

PAPER



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Tailoring in-gap states for optimizing the band gap in mixed-valent bromometallates, towards lead-free photovoltaics

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Motivated by the task to replace toxic lead halide perovskites with lead-free environmentally benign light-harvesting materials for photovoltaics, we have synthesized two new hybrid bromometallates, $(\text{AH}_2)_4[\text{Sb}_2\text{Br}_{10}(\text{SbBr}_6)_2(\text{Br})_2]$ (**1**) and $(\text{AH}_2)_2[(\text{BiBr}_6)(\text{SbBr}_6)] \cdot 2\text{H}_2\text{O}$ (**2**), where A = 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane. Their crystal structures show combinations of $\text{Sb}^{3+}/\text{Sb}^{5+}$ (**1**) or $\text{Bi}^{3+}/\text{Sb}^{5+}$ (**2**) centers each surrounded by six Br^- anions forming distorted (Sb^{3+} or Bi^{3+}) or almost regular (Sb^{5+}) octahedra. These octahedra are arranged in the crystal structure in a perfectly ordered way owing to weak $\text{Br} \cdots \text{Br}$ interactions within the inorganic anionic part and to hydrogen bonds linking inorganic anions and organic cations. The electronic structures of both compounds are alike in that they have $\text{M}^{3+}/\text{Br}^-$ states ($\text{M} = \text{Sb}$ or Bi) dominating the top of the valence band and acceptor in-gap states formed by the $\text{Sb}^{5+}/\text{Br}^-$ interactions. Such an electronic structure leads to the reduced band gap of 1.27 (**1**) and 1.58 eV (**2**), favorable for creating light-harvesting materials for photovoltaics. We support our data by powder and single-crystal X-ray diffraction study, ^{121}Sb Mossbauer spectroscopy, and optical spectroscopy. We infer that tailoring the band gap is a very important step on the way to lead-free light-harvesting materials for photovoltaic applications.

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Introduction

The efficiency of light-absorbing haloplumbates has already exceeded 26%, making them very attractive for modern photovoltaics.¹ Their drawback is the neurotoxicity of lead compounds that raises doubts about the prospects of lead-based light-harvesting materials and motivates looking for analogues among halide complexes of other post-transition metals containing a lone ns^2 pair.^{2–6} The obvious solution to replace lead with much less toxic tin gained only moderate success because of the low chemical stability of Sn^{2+} derivatives that are prone to oxidation in air and to disproportionation into Sn^0 and Sn^{4+} when exposed to light in anaerobic conditions.^{7–9}

Complex halides of antimony and bismuth have much greater stability coupled with low toxicity. However, they, as a rule, do not meet the very first demand for light-harvesting

materials, which is the optimal band gap of 1.3–1.5 eV, which enables the highest power conversion efficiency.¹⁰ The majority of antimony and bismuth halide complexes are characterized by a band gap of 2 eV and higher, which brings about the central task to develop methods for reducing the band gap down to acceptable values. Expectedly, the width of the band gap in complex bismuth and antimony halides increases on going from iodine to bromine and chlorine, and from bismuth to antimony. Complex bismuth iodides that contain BiI_6^{3-} anions display narrower band gaps near 2.0 eV,^{11–16} whereas those for complex antimony chlorides exceed 3.0 eV.^{17,18} Mainly, complex iodides were considered as potential lead-free light-harvesting materials, and several methods to diminish their band gap have been reported in the literature.

Condensation of MI_6^{3-} anions ($\text{M} = \text{Sb}, \text{Bi}$) into 1D or 2D structures was the first method. Many motifs of forming linear, zigzag, or spiral chains or layers by stitching MI_6^{3-} octahedra through common vertices and/or edges have been documented.^{19–24} These compounds frequently display band gaps of 1.75–1.85 eV.^{25–27} In this case, multiple M–I interactions provide greater dispersion in the band structure thus leading to lowering the band gap width, where the charge

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transfer proceeds from occupied iodine p-states at the top of the valence band to empty bismuth or antimony p-states at the bottom of the conduction band. Additional interactions that include hydrogen bonding, secondary I...I bonds, and charge transfer from iodine p-orbitals to the aromatic system of an organic cation can further narrow the band gap down to 1.6 eV,^{28–31} which is still above the optimal range of 1.3–1.5 eV.

Another approach is based on linking the MI_6^{3-} anions by additional I_2 molecules or I_n^- anions.^{32–35} In particular, I_2 molecules link MI_6^{3-} anions such that I...I bonds between iodine atoms of a I_2 molecule and MI_6^{3-} octahedra form interatomic interactions at about 3.5 Å. Such a distance is known as a secondary bond;³⁶ it is observed in crystalline iodine³⁷ and in several polyiodometallates.^{38,39} In the case of iodobismuthates and iodoantimonates, I_2 molecules form states at the top of the valence band thus reducing the band gap to the values of 1.17–1.51 eV, depending on the crystal structure and the length of the I...I bond, which fall into the desired range of 1.3–1.5 eV.^{40–43}

Although the required band gap can be achieved, another obstacle prevents one from using these compounds as light-harvesting materials. They have low chemical and thermal stability, they readily decompose upon slight heating, and they cannot be recrystallized from any solution except aqueous HI, which so far makes their use in photovoltaics doubtful.

Here, we propose another approach to optimizing the band gap of complex bismuth and antimony halides. It relies on the formation of in-gap states in the band structure. Their formation is achieved by combining empty and occupied p-states of bismuth and antimony, for which a combination of M^{3+} and M^{5+} is required. In such a case, the charge transfer proceeds from M^{3+}/X^- p-states at the top of the valence band to M^{5+}/X^- in-gap acceptor states ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) as shown schematically in Fig. 1 ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$).

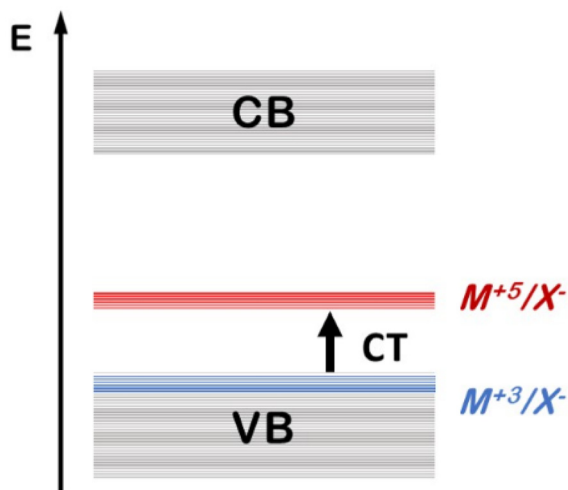


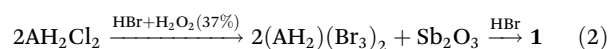
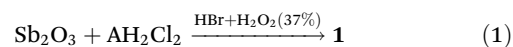
Fig. 1 A scheme of the band structure showing the charge transfer from M^{3+}/X^- p-states at the top of the valence band (VB) to M^{5+}/X^- in-gap acceptor states.

Of course, in the formal oxidation state of +5 bismuth behaves as a strong oxidizer, making its combination with chloride, bromide, and iodide anions impossible. Therefore, it is logical to turn to antimony, which is rather stable in this oxidation state except for iodide complexes. Naturally, Sb^{5+} in the bromide environment in combination with Sb^{3+} or Bi^{3+} is chosen for constructing halometallate anions having in-gap states. The choice of 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane, belonging to a family of bispidines (Fig. 2), as a source of a strong ammonium cation is based on two considerations. First, bispidines are stable in a strong acidic medium unlike their congeners, such as urotropine, and resistant towards oxidation by moderate oxidants. Second, bispidines form relatively strong hydrogen bonds with halides ensuring strict positioning of halometallate anions in the crystal structure with no positional disorder; moreover, the ability of bispidines to use all their hydrogen atoms bound to nitrogen atoms to form hydrogen bonds can be used to predict the arrangement of halometallates in the crystal structure of a desired organic–inorganic hybrid.^{44–47}

In this paper, we describe the synthesis, crystal and electronic structure, and optoelectronic properties of two new compounds, $(\text{AH}_2)_4[\text{Sb}_2\text{Br}_{10}(\text{SbBr}_6)_2(\text{Br})_2]$ (**1**) and $(\text{AH}_2)_2[(\text{Bi}^{\text{III}}\text{Br}_6)(\text{Sb}^{\text{V}}\text{Br}_6)] \cdot 2\text{H}_2\text{O}$ (**2**), where $\text{A} = 1,5\text{-dimethyl-3,7-diazabicyclo[3.3.1]nonane}$. We show that both new complexes can be reproducibly prepared by different synthetic methods and are chemically stable. They indeed have in-gap states in their band structures formed by $\text{Sb}^{5+}/\text{Br}^-$ hybridized states. This ensures charge transfer between $\text{Sb}(\text{Bi})^{3+}$ and Sb^{5+} states across the gap of nearly 1.5 eV. Details of the crystal and electronic structure as well as the interaction between $(\text{Sb}^{5+}\text{Br}_6)^-$ and $(\text{M}^{3+}\text{Br}_6)^{3-}$ octahedra are discussed in this paper.

Results and discussion

Three different procedures were employed to synthesize compound **1**. In two of them, partial oxidation of $\text{Sb}(\text{III})$ was achieved by applying moderate oxidizers. In the first method, commercial 37% hydrogen peroxide was used (eqn (1)). In the second method, specially designed and synthesized (see SI for details) tribromide $\text{AH}_2(\text{Br}_3)_2$ served as an oxidizer (eqn (2)). In both cases only half of Sb^{3+} cations transformed into Sb^{5+} ones, leading to the $\text{Sb}^{3+}:\text{Sb}^{5+}$ ratio of 1:1 in the resulting compound. In the third method, antimony oxides Sb_2O_3 and Sb_2O_5 were taken in a 1:1 ratio as the source of antimony in two different oxidation states such that no oxidizer was required (eqn (3)). In all three synthetic routes, 47% hydrobromic acid was used both as a source of Br^- anions and as a medium. The latter protects both Sb^{3+} and Sb^{5+} species from hydrolysis, yet it is harmless to bisidine **A**, which survives in a highly acidic medium.



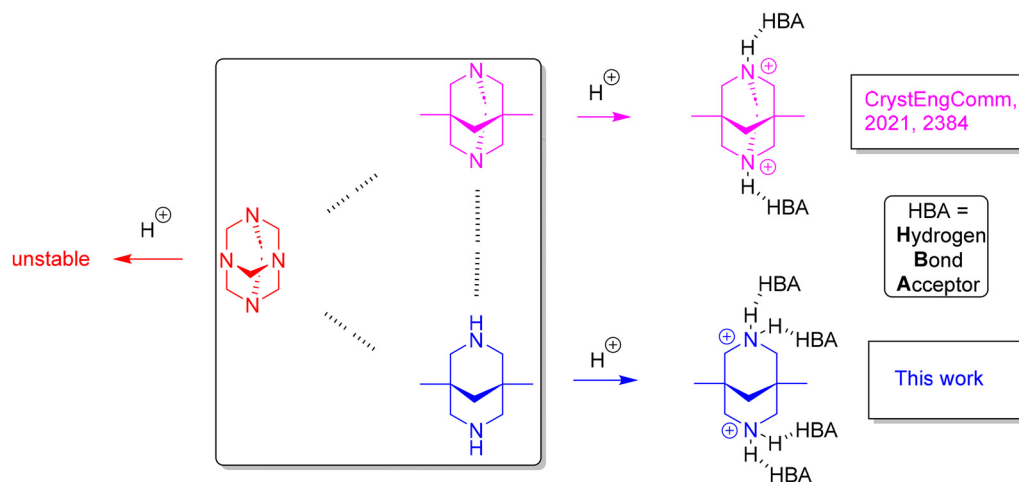
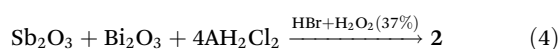
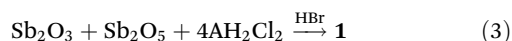


Fig. 2 Bispidine (bottom), its congeners urotropine (left) and diazaadamantane (top), and the modes of their interactions with strong acids.



Although the above three synthetic methods demonstrate comparable yields, the method that exploits hydrogen peroxide as a moderate oxidizer was chosen as the best because it was the easiest to accomplish and to control, whereas other methods produced the target phase slightly contaminated by an unknown impurity (Fig. S4). Consequently, for the synthesis of compound 2, the method involving oxidation of Sb(III) by hydrogen peroxide in the presence of Bi(III) in the HBr medium was chosen and successfully led to crystals of 2 (eqn (4)).

The resulting products were tested by PXRD, and good agreement between PXRD and those simulated from the crystal data showed that compounds 1 and 2 were phase-pure (see Fig. S4 and S5 of SI). Both compounds display long-term stability in air at ambient temperature but decompose upon heating at about 115 (1) or 90 (2) °C (Fig. S6 and S7 of SI).

The crystal structures of compounds 1 and 2 contain two distinct parts, an organic cation and inorganic anions (Fig. 3). Although the inorganic part of the crystal structures is based on $[\text{MBr}_6]$ octahedra, there are several important differences between 1 and 2. In the former, two octahedra that contain Sb^{3+} share edges to form a $[\text{Sb}_2\text{Br}_{10}]$ bioctahedron, whereas Sb^{5+} is surrounded by a regular octahedron of six bromines; furthermore, the anionic part is supplemented by Br^- anions. The interatomic distances in the $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedron are nearly the same, from 2.5323(6) to 2.5646(6) Å, similar to those found in other compounds with $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra.^{48,49} Contrastingly, the Sb–Br distances in the $[\text{Sb}_2^{\text{III}}\text{Br}_{10}]$ bioctahedron clearly reveal the influence of the $5s^2$ lone pair of antimony; there are three shorter bonds of 2.5756(6)–2.6147(6) Å and three much longer distances of 3.0279(7)–3.2702(6) Å (see Fig. S8 of SI for a full list of Sb–Br distances in 1).

In the structure of 2, both bismuth and antimony form $[\text{MBr}_6]$ octahedra, which are different in their actual geometry (see Fig. S9 of SI for a full list of Sb–Br and Bi–Br distances in 2). Similar to 1, $\text{Sb}^{\text{V}}\text{–Br}$ distances fall into the range of 2.5393(11)–2.5627(11) Å, whereas the $[\text{BiBr}_6]$ octahedron is

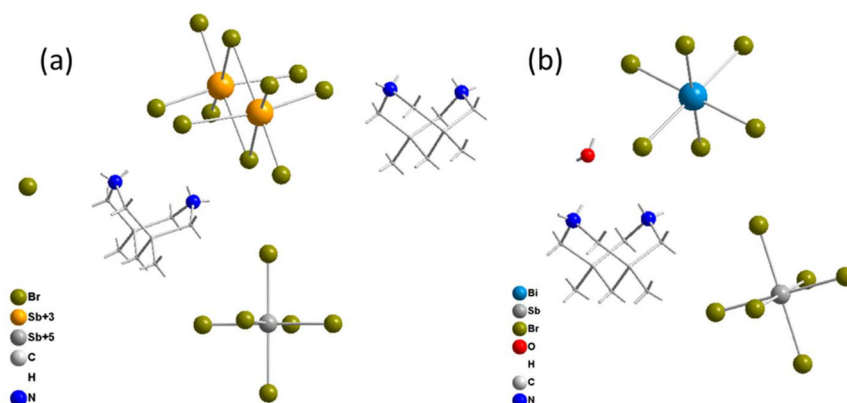


Fig. 3 Building blocks in the crystal structures 1 (a) and 2 (b).

only slightly distorted, the $\text{Bi}^{\text{III}}\text{-Br}$ distances ranging from 2.8074(11) to 2.8438(11) Å. While the +3 oxidation state for bismuth is apparent, the stereochemical inactivity of the $6s^2$ lone pair of bismuth is typical owing to its low-lying valent $6s$ orbital.

Both crystal structures demonstrate patterns of secondary $\text{Br}\cdots\text{Br}$ bonds, owing to which separate octahedra and bioctahedra are assembled into polymers.

In the crystal structure of **2** (Fig. 4), the $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra are linked by the $\text{Br}\cdots\text{Br}$ distance of 3.3509(15) Å to form layers running parallel to each other. The layers are further linked in the perpendicular direction by $[\text{Bi}^{\text{III}}\text{Br}_6]$ octahedra with the $\text{Br}\cdots\text{Br}$ distance of 3.5785(16) Å. The former distance is the same as the secondary $\text{Br}\cdots\text{Br}$ distance found in the crystal structure of Br_2 ,⁵⁰ whereas the latter distance, although being longer, is still below the interlayer $\text{Br}\cdots\text{Br}$ distance in Br_2 (3.89 Å), which can be treated as a van-der-Waals distance between two bromine atoms.⁵¹ In total, each $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedron has four $\text{Br}\cdots\text{Br}$ contacts within the plane of the same units and two $\text{Br}\cdots\text{Br}$ contacts in the axial direction with

$[\text{Bi}^{\text{III}}\text{Br}_6]$ octahedra. The system of $\text{Br}\cdots\text{Br}$ bonds is more complex in **1** (Fig. 5). The $[\text{Sb}_2^{\text{III}}\text{Br}_{10}]$ bioctahedra form columns running along the (100) direction and linked by $\text{Br}\cdots\text{Br}$ distances of 3.5997(8) Å. Each bioctahedron is decorated at both sides by a monoatomic Br^- anion separated by a distance of 3.5846(8) Å. The columns are linked to the zigzag chains of $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra with the help of $\text{Br}\cdots\text{Br}$ interactions of 3.6927(7) Å, whereas within the zigzag chains the $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra are linked to each other by $\text{Br}\cdots\text{Br}$ distances of 3.4394(11) Å. In such a way, a 3D system of inorganic anions is formed.

The organic part of the crystal structures is presented by diprotonated 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane, referred to as AH_2^+ . Two independent organic cations are observed in the crystal structure of **1**.

They use all hydrogen atoms bound to nitrogen atoms to form the total of eight $(\text{N})\text{H}\cdots\text{Br}$ bonds, with the distances ranging from 2.38 to 2.67 Å (Tables 1 and 2), which are significantly shorter than the van-der-Waals $\text{H}\cdots\text{Br}$ bond of 3.03–3.06 Å.⁵² Interestingly, one of AH_2^+ dicationic form $(\text{N})\text{H}\cdots\text{Br}$

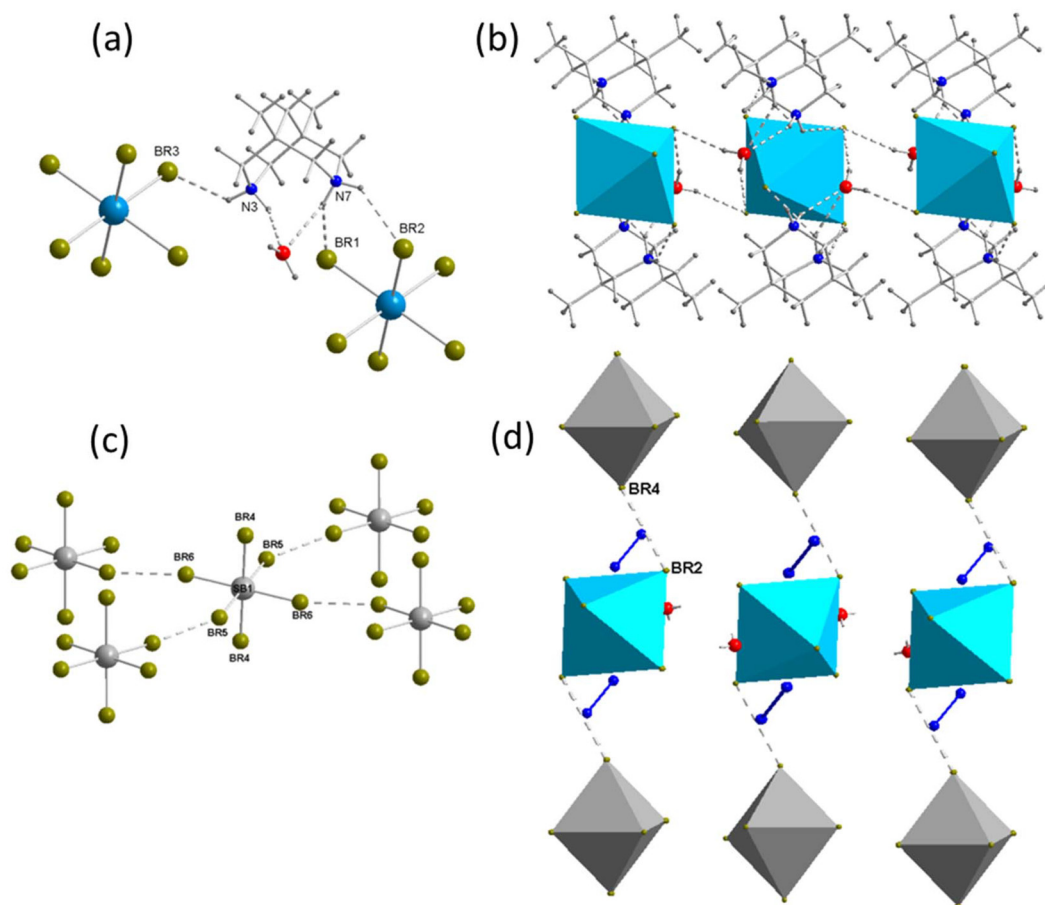


Fig. 4 Crystal structure of **2**. Doubly protonated bispidine AH_2^{2+} coordinating a water molecule and two BiBr_6^{3-} octahedra by means of hydrogen bonds (a); a fragment of a layer made of bispidine, water, and BiBr_6^{3-} octahedra (b); a fragment of a layer composed of SbBr_6^{3-} octahedra linked by $\text{Br}\cdots\text{Br}$ interactions (c); formation of a 3D structure (d). Weak interactions are shown by dotted lines, octahedra BiBr_6^{3-} are blue and octahedra SbBr_6^{3-} are grey. For the sake of simplicity, in (d), the AH_2^{2+} cations are shown as blue dumbbells symbolizing a pair of nitrogen atoms at one bispidine.

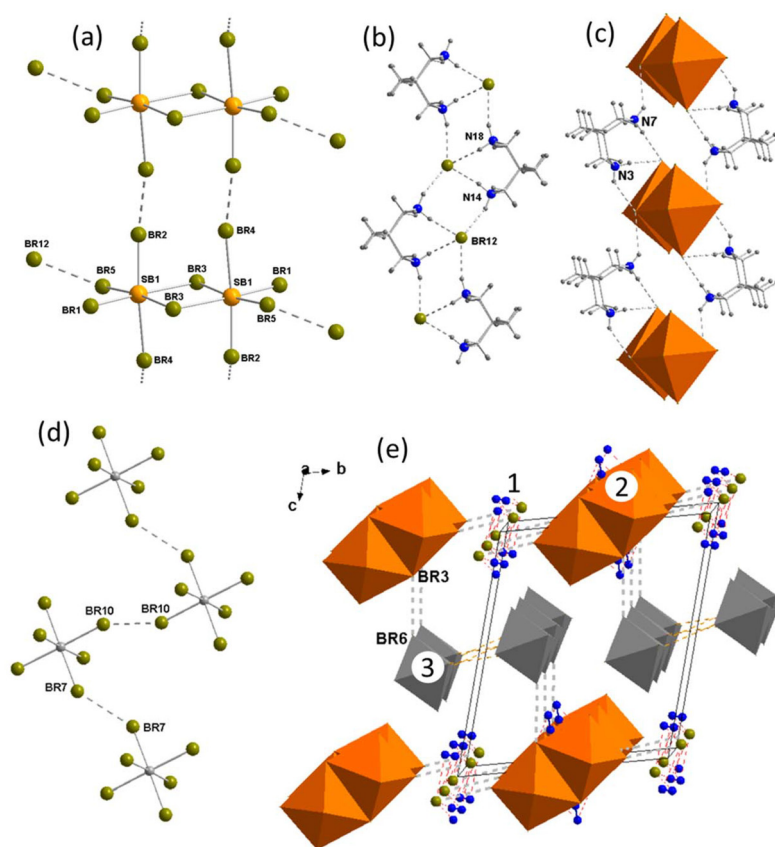


Fig. 5 Crystal structure of **1**. Ribbons of $\text{Sb}_2\text{Br}_{10}^{4-}$ bioctahedra linked by $\text{Br}\cdots\text{Br}$ interactions and decorated by additional Br^- anions (a); Br^- anions forming four hydrogen bonds to link AH_2 bication into a chain (b) and connection of such chains with $\text{Sb}_2\text{Br}_{10}^{4-}$ bioctahedra (c); SbBr_6^- octahedra linked by $\text{Br}\cdots\text{Br}$ interactions into a zigzag chain (d); connection of structural units into a 3D structure (e). Weak interactions are shown as dotted lines; bioctahedra $\text{Sb}_2\text{Br}_{10}^{4-}$ are orange and octahedra SbBr_6^- are grey. For the sake of simplicity, in (e), the AH_2^{2+} cations are shown as blue dumbbells symbolizing a pair of nitrogen atoms at one bispidine.

Table 1 Hydrogen bonds in the crystal structure of **1**

D	H	A	D–H, Å	H $\cdots$ A, Å	D $\cdots$ A, Å	Angle D–H $\cdots$ A, °
N3	H3A	Br3 ⁱ	0.91	2.67	3.339(5)	131
N3	H3A	Br6	0.91	2.85	3.513(5)	130.9
N3	H3B	Br4	0.91	2.42	3.260(4)	152.8
N7	H7A	Br4	0.91	2.47	3.319(5)	154.9
N7	H7B	Br3 ⁱⁱ	0.91	2.60	3.308(5)	135.6
N14	H14A	Br12 ⁱ	0.91	2.62	3.404(5)	144.3
N14	H14B	Br12 ⁱⁱⁱ	0.91	2.52	3.314(5)	146.1
N18	H18A	Br5 ^{iv}	0.91	2.88	3.599(5)	136.8
N18	H18A	Br12 ⁱ	0.91	2.61	3.367(5)	140.5
N18	H18B	Br12 ^v	0.91	2.38	3.259(5)	163.5

Symmetry code: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x + 2, -y + 1, -z + 2$; (iii) $-1 + x, y + 1, z$; (iv) $-x + 1, -y + 2, -z + 2$; (v) $x, y + 1, z$.

Table 2 Hydrogen bonds in the crystal structure of **2**

D	H	A	D–H, Å	H $\cdots$ A, Å	D $\cdots$ A, Å	Angle D–H $\cdots$ A, °
O1	H1A	Br3 ⁱ	0.9	2.64	3.522(9)	165.2
O1	H1B	Br3 ⁱⁱ	0.9	2.76	3.640(8)	165.3
N3	H3A	O1	0.9	2.26	3.020(13)	142.0
N3	H3B	Br1 ⁱⁱⁱ	0.9	2.81	3.446(9)	129.2
N3	H3B	Br3 ⁱⁱⁱ	0.9	2.74	3.421(10)	133.2
N7	H7A	Br1 ⁱ	0.9	2.77	3.466(10)	135.3
N7	H7A	O1	0.9	2.35	3.092(14)	140.2
N7	H7B	Br2	0.9	2.54	3.298(10)	141.6

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + 3/2, z + 1/2$; (iii) $x, y + 1, z$.

bonds with bromines of $[\text{Sb}_2^{\text{III}}\text{Br}_{10}]$ bioctahedra, whereas another cation is bound only to monoatomic Br^- , which forms four $\text{Br}\cdots\text{H}(\text{N})$ bonds at the time (Fig. 5).

There is only one independent AH_2 cation in the structure of **2**. It uses all four hydrogen atoms of the NH_2 group to form hydrogen bonds, two with bromine atoms of the $[\text{Bi}^{\text{III}}\text{Br}_6]$ anions and two with water oxygen (Fig. 4). The $(\text{N})\text{H}\cdots\text{O}$ dis-

tances of 2.26 and 2.35 Å are slightly longer than for a typical H-bond of this type and can be considered as weak hydrogen bonds.⁵² The $(\text{N})\text{H}\cdots\text{Br}$ distance to the Br2 atom is rather short, 2.54 Å, whereas the distance to Br3 is much longer, 2.74 Å, which is still below the van-der-Waals $\text{H}\cdots\text{Br}$ distance of 3.03–3.06 Å.⁵¹ The reason for such an elongation is that the Br3 atom also forms two $\text{Br}\cdots\text{H}(\text{O})$ bonds with water. Analyzing the pattern of weak interactions, one can notice that

the AH_2 cations are involved in intermolecular bonding with $[\text{M}^{\text{III}}\text{Br}_6]$ octahedra and in the case of **2** also with water. In contrast, the $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra form only $\text{Br}\cdots\text{Br}$ secondary bonds (Fig. 4).

The doubly protonated bispidine cations, although showing dissimilar coordination in **1** and **2**, demonstrate alike IR spectra (Fig. S10 of SI), the main difference being the pronounced bands near 3500 cm^{-1} reflecting the presence of water in the latter compound.

Compounds with coexisting $[\text{Sb}^{\text{V}}\text{Br}_6]^-$ and $[\text{Sb}^{\text{III}}\text{Br}_6]^{3-}$ anions have previously been reported in the literature. $\text{Rb}_2\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_6$ that crystallizes in the K_2PtCl_6 type was reported as early as 1956.⁵³ A little later, the use of pyridinium cation enabled preparation of $(\text{C}_5\text{H}_5\text{NH})_6\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{24}$.⁵⁴ Recent reports of the Adonin group introduced several new compounds containing $[\text{Sb}_2^{\text{III}}\text{Br}_9]^{3-}$ and $[\text{Sb}^{\text{V}}\text{Br}_6]^-$ anions in a 1 : 1 ratio.^{55,56} In all compounds, Sb^{3+} and Sb^{5+} differ in coordination polyhedra such that $[\text{Sb}^{\text{V}}\text{Br}_6]$ octahedra are nearly regular, whereas $[\text{Sb}^{\text{III}}\text{Br}_6]$ octahedra are severely distorted. Although optical and/or optoelectronic properties were not reported for any of the above compounds, the latter two papers provided the insights into weak $\text{Br}\cdots\text{Br}$ interactions, including their energy and the role they play in assembling the crystal structures.

The oxidation states of +3 and +5 were additionally proven by ^{121}Sb Mössbauer spectroscopy in the case of compound **1** (Fig. 6). ^{121}Sb Mössbauer spectrum recorded at 77 K can be represented as a superposition of two components Sb(1) and Sb(2) with very different isomer shift values ($\delta_1 \ll \delta_2$). The fitted parameters of the spectrum are shown in Table 3. The first component with a more negative value of δ_1 is a multiplet due to the hyperfine electric quadrupole interactions.⁵⁷ The

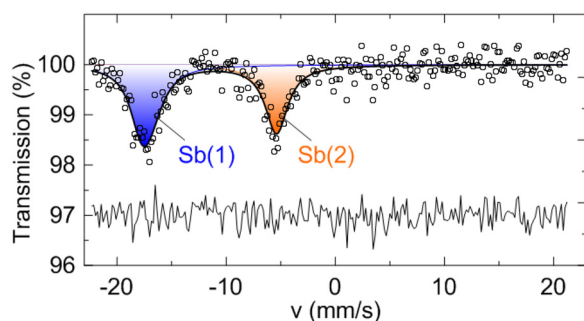


Fig. 6 ^{121}Sb Mössbauer of compound **1** collected at $T = 77\text{ K}$.

observed large quadrupole splitting ($eQ_{5/2}V_{zz,1}$) underlines that antimony cations are located in crystal sites with a very strong electric field gradient $V_{zz,1}$ (EFG) at ^{121}Sb nuclei. Based on the obtained values of both hyperfine parameters (Table 3), we can surely conclude that the spectral component Sb(1) corresponds to trivalent ions Sb^{3+} in a distorted crystalline environment. The second component Sb(2) with a higher isomer shift (δ_2) and nearly zero quadrupole splitting ($V_{zz,2} \approx 0$) corresponds to pentavalent Sb^{5+} ions in an almost undistorted crystal surrounding. The pronounced difference of δ values between related trivalent and pentavalent ions mainly arise from a different 5s orbital population.⁵⁷ Therefore, a significantly less negative isomer shift δ_2 is consistent with a lower 5s orbital population for Sb^{5+} ions. Relative intensities A_i ($\sim f_{\text{LM}}n_i$) of Sb (1) and Sb(2) subspectra are proportional to both the Lamb-Mössbauer factor (f_{LM}) and the content (n_i) of the relevant kind of antimony ions. Assuming the approximate equality of the f_{LM} factors for both antimony ions and given the noisy background of the spectra from the experimental ratio A_1/A_2 we estimated the ratio of Sb^{3+} to Sb^{5+} centers is near unity.

Optical diffuse reflectance measured using polycrystalline powders were converted into absorbance. The Kubelka-Munk transformation provided the band gap of 1.27 and 1.58 eV for **1** and **2**, respectively (Fig. 7), assuming the indirect gap model inferred from the DFT calculations (below). These values are not typical for bromoantimonates and bromobismuthates,^{58–62} and to analyze the grounds for low band gaps, quantum-chemical calculations at the DFT level were performed.

Calculated band structure plots for **1** and **2** are shown in Fig. 8. According to the calculations, both compounds are indirect gap semiconductors with high degree of degeneracy. Their calculated band gap values are *ca.* 0.39 eV (**1**) and 0.57 eV (**2**). Main contributions both to the top of the valence band and to the bottom of the conduction band arise from the 4p-states of bromine. Valence band maximum in both compounds show high degree of degeneracy, particularly in the case of the Bi-containing compound, where direct and indirect gaps differ only by *ca.* 0.01 eV due to the virtually flat nature of the maximum around the Γ point.

The results of the calculations only qualitatively agree with the optical gap data, as calculated electronic gaps are significantly smaller than measured optical ones. Even considering the trend for all local and semi-local DFT functionals to underestimate band gaps, this calls for further investigation, as it appears that in both structures there are small localized states around the Fermi level appearing between the majority of

Table 3 Hyperfine parameters of the ^{121}Sb Mössbauer spectra collected at 77 K. Here, δ is the isomer shift relative to the $\text{Ca}^{121\text{m}}\text{SnO}_3$ source, $eQ_{5/2}V_{zz}$ is the quadrupole coupling constant for the ground nuclear state, η is the asymmetry parameter, Γ is the linewidth, and A is the relative intensity

Subspectrum	$\delta, \text{mm s}^{-1}$	$eQ_{5/2}V_{zz}, \text{mm s}^{-1}$	η	$\Gamma, \text{mm s}^{-1}$	$A, \%$
Sb(III)	-17.38 ± 0.07	-5.15 ± 1.37	~ 0	2.5(2)	57.5(8)
Sb(V)	-5.39 ± 0.087	~ 0	~ 0	2.5(2)	42.5(8)

^a The corresponding values were taken to be equal to each other.

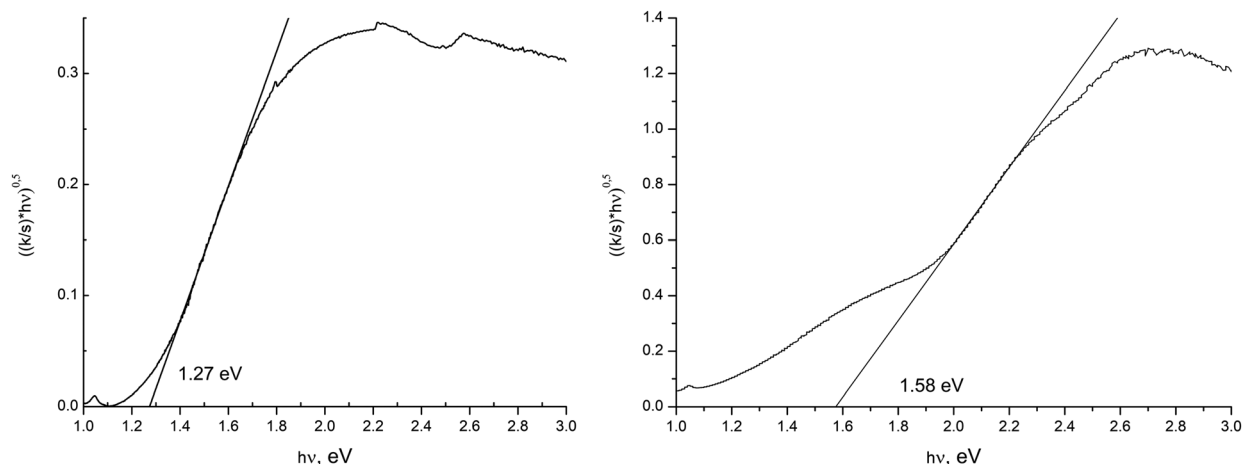


Fig. 7 Kubelka–Munk plots for **1** (left) and **2** (right).

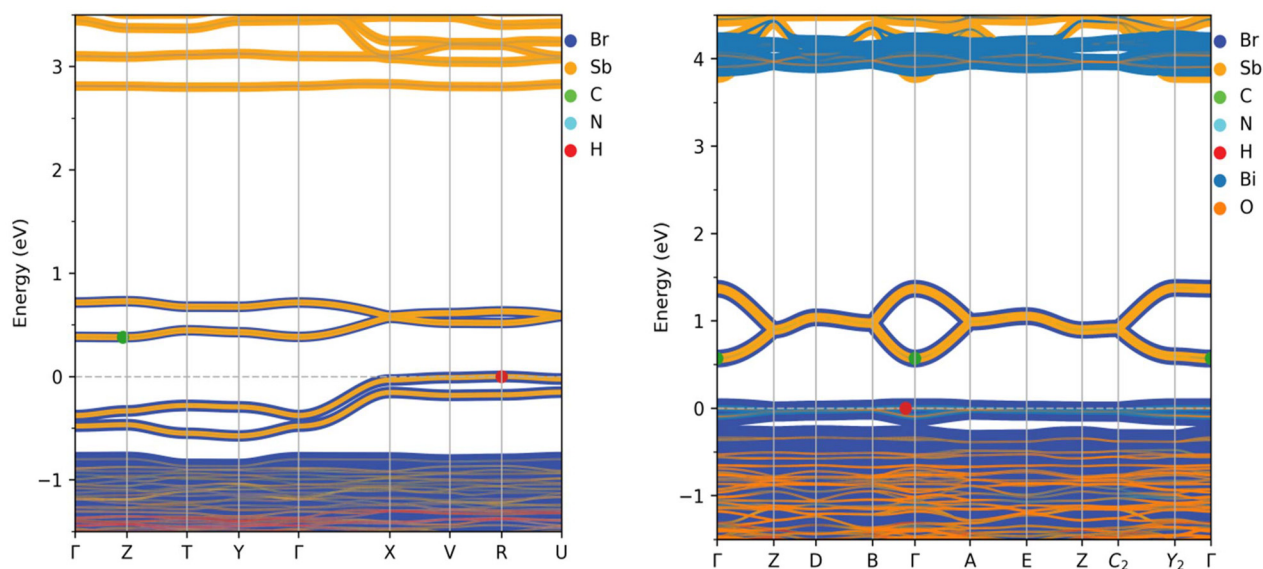


Fig. 8 Calculated band structures for **1** (left) and **2** (right) near the Fermi level. The thickness of a band is proportional to its contribution to the band structure. Fermi energy is at zero. Valence band maximum (VBM) and conduction band minimum (CBM) are shown by red and green dots, respectively.

valence and conduction bands, which have the appearance of in-gap states. These states arise from the mixture of bromine and antimony or bismuth states. The calculations of projected band structures reveal the nature of these states (see Fig. 9).

As seen from the plots, in the band structure of **1**, the contributions to the lower band, between -0.5 and 0 eV, arise from mixed Sb 5p- and 5s-states (also mixed with Br 4p-states, according to Fig. 8). Localized bands in the 0.4 – 0.8 eV range are mainly contributed to by Sb 5s-states, which are vacant, and also by Br 4p-states. Since vacant 5s-states are the feature of Sb^{5+} , and filled of Sb^{3+} , we can assume that the lower in-gap states are the product of the latter, and higher of the former. This conclusion is supported by calculated Bader charges,

showing that there are two distinct forms of antimony present: atoms corresponding to the Sb1 position have an effective charge of *ca.* $+2.9$, *i.e.* represent Sb^{III} , while the ones at the Sb2 position show *ca.* $+4.9$ charge, *i.e.* represent Sb^{V} , which confirms the existence of two types of bromometallate anions and their different roles in the electronic structure.

Moving to the mixed bismuth and antimony structure **2**, we see that the in-gap state between 0.7 and 1.7 eV shows major contributions from Sb 5s- and Br 4p-states, along with a minor contribution from Sb 5p-states. The lower in-gap bands around 0 eV, however, are contributed not by Sb but by filled Bi 6s-states, which means that this contribution arises from Bi^{III} . The lack of empty Bi 6s-states supports the idea that Bi is in a single formal oxidation state of $+3$ and takes place of Sb^{III}

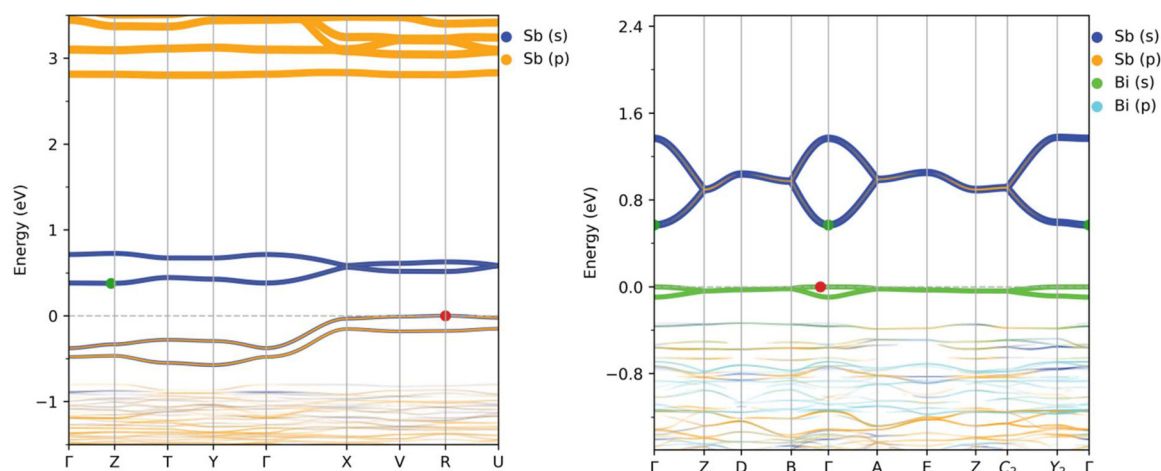


Fig. 9 Bismuth and antimony contributions to the band structures for **1** (left) and **2** (right) near the Fermi level. The thickness of a band is proportional to its contribution to the band structure. Fermi energy is at zero. The VBM and CBM are shown by red and green dots, respectively.

in the structure. This is, once again, supported by the Bader charges, which assign *ca.* +1.9 effective charge to Bi1, and *ca.* +4.9 charge to Sb1.

Thus, considering the nature of the in-gap states, we may suggest a possible explanation for the discrepancies in the calculated and optical gaps. The calculated gaps refer to the electronic ones at 0 K, and, due to the presence of in-gap states, they are rather small. Optical gaps, however, are measured at room temperature, and for some semiconductors, particularly degenerate ones and featuring strong intermolecular interactions, the Fermi level can be pushed into or even above the conduction band (Burstein–Moss shift),^{63,64} which was previously observed for halide perovskites.⁶⁴ This means that the gap should be estimated at least from the top of the in-gap states till the bottom of the nearest conduction band. In this case, the calculated gaps for **1** and **2** would be *ca.* 1.9 and 2.1 eV, respectively. These values are closer to the measured optical gaps, however, this time they appear to overestimate gaps. However, we must take into account both the fact that standard DFT is not expected to correctly describe excited states, and that we do not know the exact position of the Fermi level at room temperature. Nevertheless, we believe that these considerations combined provide a plausible explanation of the differences between optical and electronic gaps.

In the structure of **1**, the –ICOHP values for the Br⋯Br contacts, linking [Sb^{III}Br₁₀] bioctahedra at 3.5997(8) Å, are *ca.* 0.03–0.04 eV (and the averaged –ICOHP for the Sb–Br bond is *ca.* 3.45 eV), *i.e.* around 1% of the covalency of the Sb–Br bond. The –ICOHP for the contacts between Br[–] anion and Br from the bioctahedra is even smaller, *ca.* 0.02 eV, despite the respective distance being slightly shorter, 3.5846(8) Å. Br⋯Br contacts at 3.4394(11) Å, linking octahedra into zigzag chains, have average –ICOHP values of *ca.* 0.10 eV (*ca.* 2.9% of the Sb–Br bond), with Br⋯Br contacts linking zigzag chains having –ICOHP of *ca.* 0.03 eV (less than 1% of the covalent Sb–Br bond).

This picture confirms that in both compounds, a complex system of intermolecular bonds exists to stabilize the regularity and order in the structures.

Experimental

Synthesis

For the synthesis of target compounds, 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane dichloride (**A**) was first obtained according to a published procedure;⁶⁵ for details, see SI and Fig. S1 therein. Sb₂O₃ (Chemcraft Ltd, Russia, pure for analysis, >99.5%), Sb₂O₅ (≥99.9%, Reakhim, Russia), Bi₂O₃ (99.99%, Changsha Santech Materials Co., China), H₂O₂ (≥99.9%, Khimsintex Ltd, Russia), aqueous hydrogen peroxide H₂O₂, 37% (Reakhim, Russia), and hydrobromic acid HBr, 46% (pure for analysis, GOST 2062-77, Reakhim, Russia) were used as precursors.

For the synthesis of (AH₂)₄[Sb₂Br₁₀(SbBr₆)₂(Br)₂] (**1**) three methods were used.

A solution of 0.1249 g (0.56 mmol) of AH₂Cl₂ in 5 mL of distilled water was added to a solution of 0.1621 g (0.21 mmol) of Sb₂O₃ in 12.5 mL of concentrated HBr. After stirring, 0.5 mL of H₂O₂ (37%) was added to the solution. Black crystals in the shape of long needles appeared in 15–20 minutes.

A solution of 0.1249 g (0.56 mmol) AH₂Cl₂ was dissolved in 5 mL of distilled H₂O. Antimony oxide Sb₂O₃ (0.1621 g, 0.56 mmol) was dissolved in 12.5 mL of concentrated HBr. Upon mixing these solutions, 0.5 g of pre-prepared cationic tribromide AH₂(Br₃)₂ (see SI for its synthesis and Fig. S2 for the crystal structure) was added. Black needle-like crystals of compound **1** formed within 10 min at room temperature.

A solution of 0.1500 g AH₂Cl₂ (0.97 mmol) was dissolved in 5 mL of distilled H₂O. Antimony oxides Sb₂O₃ (0.0711 g, 0.24 mmol) and Sb₂O₅ (0.0789 g, 0.24 mmol) were separately dissolved in 5 mL of concentrated HBr each. The three solu-

tions were mixed, yielding black crystals after 20 min at room temperature (Fig. S3).

In all three methods, the resulting crystals were left for additional crystallization for one hour and then filtered under vacuum and dried in air at room temperature.

For the synthesis of $(\text{AH}_2)_2[(\text{Bi}^{\text{III}}\text{Br}_6)(\text{Sb}^{\text{V}}\text{Br}_6)] \cdot 2\text{H}_2\text{O}$ (**2**), a solution of 0.1249 g (0.56 mmol) of **A** in 5 mL of distilled water was prepared. Separately, 0.0624 g (0.21 mmol) of Sb_2O_3 and 0.0997 g (0.21 mmol) of Bi_2O_3 were dissolved in 12.5 milliliters of HBr. After mixing both solutions, 0.5 mL of 37% H_2O_2 was added. Within one day, dark red plate crystals of **2** formed and were filtered off and dried in air at room temperature.

Thermal analysis

Thermogravimetric analysis was performed using a NETZSCH TG 209 F1 Libra thermo-microbalance. The samples were heated in an alumina crucible under dry nitrogen flow up to 300 °C with the ramp rate of 5 °C min⁻¹. The NETZSCH Proteus Thermal Analysis program was used for data processing.

Powder X-ray diffraction analysis

Powder X-ray diffraction analysis (PXRD) was performed on an Imaging Plate Guinier Camera (Huber G670, Cu- $K\alpha_1$ radiation, $\lambda = 1.540598$ Å). For the data collection, crystals were finely crushed in an agate mortar, and the resulting powder was fixed on a holder between two X-ray amorphous films.

Crystal structure determination

Well-shaped single crystals of the title compounds were selected from the reaction product. The single-crystal X-ray diffraction data for **1**, **2**, and $\text{AH}_2(\text{Br}_3)_2$ were collected on a four-circle XtaLAB Rigaku Synergy-S diffractometer equipped with a HyPix-6000HE area-detector ($T = 100$ K, $\lambda(\text{CuK}\alpha)$ -radiation, graphite monochromator, shutterless ω -scan mode). The data were integrated and corrected for absorption by the CrysAlisPro program.⁶⁶ For details, see Table 4 and SI. The structures were solved by intrinsic phasing modification of direct methods⁶⁷ and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. In the structure of $\text{AH}_2(\text{Br}_3)_2$, the two bromide anions were disordered over two sites with the occupancies of 0.9 : 0.1. The X-ray absorption was analytically considered using the crystal faceting. For all structures, there are the relatively high positive electron density residues near the Bi, Sb and/or Br atoms due to the significant absorption effects, which cannot be corrected completely. Moreover, the crystal of **2** has a very high X-ray absorption coefficient of 28.614 mm⁻¹, so the quality of its structure is relatively low. The hydrogen atoms of the >NH₂-groups in **1**, **2**, and $\text{AH}_2(\text{Br}_3)_2$ as well as the water solvate molecules in **2** were objectively localized in the difference-Fourier maps and refined within the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $1.5U_{\text{eq}}(\text{O})$]. The other hydrogen atoms were placed in calculated positions and refined within the

Table 4 Crystal data and structure refinement for **1**, **2**, and $\text{AH}_2(\text{Br}_3)_2$

Identification code	1	2	$\text{AH}_2(\text{Br}_3)_2$
Empirical formula	$\text{C}_{18}\text{H}_4\text{Br}_{12}\text{N}_4\text{Sb}_2$	$\text{C}_{18}\text{H}_{44}\text{BiBr}_{12}\text{N}_4\text{O}_2\text{Sb}$	$\text{C}_9\text{H}_{20}\text{Br}_6\text{N}_2$
Formula weight	1514.86	1638.11	635.67
Crystal size, mm	$0.05 \times 0.08 \times 0.22$	$0.14 \times 0.19 \times 0.31$	$0.05 \times 0.09 \times 0.16$
Wavelength, Å	1.54184	1.54184	1.54184
T , K	100	100	100
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a , Å	9.0171(3)	15.3442(2)	8.56780(19)
b , Å	14.1829(3)	9.77582(17)	15.8051(3)
c , Å	15.7288(3)	13.11027(18)	13.6322(3)
α , °	104.6927(18)	90	90
β , °	92.663(2)	90.5767(13)	96.1095(19)
γ , °	106.224(2)	90	90
V , Å ³	1853.31(9)	1966.47(5)	1835.52(7)
Z	2	2	4
Density (calc.), Mg m ⁻³	2.715	2.767	2.300
μ , mm ⁻¹	26.864	28.614	15.683
$F(000)$	1396	1500	1192
Absorption correction	Analytical	Analytical	Gaussian
Theta range, °	3.379–80.130	2.880–80.738	4.297–80.222
Index ranges	$-11 \leq h \leq 9$ $-18 \leq k \leq 18$ $-20 \leq l \leq 19$	$-19 \leq h \leq 18$ $-12 \leq k \leq 12$ $-16 \leq l \leq 14$	$-10 \leq h \leq 10$ $-20 \leq k \leq 20$ $-17 \leq l \leq 16$
Reflections collected	37 222	25 929	24 581
Independent reflections, R_{int}	7888, 0.0641	4252, 0.0679	3961, 0.0442
Reflections observed	7425	4184	3800
R_1/wR_2 ($I > 2\sigma(I)$)	0.0501/0.1304	0.0717/0.1811	0.0573/0.1598
R_1/wR_2 (all data)	0.0521/0.1330	0.0724/0.1818	0.0588/0.1608
Goodness-of-fit on F^2	1.010	1.044	1.129
$T_{\text{min}}/T_{\text{max}}$	0.045/0.315	0.017/0.183	0.591/1.000
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e Å ⁻³	2.834/-2.172	3.237/-2.667	2.457/-1.547

riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the CH_3 -groups and $1.2U_{\text{eq}}(\text{C})$ for the other groups]. All calculations were carried out using the SHELXTL program.⁶⁹

Crystallographic data for all investigated compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC 2494589 (1), 2494590 (2), and 2494591 ($\text{AH}_2(\text{Br}_3)_2$).

Infrared spectroscopy

Infrared (IR) spectra of the title compounds were collected by Fourier Transform Infrared (FT-IR) spectrometer Perkin Elmer Frontier. Samples were initially kept in a desiccator with anhydrous calcium chloride for 24 hours. Then 0.25 mg of the analyzed powder and 49.75 mg of dry KBr were crushed together in an agate mortar, mixed, and pressed into a tablet. The spectra were recorded in the wavenumber range from 400 to 4000 cm^{-1} with a 1 cm^{-1} step at room temperature. Correction of the baseline was performed using a tablet of pure KBr.

Mössbauer spectroscopy

¹²¹Sb Mössbauer experiments were performed in transmission geometry using $\text{Ca}^{121\text{m}}\text{SnO}_3$ as the radiation source with an activity of 0.32 mCi. The spectra were recorded using an escape peak of 8.5 keV from the resonance γ -quanta with an energy of 37.2 keV in a thin NaI(Tl) scintillator. During the measurements, both the radiation source and the absorber were held in the cryogen-free closed cycle cryostat for Mössbauer spectroscopy CFPR-221-MESS at a liquid nitrogen temperature of ~ 77 K. The isomer shift values are given relative to the $\text{Ca}^{121\text{m}}\text{SnO}_3$ source at 77 K. The spectra were fitted using a computer program to an eight-line quadrupole pattern (the ratio of the quadrupole moment of the excited state ($eQ_{7/2}$) to the ground state ($eQ_{5/2}$) was taken as 1.33).⁶⁸

Diffuse reflectance spectroscopy

Optical diffuse reflectance spectra were recorded using a PerkinElmer Lambda 950 UV-visible spectrometer (Perkin-Elmer, Waltham, MA, USA) with an attached diffuse reflectance accessory. Measurements were performed at 298 K in the spectral range of 160–1400 nm, with a scanning rate of 2 nm s^{-1} and 1 nm step using a finely ground polycrystalline sample. The data were transformed into absorbance using the Kubelka–Munk method and plotted as $[(k/s) \cdot h\nu]^{1/2}$ against $h\nu$, where k is the absorption coefficient, s is the scattering coefficient, h is the Planck constant, $\gamma = 2$ for the indirect band gap model. Optical band gap, E_g , was approximated by extrapolation to $k = 0$.⁷⁰

Electronic structure calculations

DFT calculations on the periodic structures of 1 and 2 were performed using the projector augmented-wave method (PAW) as implemented in the Vienna *Ab initio* Simulation Package (VASP).^{71,72} The PBE exchange-correlation functional⁷³ of the GGA type combined with the DFT-D3 correction for dispersive interactions by Grimme *et al.*⁷⁴ was used for calculations.

Brillouin zone samplings were done using gamma-centered grids, and the number of k -points in the first Brillouin zone was chosen so as to provide a step between k -points of no more than 0.02 $\text{\AA}^{-1}$ in each case. Experimental structural information was used for the modeling, with the structures converted to the $P1$ space group. The energy cutoff was set to 500 eV, and the energy-convergence criterion was at 10^{-5} eV. Effective charges were calculated using the Bader routine from Henkelmann group.⁷⁵ Band structure plots were produced using sumo 2.3.12 package.⁷⁶ COHP analysis was performed using the LOBSTER 5.1.1 package.^{77–80}

Conclusions

We have synthesized two new hybrid bromometallates containing group 15 elements Sb and Bi in two different oxidation states, +3 and +5, $(\text{AH}_2)_4[\text{Sb}_2\text{Br}_{10}(\text{SbBr}_6)_2(\text{Br})_2]$ (1) and $(\text{AH}_2)_2[(\text{Bi}^{\text{III}}\text{Br}_6)(\text{Sb}^{\text{V}}\text{Br}_6)] \cdot 2\text{H}_2\text{O}$ (2), where A = 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane. Having bispidine cation as a powerful structure-directing agent withstanding a strong acid medium and oxidizing conditions, we were able to synthesize organic–inorganic hybrids featuring a combination of $\text{Sb}^{\text{III}}/\text{Sb}^{\text{V}}$ or $\text{Bi}^{\text{III}}/\text{Sb}^{\text{V}}$ cations. Their crystal structures feature different patterns of weak $\text{Br} \cdots \text{Br}$ interactions that ensure bonding within the anionic substructure as well as hydrogen bonds linking organic cations and inorganic anions. Altogether this leads to perfect positioning of structural building blocks with no sign of disorder. The electronic structure of both compounds displays the dominant role of $\text{M}^{3+}/\text{Br}^-$ states at the top of valence bands and formation of in-gap acceptor states dominated by $\text{Sb}^{5+}/\text{Br}^-$ interactions. As a result, the band gap width is reduced from typical for bromometallates values of 2.5–3.0 eV down to 1.27 (1) and 1.58 eV (2). We infer that tailoring in-gap states should become a powerful tool for designing halo-metallates with desired band gaps in order to create effective light-absorbing compounds for photovoltaic applications.

Author contributions

Conceptualization, A. V. S.; methodology T. A. S. and A. V. S.; formal analysis, T. A. S., A. N. K., and A. V. S.; investigation T. A. S., A. P. K., A. V. M., M. A. B., V. N. K., D. A. P., A. N. K.; resources, T. A. S., S. Z. V., I. A. P., A. N. K. and A. V. S.; data curation T. A. S., V. N. K., A. N. K., I. A. P., and A. V. S.; writing – original draft preparation T. A. S., and A. V. S.; writing – review and editing A. V. S., T. A. S., I. A. P., A. N. K., and S. Z. V.; visualization, A. V. S., T. A. S., I. A. P., A. N. K., and S. Z. V.; supervision, A.V. S. All authors have read and agreed to the submitted version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: synthesis of AH_2Cl_2 and $\text{AH}_2(\text{Br}_3)_2$, crystal structure of $\text{AH}_2(\text{Br}_3)_2$, photo of the crystals of compound **1** and **2**, experimental and simulated powder X-ray diffraction patterns for compounds **1** and **2**, thermal analysis data for **1** and **2**, figures with interatomic Sb–Br distances (Å) in **1** and interatomic Bi–Br and Sb–Br distances (Å) in **2**, a figure of IR spectra of **1** and **2**. See DOI: <https://doi.org/10.1039/d5dt02874d>.

CCDC 2494589 (**1**), 2494590 (**2**), and 2494591 ($\text{AH}_2(\text{Br}_3)_2$) contain the supplementary crystallographic data for this paper.^{81a–c}

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