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Mixed halide hybrid halobismuthates and their *in situ* transformations

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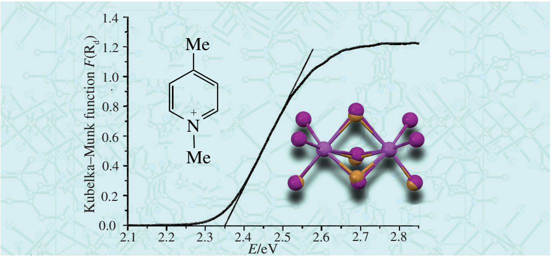
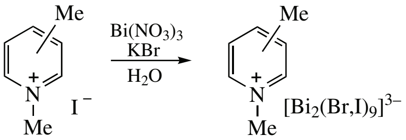
During a formation of four mixed hybrid halobismuthates (two of them have new structures) from solutions containing both Br$^-$ and I$^-$ ions, solid products enriched with iodine were isolated. Either oxidation or drying of mother liquors resulted in products with even higher iodine contents, up to pure iodobismuthates. All the compounds were characterized by a set of comprehensive methods (NMR, X-ray, DRS, *etc.*).



Hybrid halobismuthates attract an attention due to their interesting physical and chemical properties.[1–6] Researchers usually obtain compounds containing one halogen atom using derivatives of only this particular halogen in the synthesis or by removal of interfering halogens from the reaction mixture *via* chemical methods.[7] There are much less reports on systems, wherein two halogens are simultaneously present, since it is almost impossible to predict the nature of products that would be formed from such systems. Thus, a work on mixed methyl viologen halobismuthates revealed that the replacement of chlorine with bromine in these compounds proceeds *via* a formation of the continuous series of solid solutions.[8] In the case of chlorine and iodine pair, a compound possessing the halogen ratio of 2 : 3 was formed from the solution,[9] while in the presence of bromine and iodine, the solid solution different in structure from both the pure bromobismuthate and pure iodobismuthate was formed.[8] All the obtained compounds demonstrated interesting photophysical properties, while a mixed iodochlorobismuthate possesses ferroelectric properties, which have never been observed in halobismuthates containing a single halogen. Previously we investigated the reactions of bromobismuthates of bis(4-cyanopyridino)alkanes with iodide ions. A mixed hybrid halobismuthate was obtained as the reaction product from bis(4-cyanopyridino)propane,[10] while a hybrid iodobismuthate was formed from bis(4-cyanopyridino)pentane.[11] Both the products possess low values of optical band gap and are promising light absorbing materials. Thus, a study of previously unexplored mixed halobismuthates may afford hybrid compounds with unusual properties. Iodide ions can be oxidized in air in the presence of moisture. The appearance of polyhalide ions in the system may often result in poorly soluble compounds containing polyhalide and halobismuthate anions or polymeric frameworks, where halobismuthate anions are bound through polyhalide chains.[12–14] Halobismuthate compounds bearing BrIBr$^-$ ligands can also be produced but more rarely.[15] All these compounds were discovered and reported over recent years. This work was aimed at studying the composition and properties of 1,*n*-dimethylpyridinium (*n* = 2–4) and 4-cyano-1-methylpyridinium halobismuthates, which were obtained in solutions containing both bromobismuthate and iodide anions, and at clarifying how these compounds change in the air atmosphere.

Reactions of isomeric picolines and 4-cyanopyridine with methyl iodide were performed in ethyl alcohol at room temperature. The structure and purity of the obtained products were confirmed by ^{1}H NMR (Figure S3, see Online Supplementary Materials). Pure 1,*n*-dimethylpyridinium iodides **1a**–**3a** (**1** *n* = 2, **2** *n* = 3, **3** *n* = 4, Scheme 1) and 1-methyl-4-cyanopyridinium iodide **4a** (Scheme 2) were obtained in yields varying from 31% (**4a**) to 79% (**1a**). Iodide **2a** was highly hygroscopic, and all the attempts to isolate it in a dry form failed. Iodides **1a**–**3a** were used as the starting materials in the synthesis of corresponding 1,*n*-dimethylpyridinium halobismuthates. The reaction of bromobismuthate anions with iodides **1a**–**3a** in aqueous solution afforded fine-crystalline yellowish-orange precipitates of compounds **1b**–**3b**[†] in 10–23% yields.

We examined the crystal structures of obtained halobismuthates.[‡] The structure of salt **1b** is formed by six



1a–**3a** **1b**–**3b**

Scheme 1

[†] See Online Supplementary Materials for the synthesis procedures.

[‡] *Crystallographic data*. Experimental data for compounds **2b**,**c**, **3c**, **4b**–**e** were acquired on a Bruker SMART APEX2 instrument.[15] Absorption was taken into account by a semiempirical method based on equivalents using SADABS.[16] The data for **1b** and **3b** were collected on a PILATUS@SNBL diffractometer at BM01 End Station of European Synchrotron Radiation Facility (Grenoble, France).[17]

crystallographically independent [1,2-Me_2Py]$^+$ cations and [$Bi_2Br_6I_3$]$^{3-}$ and [$Bi_2Br_{6.85}I_{2.15}$]$^{3-}$ anions. All 18 independent Br/I positions are mixed, the Br : I ratio varies from 42 : 58 to 90 : 10, and one of the cations is disordered [Figure S4(*a*)]. Two cations are involved in stacking interactions [Figure S4(*b*)], and the shortest I···I contacts are 3.87, 3.90 and 3.95 Å.

The crystal structure of **2b** is derived from the structure of [1,3-Me_2Py]$_3$[Bi_2Br_9]^7 and formed by [1,3-Me_2Py]$^+$ cations and [$Bi_2Br_{6.26}I_{2.74}$]$^{3-}$ anions. In the structure of **2b** (Figure S5), all nine Br/I positions are mixed, and the Br : I ratio varies from 48 : 52 to 90 : 10.

The crystal structure of **3b** is derived from the structure of [1,4-Me_2Py]$_3$[Bi_2Br_9]^{16} and formed by three crystallographically independent [1,4-Me_2Py]$^+$ cations and [$Bi_2Br_{6.60}I_{2.40}$]$^{3-}$ anions (Figure S6), all 9 independent Br/I positions are mixed, the Br : I ratio varies from 42 : 58 to 82 : 18.

According to X-ray powder diffraction data,§ the resulting solid solutions **1b–3b** were single-phased ones.

According to EDX data¶ (Tables S1–S3), the percentage of bromine relative to the total content of halogens in samples **1b–3b** was 74.2, 70.0 and 75.0%, respectively. These results are close to the corresponding values of 71.4, 69.6 and 73.3% obtained by XRD. According to the EDX data for two random points, the percentage of bromine relative to the total halogen content in samples **1b–3b** was 71.6±0.05, 70.6±0.5 and 73.5±3.7%, *i.e.*, the obtained samples were fairly homogeneous.

Values of the optical band gap for compounds **1b–3b** were 2.35, 2.32 and 2.38 eV, respectively, according to the diffuse reflectance spectroscopy (DRS) data†† [Figure S2(*a–c*)]. These values are smaller than those characteristic of bromobismuthates possessing 0D structure of anions, but larger than those for iodobismuthates of 0D structure, and correlate with the relative content of halogens in a series of compounds **1b–3b** with similar compositions.

The reaction of bromobismuthate anions with iodide **4a** in an aqueous solution yielded a fine-crystalline yellowish-orange

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The temperature was controlled with CryoStream 700+ nitrogen blower (Oxford Cryosystems) and set to 150 K. The synchrotron data were pre-processed with SNBL ToolBox^{17} and processed using CrysAlis software (Rigaku Oxford Diffraction). The structures were determined using a combination of the direct method and Fourier syntheses. The positions of (C)–H hydrogen atoms were calculated from geometrical considerations. All the calculations were carried out using SHELXS and SHELXL software.^{18}

Crystal data for **1b**. $C_{42}H_{60}Bi_4Br_{12.86}I_{5.14}N_6$ (M = 3164.79), orthorhombic, space group $P2_12_12_1$, a = 10.2477(3), b = 16.8771(3) and c = 42.4017(9) Å, V = 7333.4(3) Å^3, Z = 4, T = 150 K, d_{calc} = 2.866 g cm^{-3}. Total 52603 reflections were collected (1.465° < θ < 26.753°), μ = = 16.382 mm^{-1}, 16331 independent reflections (R_{int} = 0.0412). Data/restraints/parameters: 16331/54/695. The final refinement parameters were: R_1 = 0.0348, wR_2 = 0.0881 for reflections with $I > 2\sigma(I)$; R_1 = = 0.0384, wR_2 = 0.0897 for all the reflections; largest diff. peak/hole was 2.026–1.349 eÅ^{-3}. GOF = 1.049.

Crystal data for **2b**. $C_{21}H_{30}Bi_2Br_{6.26}I_{2.74}N_3$ (M = 1590.38), monoclinic, space group $P2_1$, a = 11.8243(4), b = 11.8539(4) and c = 13.3778(4) Å, β = 95.8019(11)°, V = 7333.4(3) Å^3, Z = 2, T = 150 K, d_{calc} = 2.831 g cm^{-3}. Total 64774 reflections were collected (2.192° < θ < 30.052°), μ = = 18.408 mm^{-1}, 10938 independent reflections (R_{int} = 0.0411). Data/restraints/parameters: 10938/1/367. The final refinement parameters were: R_1 = 0.0450, wR_2 = 0.1108 for reflections with $I > 2\sigma(I)$; R_1 = = 0.0490, wR_2 = 0.1128 for all the reflections; largest diff. peak/hole was 2.386–1.198 eÅ^{-3}. GOF = 1.198.

Crystal data for **3b**. $C_{21}H_{30}Bi_2Br_{6.60}I_{2.40}N_3$ (M = 1574.40), monoclinic, space group $P2_1/n$, a = 18.7476(7), b = 11.7296(3) and c = 19.0123(7) Å, β = 118.158(5)°, V = 7333.4(3) Å^3, Z = 4, T = 150 K, d_{calc} = 2.837 g cm^{-3}. Total 19649 reflections were collected (1.994° < θ < 23.697°), μ = = 16.335 mm^{-1}, 6245 independent reflections (R_{int} = 0.0344). Data/restraints/parameters: 6245/108/379. The final refinement parameters were: R_1 = 0.0289, wR_2 = 0.0825 for reflections with $I > 2\sigma(I)$; R_1 = 0.0327, wR_2 = 0.0848 for all the reflections; largest diff. peak/hole was 1.266–1.070 eÅ^{-3}. GOF = 0.945.

Crystal data for **3c**. $C_7H_{10}BiI_4N$ (M = 824.74), monoclinic, space group $P2_1/c$, a = 14.4469(10), b = 14.0102(10) and c = 7.7784(5) Å, β = 104.175(2)°, V = 1526.44(18) Å^3, Z = 4, T = 100 K, d_{calc} = 3.589 g cm^{-3}. Total 15899 reflections were collected (2.908° < θ < 26.373°), μ = 19.608 mm^{-1}, 3116 independent reflections (R_{int} = 0.0387). Data/restraints/parameters: 3116/0/121. The final refinement parameters were: R_1 = 0.0284, wR_2 = 0.0614 for reflections with $I > 2\sigma(I)$; R_1 = 0.0294, wR_2 = 0.0616 for all the reflections; largest diff. peak/hole was 2.346–1.167 eÅ^{-3}. GOF = 1.326.

To check the reproducibility of determining the composition of anion in **4b**, two experiments were performed for different single crystals (**4b**_100 K and **4b**_150 K). The populations were refined isotropically with fixed Uiso(Br, I) = 0.03 Å^2. Br and I atoms were placed pairwise at the same position. In subsequent calculations, the population values (rounded to 0.01) were fixed. In the anisotropic position refinement, the Br and I atoms were refined independently, but only in the one position of **4b**_100K experiment, did the Br(4) and I(4) atoms 'diverge' by 0.26 Å. In the other cases, the Br···I distances did not exceed 0.08 Å, and significant correlations between the thermal parameters of these atoms were observed. In the final refinement, all the positions of Br/I atoms [except for Br(4) and I(4) in the **4b**_100 K experiment] were considered to be mixed. The populations in three of the five positions of the two experiments were equal to within 0.01, in one position they differed by 0.01, and only in X(4) position, the Br : I ratios were 0.51 : 0.49 (**4b**_100 K) and 0.57 : 0.43 (**4b**_150 K). The molecular formulas of dimeric anions in **4b**_100 K and **4b**_150 K differ by 0.10, which is probably due to the accuracy of composition determination by routine single-crystal XRD. The main crystallographic data are given in Table S6, while the Bi–Br (or I) bond lengths are listed in Table S7.

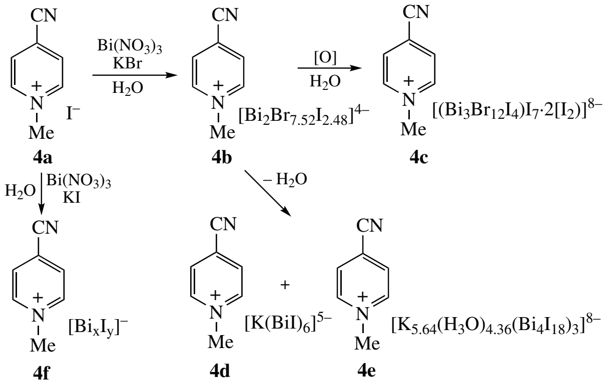
Crystal data for **4b** (experiment **4b**_100K). $C_{28}H_{28}Bi_2Br_{7.42}I_{2.58}N_8$ (M = 1814.88), orthorhombic, space group $Pbca$, a = 16.7680(5), b = 9.8073(3) and c = 27.5212(7) Å, V = 4525.8(2) Å^3, Z = 4, T = 100 K, d_{calc} = 2.664 g cm^{-3}. Total 53397 reflections were collected (2.429° < θ < 28.315°), μ = 16.107 mm^{-1}, 5623 independent reflections (R_{int} = 0.0759). Data/restraints/parameters: 5623/0/226. The final refinement parameters were: R_1 = 0.0353, wR_2 = 0.0788 for reflections with $I > 2\sigma(I)$; R_1 = 0.0552, wR_2 = 0.0866 for all the reflections; largest diff. peak/hole was 1.882–1.386 eÅ^{-3}. GOF = 1.007.

Crystal data for **4b** (experiment **4b**_150K). $C_{28}H_{28}Bi_2Br_{7.52}I_{2.48}N_8$ (M = 1810.18), orthorhombic, space group $Pbca$, a = 16.8149(6), b = 9.8623(4) and c = 27.5955(10) Å, V = 4576.3(3) Å^3, Z = 4, T = 150 K, d_{calc} = 2.627 g cm^{-3}. Total 51753 reflections were collected (2.422° < θ < 27.156°), μ = 15.949 mm^{-1}, 5076 independent reflections (R_{int} = 0.0782). Data/restraints/parameters: 5076/0/217. The final refinement parameters were: R_1 = 0.0398, wR_2 = 0.0858 for reflections with $I > 2\sigma(I)$; R_1 = 0.0644, wR_2 = 0.0953 for all the reflections; largest diff. peak/hole was 1.399–1.460 eÅ^{-3}. GOF = 1.060.

Crystal data for **4c**. $C_{56}H_{56}Bi_3Br_{12}I_{15}N_{16}$ (M = 4442.52), tetragonal, space group $I4/m$, a = 14.7016(6), b = 14.7016(6) and c = 24.3159(10) Å, V = 5255.6(5) Å^3, Z = 2, T = 150 K, d_{calc} = 2.807 g cm^{-3}. Total 37819 reflections were collected (2.578° < θ < 31.023°), μ = 14.017 mm^{-1}, 4258 independent reflections (R_{int} = 0.0553). Data/restraints/parameters: 4258/0/149. The final refinement parameters were: R_1 = 0.0339, wR_2 = 0.0904 for reflections with $I > 2\sigma(I)$; R_1 = 0.0549, wR_2 = 0.1003 for all the reflections; largest diff. peak/hole was 1.665–1.235 eÅ^{-3}. GOF = 1.010.

Crystal data for **4d**. $C_{35}H_{35}Bi_2I_{12}KN_{10}$ (M = 2575.59), monoclinic, space group $P2_1/n$, a = 9.8150(2), b = 14.9572(3) and c = 20.8682(4) Å, β = 92.0850(10)°, V = 3061.53(11) Å^3, Z = 2, T = 150 K, d_{calc} = 2.794 g cm^{-3}. Total 72867 reflections were collected (2.262° < θ < 31.552°), μ = 11.891 mm^{-1}, 10022 independent reflections (R_{int} = 0.0631). Data/restraints/parameters: 10022/20/313. The final refinement parameters were: R_1 = 0.0309, wR_2 = 0.0743 for reflections with $I > 2\sigma(I)$; R_1 = 0.0495, wR_2 = 0.0838 for all the reflections; largest diff. peak/hole was 2.136–0.982 eÅ^{-3}. GOF = 0.925.

CCDC 1905348–1905352 and 1905354–1905356 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data *via* http://www.ccdc.cam.ac.uk.



Scheme 2

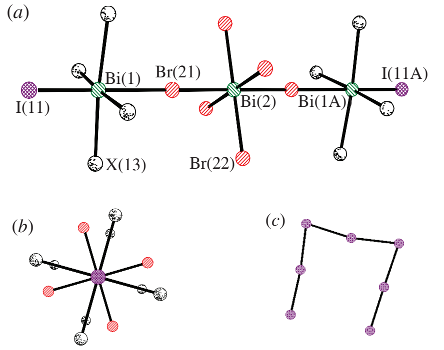


Figure 1 (*a*),(*b*) Two projections of the complex anion in the structure of [4-NCMePy]$_8$[Bi$_3$Br$_{12}$I$_4$]I$_7$·2(I$_2$) (compound **4c**), where position X(13) = = 0.75 Br + 0.25 I; and (*c*) the structure of I$_7^-$ anion.

precipitate. After few days, the orange crystals of **4b** were formed (see Scheme 2). Its structure (**4b**_100K experiment)[‡] is formed by two crystallographically independent [4-NCMePy]$^+$ cations and [Bi$_2$Br$_{7.52}$I$_{2.48}$]$^{4-}$ anions. All the five independent Br/I positions are mixed; the Br : I ratio varies from 51 : 49 to 87 : 13, and the both independent cations are ordered. In structure **4b**, layers perpendicular to the *c* axis consisting of cations only, as well as layers formed by cations and anions can be distinguished [Figure S7(*b*)]. The length of I...I contacts exceeds 4.7 Å.

According to the powder XRD data [Figure S1(*d*)], the obtained compound corresponds to structure **4b** and is single-phased.[§] According to the EDX data (Table S4) for a sample of **4b**, the percentage of bromine relative to the total amount of halogens was 75.0% in the whole sample and 76.4±2.7% in 3 random points. These values are fairly close to 75.2% obtained using the powder XRD and indicate that the obtained solid solution is homogeneous. The optical band gap for compound **4b** is 2.48 eV according to the DRS data [Figure S2(*d*)]. It is higher by about 0.1 eV than that for mixed bromoiodobismuthate **3b**, which possesses the same relative bromine content in the halobismuthate.

To determine whether oxidation products can be formed in the considered systems, the reaction mixtures containing **1b–4b** and the mother liquors were kept in air for a few days. Resulting dark brown crystals of oxidation products **2c** and **4c** (of **2b** and **4b** oxidation, respectively) were isolated from two of the four systems. The quality of crystals of admixture phase **2c** was poor due to pseudo-monohedral and centrosymmetric twinning. Structural investigation of the crystals of **2c** revealed the molecular formula [1,3-Me$_2$Py]$_4$[Bi$_2$I$_9$][I$_3$] and the following unit cell parameters: $P2_1$, $a = 8.672$, $b = 28.097$ and $c = 11.635$ Å, and $\beta = 109.880°$ (Figure S8).[23]

Compound **4c** was formed from [4-NCMePy]$^+$ cation, [Bi$_3$Br$_{12}$I$_4$]$^{7-}$ complex anion, I$_7^-$ polyiodide anion, and I$_2$ molecules (Figure 1).

In the centrosymmetric trinuclear anion (4/m symmetry), the central Bi(2) atom coordinates with six Br atoms, and the X(13) position at the terminal Bi(1) atom is mixed (0.75 Br + 0.25 I). The I$_7^-$ anion is disordered around the 4/m position, and the I$_2$ molecule is disordered around the –4 position. Nine compounds containing the I$_7^-$ anion were known (CCDC version 5.39, November 2018).[24] In all the 11 cases (two compounds contain two crystallographically independent anions), the anion contains three linear I$_3$ fragments, similarly to the compound that was isolated in the present work. The I$_3$ moieties can have *cis*, *gauche* and *trans* mutual arrangement. The I$_2$ molecules bind the complex anions through short contacts X(13)···I(15) of 3.192 Å (Figure S10) into 1D chains (the disordered I$_2$ molecule located in a particular position can bind only two complex anions to each other). The I···X contacts of 4.19–4.21 Å bind the anions into 2D-layers, while the I$_7^-$ anions are involved in ‘medium’ interactions (I···I of 3.67 and 3.87 Å) with complex anions to form a 3D-structure (Figure S10). A few crystals of **4c** were collected and additionally characterized by DRS. According to our estimation [see Figure S2(*e*)], the E_g value for **4c** is 1.90 eV.

Upon drying the reaction mixture containing **4b** and the mother liquor for about a week, the formation of large KBr crystals was observed. Light-red crystals of **4d** ([4-NCMePy]$_5$[K(BiI$_6$)$_2$]) were found in the brine under these crystals. In the structure of **4d**, one of the three aromatic cations is disordered around the center of inversion, while the K atom binds two [BiI$_6$]$^{3-}$ anions into a trinuclear centrosymmetric anion [K(BiI$_6$)$_2$]$^{5-}$ (Figure 2).

The shortest I···I contact length is 4.44 Å. In addition to the light-red crystals of **4d**, the brine obtained upon drying the

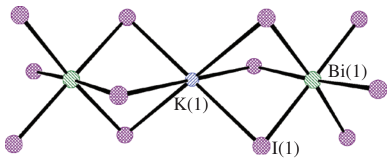


Figure 2 Structure of trinuclear anion [K(BiI$_6$)$_2$]$^{5-}$ in product **4d** ([4-NCMePy]$_5$[K(BiI$_6$)$_2$]).

[§] X-ray powder diffraction analysis was carried out using a Bruker D8 ADVANCE X-ray diffractometer (CuKα, Ni-filter, LYNXEYE detector, reflection geometry). Full-profile X-ray analysis of patterns of crystalline substances was performed using TOPAS 4.2 software.[19] The refinement was carried out using the structural models **1b–4b**. The unit cell parameters and the scale factor were refined.

Details of clarification using the Rietveld method are as follows. Solution **1b**: $P2_12_12_1$, $a = 10.3878(15)$, $b = 17.0883(19)$ and $c = 42.7748(42)$ Å, R_{exp} 2.36%, R_{wp} 6.07%, R_{p} 4.39%, GOF 2.57; **2b**: $P2_1$, $a = 11.9766(20)$, $b = 11.9571(13)$ and $c = 13.4119(8)$ Å, $\beta = 95.579(15)°$, R_{exp} 3.69%, R_{wp} 9.08%, R_{p} 6.24%, GOF 2.46; **3b**: $P2_1/n$, $a = 18.9129(30)$, $b = 11.9290(20)$ and $c = 19.2431(24)$ Å, $\beta = 118.584(9)°$, R_{exp} 2.42%, R_{wp} 7.71%, R_{p} 5.68%, GOF 3.19; **4b**: *Pbca*, $a = 16.8474(13)$, $b = = 9.9959(7)$ and $c = 27.6833(20)$ Å, R_{exp} 2.54%, R_{wp} 4.81%, R_{p} 3.60%, GOF 1.90.

[¶] Energy-dispersive X-ray spectroscopy (EDX) was performed using a Carl Zeiss NVision 40 scanning electron microscope equipped with Oxford Instruments X-Max (80 mm^2) detector and operating at an accelerating voltage of 20 kV.

[††] The diffuse reflectance spectra (DRS) were measured on an Ocean Optics QE65000 spectrophotometer within the frequency range 11000–50000 cm^{-1} at room temperature. The spectra were presented as the Kubelka–Munk function[20] *vs.* light energy. The Kubelka–Munk equation is expressed as follows: $F(R_d) = (1-R_d)^3/2R_d$, where R_{d} is the absolute reflectance of the sample layer. The optical band gap energies were estimated from extrapolation of the linear parts of the corresponding curves to $F(R_{\text{d}}) = 0$.

solution of **4b** contained dark-red single crystals of rather poor quality.

Structural studies of the crystals revealed the molecular formula $K_{5.64}(H_3O)_{4.36}[4\text{-NCMePy}]_8[Bi_4I_{18}]_3\cdot 4.13H_2O$ (**4e**) and the following unit cell parameters: $C2$, a = 49.305, b = 10.4676 and c = 40.012 Å, β = 107.373° (Figure S11).[25] Both the isolated iodobismuthates contained potassium ions. We assumed that the same products could be obtained by a direct reaction of potassium iodobismuthate with iodide **4a**. However, the resulting red powder (**4f**) was found to be unsuitable for single-crystal X-ray diffraction analysis. Powder XRD data (Figure S12) revealed that products **4d** and **4e** were not the major ones in the reaction of potassium iodobismuthate with iodide **4a**. According to the EDX data, product **4f** was not homogeneous (Table S5) and contained almost no potassium, unlike **4d** and **4e** (see Scheme 2).

In conclusion, the solid products enriched with iodine were isolated during the formation of mixed hybrid halobismuthates from solutions containing both bromine and iodine. The structures of mixed halobismuthates **2b** and **3b** were derived from the structures of corresponding hybrid bromobismuthates.[5,14] The structure of single-phase product **1b** was markedly different from that of bromobismuthate $[1,2\text{-Me}_2Py]_3[Bi_2Br_9]$ reported previously.[5] Isolated halobismuthates **1b–4b** were enriched with iodine as compared to its content in the original solution. For instance, more than 50% of iodine and only 5% of bromine presented in the original solution were utilized for the formation of halobismuthate **1b**. Such Br : I ratio of *ca.* 10 : 1 was also observed for compounds **2b–4b**. The structure of iodobismuthate **3c** (it contains $[1,4\text{-Me}_2Py]^+$ cations and $[BiI_4]_n^{n-}$ 1D chains,[26] Figure S9) suggests the absence of any continuous series of solid solutions for hybrid bromobismuthates and iodobismuthates. Either oxidation or drying of mother liquors resulted in products with even higher iodine contents, up to pure iodobismuthates.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.020.

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