Research paper

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Polybromide salts of tetraalkyl and N-heterocyclic cations: new entries into the structural library

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Abstract. Reactions between Br_2 dissolved in HBr and salts of various organic cations resulted in formation of a series of polyhalide salts: (IsoquinolH)Br_3 (**1**), (2-BrPyH)Br_3 (**2**), (H_2(4,4`-bipy))$(Br_3)_2$ (**3**), Bu_4NBr_3 (**4**), (Collidinium){$(Br_3)(Br_2)$} (**5**) and $Et_4N\{(Br_3)(Br_2)_2\}$ (**6**). All compounds were characterized by X-ray diffractometry; the role of supramolecular Br···Br contacts is discussed.

Keywords: polybromides / polyhalides / X-ray diffractometry / supramolecular contacts

Introduction

Polyhalide compounds constitute a field of modern chemistry which attracts much attention [1]. Although the first example of such substances were reported almost 200 years ago [1], new exciting compounds continue to be reported. The most recent results are concentrated on the generation of non-iodide polyhalide units of higher nuclearity (usually more than 5). For example, very recently, Riedel at al. reported formation of stable $[Cl_8]^{2-}$ [2] and a 2D polychloride network [3]. It is known that the tendency to form polyhalide anions decreases dramatically in the row I >> Br > Cl > F, and, therefore, polyodides remain the best studied class [4-5].

Interest in polybromides is caused by both fundamental reasons and their potential use in several application areas. In particular, polybromides may be utilized as a form of “capturing” of Br_2 in Zn/Br redox flow batteries, decreasing their ability to spontaneous discharge [6-10]. A number of polybromides with various molecular structures have been reported to date [11-16]; the synthetic approaches towards these compounds may include the use of ionic liquids [17].

During our experiments aiming at the synthesis of novel Bi(III) polybromide complexes [18], we have noticed that in many cases reactions "Br_2 + HBr + $[BiBr_6]^{3-}$" do not lead to the formation of a desired product. Instead, there forms a mixture of bromobismuthate and polybromide (most commonly, tribromide) salts of an organic cation. Considering the fact that XRD and PXRD are the main methods for identification of the products in reactions of this type, information on the crystal structures of such salts is needed to allow their rapid identification. In this work, we describe the crystal structures of six novel polybromides of various organic cations containing different amounts of "captured" dibromine per one Br^-: (IsoquinolH)Br_3 (**1**), (2-BrPyH)Br_3 (**2**), $(H_2(4,4`\text{-bipy}))(Br_3)_2$ (**3**), Bu_4NBr_3 (**4**), (Collidinium)$\{(Br_3)(Br_2)\}$ (**5**) and $Et_4N\{(Br_3)(Br_2)_2\}$ (**6**).

Experimental section

All reagents were obtained from commercial sources (Sigma-Aldrich) and used without any additional purification. Initially, samples of **1**-**6** were precipitated from the cooled (6°C) mixtures of two solutions: (1) Bi_2O_3 + excess of Br_2 and (2) bromide of corresponding cation (both in 2M HBr). Further, the same general approach was applied: solutions of Br_2 and corresponding cation (generated in situ by protonation or taken as bromide salt), both in aqueous 2M HBr, were mixed together and cooled down to 6°C. In initial non-optimized experiments, the cation/Br_2 ratio was 1:1 (with great excess of bromide anion in solution). Crystals of **1**-**6**, suitable for XRD, were obtained within 1-2 days (see SI).

Crystallographic data and refinement details for **1**-**6** are given in Table 1. The diffraction data were collected on a New Xcalibur (Agilent Technologies) diffractometer with MoK_α radiation (λ = 0.71073) by doing ϕ scans of narrow (0.5°) frames at 130 K. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01)). Structure was solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7 [19] in ShelXle program [20]. Hydrogen atoms were refined in geometrically calculated positions. Cifcheck from http://journals.iucr.org/services/cif/checkcif.html gives Alert B-type ADDSYM suggests Possible Pseudo/New Space Group P-1 for the crystal structure of 1. But the structure was solved in P-1 and checked with PLATON [21]. The ADDSYM procedure from PLATON does not find a new space group and suggests check pseudo translations. Checking frames for violations didn't detect any results. Analyzing of all facts we suggest to submit to CCDC the crystal structure of 1 as it is. Solution the crystal structure of 4 in space group $P2_1$ as racemic twin with BASF value 0.54 gives R 3.8%. Refinement in $P2_1/n$ lead to disordering of TEA cation over two positions with occupancy around 0.5/0.5 and R value increases to 7.23%. According to this crystal structure of 4 is an asymmetric racemic twin with low domination of one part. The main geometrical parameters are summarized in Table S1 (see SI). The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition codes CCDC 1544201-1544206.

Table 1. Details of crystallographic experiments for 1-6

	1	**2**	**3**	**4**
Chemical formula	$C_9H_8Br_3N$	$C_{10}H_9Br_5N_2$	$C_{10}H_{10}Br_6N_2$	$C_{16}H_{36}Br_3N$
M_r	369.89	556.74	637.66	482.19
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2/n$	Triclinic, $P\bar{1}$
a, b, c (Å)	7.5644 (2), 10.3668 (4), 14.5156 (4)	8.3073 (5), 8.4831 (5), 11.3016 (7)	6.9211 (4), 9.5152 (6), 12.6423 (10)	8.9920 (3), 9.9237 (3), 12.5044 (6)
α, β, γ (°)	96.664 (2), 92.227 (2), 108.708 (3)	87.164 (5), 71.941 (5), 80.975 (5)	90, 103.236 (7), 90	109.539 (4), 90.649 (3), 97.727 (3)
V (Å^3)	1067.36 (6)	747.83 (8)	810.45 (10)	1040.12 (7)
Z	4	2	2	2
μ (mm^{-1})	11.29	13.42	14.85	5.81
Crystal size (mm)	0.12 × 0.12 × 0.06	0.26 × 0.12 × 0.08	0.30 × 0.12 × 0.12	0.12 × 0.10 × 0.08
T_{min}, T_{max}	0.332, 1.000	0.153, 1.000	0.236, 1.000	0.933, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9648, 5070, 3775	5772, 3492, 2643	3973, 1927, 1575	8090, 4863, 3768
R_{int}	0.032	0.055	0.019	0.018
θ values (°)	θ_{max} = 29.6, θ_{min} = 3.3	θ_{max} = 29.5, θ_{min} = 3.3	θ_{max} = 29.6, θ_{min} = 3.3	θ_{max} = 29.6, θ_{min} = 3.4
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.695	0.694	0.695	0.695
Range of h, k, l	$h = -9 \rightarrow 10$, $k = -13 \rightarrow 12$, $l = -14 \rightarrow 18$	$h = -10 \rightarrow 11$, $k = -11 \rightarrow 10$, $l = -15 \rightarrow 15$	$h = -9 \rightarrow 7$, $k = -12 \rightarrow 10$, $l = -11 \rightarrow 17$	$h = -12 \rightarrow 11$, $k = -12 \rightarrow 13$, $l = -17 \rightarrow 13$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.084, 0.98	0.045, 0.097, 0.98	0.033, 0.084, 1.27	0.074, 0.230, 1.09

No. of reflections, parameters, restraints	5070, 235, 0	3492, 154, 0	1927, 84, 0	4863, 181, 0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0136P)^2 + 4.678P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 18.1006P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ_{max}, Δ_{min} (e Å^{-3})	0.86, -0.91	0.98, -1.11	0.69, -0.78	2.83, -2.83

	5	**6**
Chemical formula	$C_8H_{12}Br_5N$	$C_8H_{20}Br_7N$
M_r	521.74	689.62
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
a, b, c (Å)	8.7294 (4), 7.4739 (4), 22.0451 (9)	9.0935 (5), 10.3722 (5), 10.2994 (6)
α, β, γ (°)	90, 91.662 (4), 90	90, 107.880 (6), 90
V (Å^3)	1437.68 (12)	924.52 (9)
Z	4	2
μ (mm^{-1})	13.94	15.17
Crystal size (mm)	0.36 × 0.08 × 0.08	0.20 × 0.08 × 0.08
T_{min}, T_{max}	0.231, 1.000	0.448, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7446, 3195, 2640	4243, 3233, 2743
R_{int}	0.027	0.018
θ values (°)	$\theta_{max} = 29.0$, $\theta_{min} = 3.3$	$\theta_{max} = 29.6$, $\theta_{min} = 3.6$
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.682	0.694
Range of h, k, l	$h = -9 \rightarrow 11$, $k = -7 \rightarrow 9$, $l = -27 \rightarrow 28$	$h = -12 \rightarrow 7$, $k = -14 \rightarrow 10$, $l = -11 \rightarrow 13$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.061, 1.08	0.038, 0.074, 1.05
No. of reflections, parameters, restraints	3195, 127, 0	3233, 146, 1
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 0.2622P]$	$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.8624P]$ where $P = (F_o^2 + 2F_c^2)/3$

	where $P = (F_o^2 + 2F_c^2)/3$	
Δ_{max},Δ_{min} (e Å^{-3})	0.76, -0.72	1.09, -0.77

Results and discussion

As mentioned above, polybromides **1**-**6** were obtained during attempted syntheses of Bi(III) polybromide complexes. In most cases, we observed the formation of crystals of two sorts: light yellow (obviously bromobismuthate complexes; the presence of Bi was confirmed by elemental analysis) and orange/red. Once the absence of bismuth in the isolated orange/red crystals was established by XRD, we decided to focus on polybromide products all experiments were reproduced according to the abovementioned scheme (the nature of crystalline samples was confirmed by comparison of measured cell parameters). It can be seen that, although the initial stoichiometry was the same (or very similar), the cation/Br_2 ratio in the products varies.

Compounds **1**-**4** belong to the most widespread type, the tribromides [22-33]. In this case, no additional contacts between the Br_3^- anions are observed. Crystal packings in **1-4** are shown in Figures **1** and **2**. The Br-Br distances in Br_3^- fit within the usual range: 2.4353(5)-2.6829(5), 2.5317(8)-2.5589(8), 2.429(1)-2.681(1) and 2.470(2)-2.468(2) Å in **1**, **2**, **3** and **4**, respectively. The crystal structure of **2** features the presence of specific supramolecular contacts between the Br atoms of 2-bromopyridinium cation and terminal Br of Br_3^- (Br···Br = 3.4588(9) Å) (Fig. 3). In all cases where N-protonated bases act as cation, there are also short NH···Br contacts.

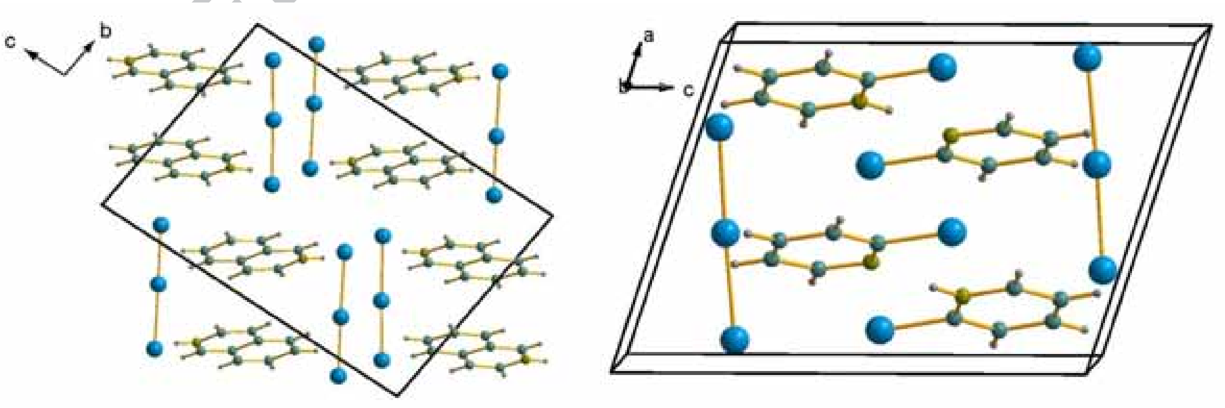

Figure 1. Crystal packings in **1** and **2**. Br blue

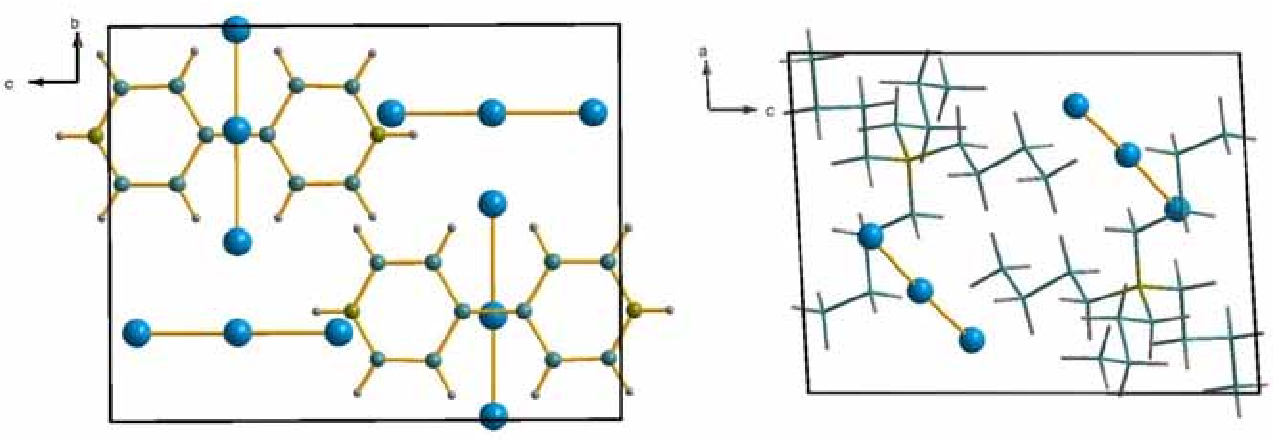

Figure 2. Crystal packings in **3** and **4**. Br blue. In 4, TBA cations are shown in wire-and-stick model for clarity

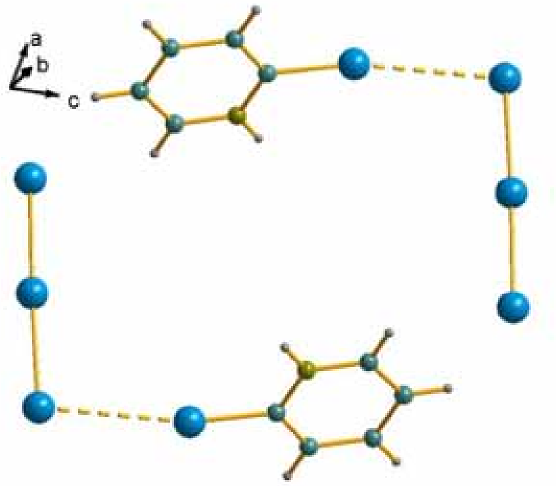

Figure 3. Specific Br···Br contacts in **2**

It must be mentioned that two polybromides containing TBA cation were reported earlier. The first compound is another polymorph of known TBABr$_3$, demonstrating higher symmetry (monoclinic *vs* triclinic in **4**) [34], while in the second case the number of {Br$_2$} units is greater [16].

In the structure of more bromine-rich polybromide **5**, the anionic part also consists of Br$_3^-$ which are supramolecularly connected to neutral {Br$_2$} units (Br···Br = 3.3261(6) Å) (Fig. 4), forming therefore a V-shaped Br$_5^-$ fragment. Therefore, it cannot be considered as "true pentabromide" described earlier [35]. It must be noted that, although such supramolecular ({Br$_3$} + {Br$_2$}) associates have been reported [36-38], their number is very limited. Analyzing the relevant structures, we noticed that there are two types of geometry, featuring different Br-Br···Br angles: either close to 120° or close to 90° (93.48(2)° in **5**).

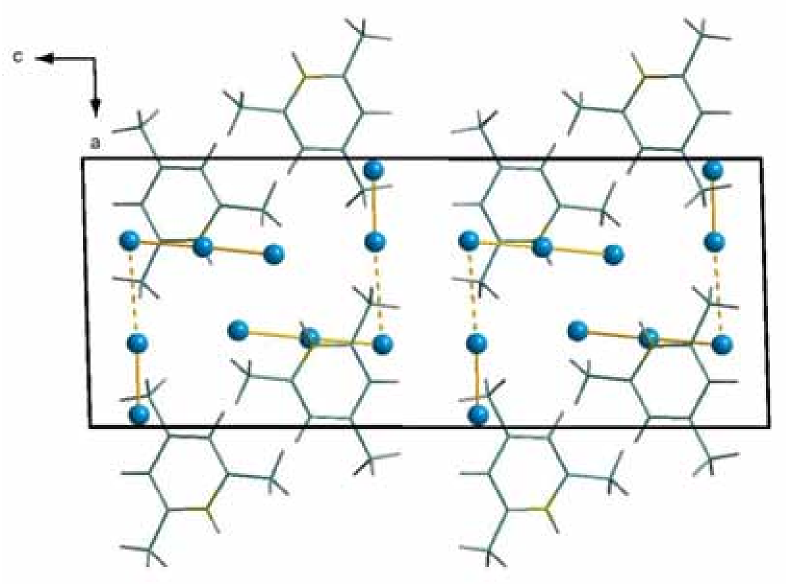

Figure 4. Crystal packing in **5.** Br blue, $\{Br_3\}\cdots\{Br_2\}$ contacts dashed

Finally, the most “Br- saturated” compound **6** demonstrates the most sophisticated structure, which may be considered as a two-dimensional supramolecular polymer. There are one Br_3^- and two $\{Br_2\}$ units per one TEA cation (Fig. 5); each Br_3^- interacts with four $\{Br_2\}$ neighbors by its terminal Br atoms (Br···Br = 3.206(2) – 3.286(2) Å). The structure reveals certain similarity with other heptabromide-based frameworks [12] [27].

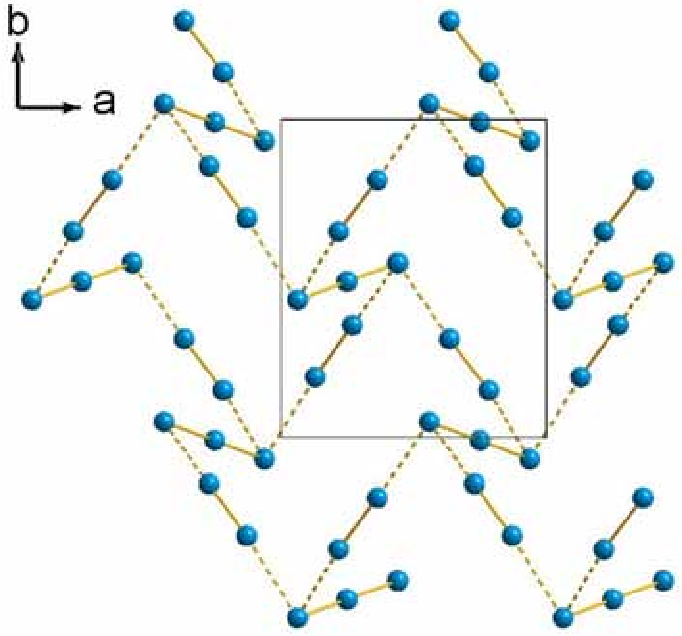

Figure 5. The system of Br···Br contacts in the structure of **6**. Br blue; TEA cations are omitted for clarity

Overall, it can be seen that polybromides containing different amounts of “captured” {Br_2} may be isolated from HBr/Br_2 system. Earlier it was noted [39] that in some cases (e.g. conducting reactions in gas phase) formation of polybromides may proceed in stoichiometric way. However, numerous reports of such compounds synthesized in ionic liquids [11, 12] allow us proposing that this is not a common situation. In our opinion, an important factor affecting the composition and structure of forming polyhalides is a nature of cation used in synthesis. Recent theoretical evaluations of halogen bonding energies in polyhalides [40] result in the values which are comparable with those of electrostatic cation···anion interactions; therefore, the role of crystal packing may be crucial.

According to our observations, a mass loss for all samples (especially for **5** and **6**) could be detected within hours when kept on air. Therefore, general safety precautions (usual when working with halogens) are recommended. As follows from the PXRD data, our numerous attempts to prepare pure phases of **1**-**6** succeeded only in the case of **1** (see SI). In some cases, there form mixtures of **2**-**6** and other polybromide phases with the same cations reported earlier (in particular, for **6**). Surprisingly, although the **4** is a tribromide salt which should be stable, in all cases we detected other known polymorphs of TBABr_3 as predominant phases. This fact, together with the limited stability (which is rather expectable for **5** and **6**), prevented us from obtaining of any reliable TGA data for the whole set of compound, as well as determination of reaction yields. However, we successfully applied TGA in the case of **1** (see SI), and results are in good agreement with our expectations.

Conclusions

A series of six novel polybromides, featuring different Br^-/Br_2 ratio, were obtained and structurally characterized. Considering that: (a) the formation of the mixture of different polyhalides is quite common and (b) the range of physical methods which can be used for their characterization is limited, X-ray diffractometry and PXRD analysis based thereupon remain the most reliable and informative approach. It is worth stressing that the formation of polybromides with higher content of {Br_2} can occur when working in HBr/Br_2 medium; this method is simple and straightforward, and it may be considered as an alternative to the use of ionic liquids (or, at least, the compounds prepared in this way may be utilized as precursors for further IL synthesis).

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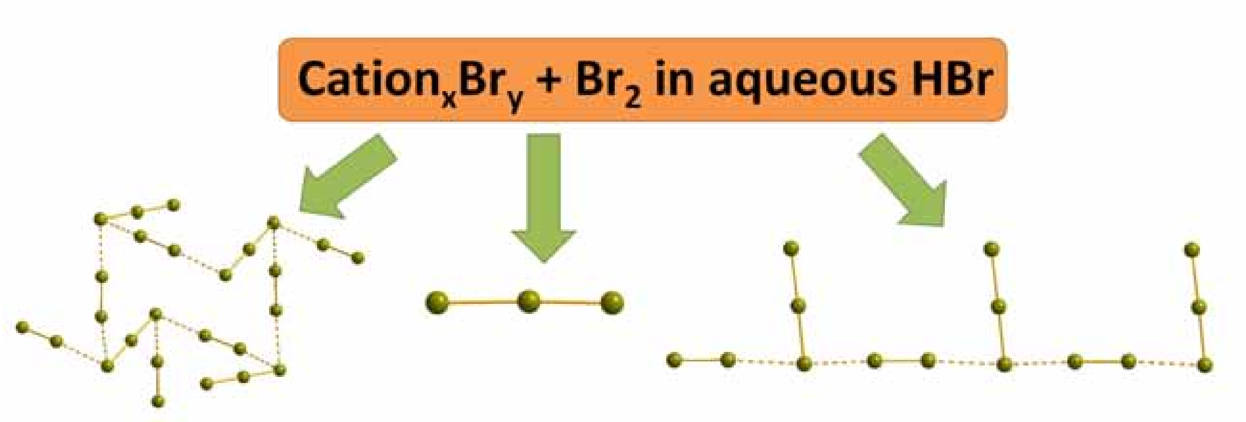
- Six novel polybromides are structurally characterized

- Br_2/Br^- ratio varies from 1 to 3

-Simple preparation strategy was proposed


$\text{Cation}_x\text{Br}_y + \text{Br}_2$ in aqueous HBr