloo L., Ruck M. *Z. Anorg. Allg. Chem.* 2009, 635, 743–752.
- Wasserscheid P., Welton T. *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, 2008.
- Merlo F., Pani M., Fornasini M. L. *J. Less Common. Met.* 1990, 166, 319–327.
- Tkachuk A. V., Mozharivskiy Y., Mar A. Z. *Kristallogr.* 2006, 221, 539–542.
- Clarke S. M., Amsler M., Walsh J. P. S., Yu T., Wang Y., Meng Y., Jacobsen S. D., Wolverton C., Freedman D. E. *Chem. Mater.* 2017, 29, 5276–5285.
- Guo K., Akselrud L., Bobnar M., Burkhardt U., Schmidt M., Zhao J.-T., Schwarz U., Grin Y. *Angew. Chem.* 2017, 129, 5712–5716; *Angew. Chem. Int. Ed.* 2017, 56, 5620–5624.
- Clarke S. M., Walsh J. P. S., Amsler M., Malliakas C. D., Yu T., Goedecker S., Wang Y., Wolverton C., Freedman D. E. *Angew. Chem.* 2016, 128, 13644–13647; *Angew. Chem. Int. Ed.* 2016, 55, 13446–13449.

41. Fenske D., Rothenberger A., Wieber S. Z. *Anorg. Allg. Chem.* 2003, 629, 929–930.
42. Wade K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1–66.
43. Weiske T., Böhme D. K., Hrušák J., Krätschmer W., Schwarz H. *Angew. Chem.* 1991, 103, 898–900; *Angew. Chem. Int. Ed. Engl.* 1991, 30, 884–886.
44. Kubozono Y., Maeda H., Takabayashi Y., Hiraoka K., Nakai T., Kashino S., Emura S., Ukita S., Sogabe T. *J. Am. Chem. Soc.* 1996, 118, 6998–6999.
45. Esenturk E. N., Fetting J., Lam Y.-F., Eichhorn B. *Angew. Chem.* 2004, 116, 2184–2186; *Angew. Chem. Int. Ed.* 2004, 43, 2132–2134.
46. Esenturk E. N., Fetting J., Eichhorn B. *J. Am. Chem. Soc.* 2006, 128, 9178–9186.
47. Stroganova E. A., Troyanov S. I., Morozov I. V., Kuznetsov A. N. *Crystals* 2020, 10, 940.
48. Shannon R. D. *Acta Crystallogr.* 1976, A32, 751–767.
49. Martin J. D., Leafblad B. R., Sullivan R. M., Boyle P. D. *Inorg. Chem.* 1998, 37, 1341–1346.
50. Rytter E., Rytter B. E. D., Øye H. A., Krogh-Moe J. *Acta Crystallogr.* 1973, B29, 1541–1543.
51. Berg R. W., Poulsen F. W., Nielsen K. *Acta Chem. Scand.* 1997, 51, 442–448.
52. Akdeniz Z., Tosi M. P. Z. *Naturforsch.* 1999, 54a, 180–186.
53. Manteghetti A., Potier A. *Spectrochim. Acta Part A Mol. Spectrosc.* 1982, 38, 141–148.
54. Baenziger N. C. *Acta Crystallogr.* 1951, 4, 216–219.
55. Bruker. *SAINT+*; Bruker AXS Inc.: Madison, Wisconsin (USA), 2017.
56. *X-SHAPE, Crystal Optimization for Numerical Absorption Correction Program*; Stoe & Cie GmbH: Darmstadt (Germany), 2008.
57. Petricek V., Dusek M., Palatinus L. *JANA2006, the Crystallographic Computing System*; Institute of Physics: Praha (Czech Republic), 2011.
58. Sheldrick G. M. *Acta Crystallogr.* 2008, A64, 112–122.
59. Sheldrick G. M. *SHELXL, Program for Crystal Structure Refinement – Multi-CPU*; Georg-August-Universität Göttingen: Göttingen (Germany), 2014.
60. Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3–8.

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/znb-2021-0159>).