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POLYHALIDE COMPLEXES OF POST-TRANSITION METALS: FASCINATING DIVERSITY OF STRUCTURAL TYPES

Solutions containing of X_2 ($X = Br, I$) in hydrohalic acids represent a virtual dynamic library of polyhalide species. In presence of $[MX_6]^{n-}$ ($M = Sb, Bi, Te$) and halide of different organic cations, there may be isolated a great number of halometalate complexes containing polyhalide units “trapped” in solid state. Here, we present an overview of structural types, as well as discussion of the potential applicability of these compounds in materials science.

Halide complexes belong to the “classic” objects of coordination chemistry, being well-known for over 100 years. From the point of view of synthetic chemist, those are rather trivial objects for study, since preparation procedures are very straightforward for many metals. Indeed, mixing a source of metal cation and source of halide ion results in formation of some anionic halometalate species $[M_aX_b]^{n-}$ which can be then precipitated as salts, commonly giving crystals suitable for X-ray diffractometry - and this is the paradigm many ordinary research papers (both earlier and current) are based upon. This simplicity, which many chemists would probably regard as the lack of “synthetic elegance” (and others would consider an advantage), is accompanied by numerous useful physical properties demonstrated by halometalates, making them attractive for materials-related studies. In particular, special attention focuses on their applicability as light absorbers in “perovskite-type” solar cells, which constitute one of the “hot topics” in modern materials science. However, there is an important point which counter-

balances the easiness of synthesis, making this area interesting from the point of view of fundamental coordination chemistry. For some metals (in particular, in the p -block), both ligand exchange kinetics and the low energies of metal-halogen bonds pre-determine that the halometalate units cannot form stable polynuclear “building blocks” in solution, thus rendering this concept, widely used in other fields, inapplicable in this case [1]. The structure and nuclearity of anions formed in each reaction depend on several factors [2], and cannot be controlled stoichiometrically. There are still no general rules and principles, which would make the outcome of synthesis predictable. The nature of cation used for isolation of a halometalate often plays the key role, but the correlations relating it to the particular structural type of the product are yet to be found.

In the beginning of our work, we set possible solution of this problem as a goal of our research. A series of closely related pyridinium-derived cations was chosen to make an extended representative series of halobismuthates, assuming that the collection

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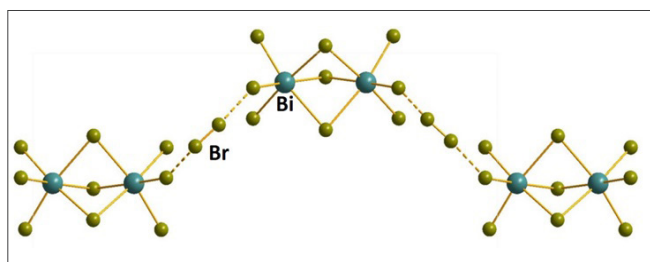


Fig. 1 - Structure of $\{[Bi_2Br_9](Br_2)\}$ units in **1**. Bi turquoise, Br olive-green, Br...Br contacts dashed

of such statistics would possibly give an idea on the relationships between the structure of the cation and structural type of polyhalobismuthate anion. However, as often happens in experimental research, we have gained unexpected results, which ultimately proved much more interesting. By accident, one of the prepared samples - crystalline polymeric bromobismuthate (N-MePy) $\{[BiBr_4]\}$ in mother liquor containing 2M HBr - was exposed to sunlight for several weeks. This exposure resulted in generation of noticeable amounts of Br₂ in solution, which turned orange. More importantly, we found that the pale yellow (N-MePy) $\{[BiBr_4]\}$ transformed into deep orange-red single crystals. Structure elucidation revealed that there are $\{Bi_2Br_9\}^{3-}$ anionic fragments, quite common for halometalates as such, but connected by neutral $\{Br_2\}$ linkers via $Br_{term} \cdots Br_{Br_2}$ interactions into a one-dimensional polymeric chain, corresponding to the composition (N-MePy) $\{[Bi_2Br_9](Br_2)\}$ (**1**) (Fig. 1). The Br-Br distances (3.22-3.38 Å) are longer than covalent bonds, but significantly shorter than the sum of the van der Waals radii (3.66 Å); therefore, the specific supramolecular contacts can be postulated. Interestingly, complex **1** demonstrates remarkable

thermal stability (loss of Br₂ begins above 150 °C); preliminary experiments show that “captured” Br₂ retains chemical activity usual for free dibromine (reaction with an excess of 1-octene yields in 1,2-dibromooctane) [3].

Inspired by this finding, we undertook a search for other supramolecular polybromides in a more straightforward way, adding solutions of bromides of different organic cations to HBr solution containing bromobismuthate species (simplified as $[BiBr_6]^{3-}$) and Br₂. The outcome was fruitful, allowing several generalizations [4, 5]. First, just as in the halometalate chemistry in general, the structure of products is extremely cationic-sensitive. Although formation of polybromide complexes is not uncommon, and we have isolated 9 compounds of this class belonging to five different structural types, in many cases it does not happen; instead, there often crystallize simple bromobismuthates, sometimes simultaneously with polybromide salts of corresponding cation. Even at this stage, although a great number (over 30 to date) of experiments were carried out, the data are still insufficient to explain this difference.

As mentioned above, the polybromobismuthates demonstrate remarkable structural diversity. The type found in **1** seems to be the most frequent; complexes containing the same moiety form also in the case of pyridinium, 4-methylpyridinium and tetraethylammonium [4-6]. The more bromine-rich type was encountered only in the *N*-ethylpyridinium salt [4]. In this case, there are also the same face-shared bromobismuthate “primary building blocks”, but there are two $\{Br_2\}$ units per one $\{Bi_2Br_9\}$, connecting them via both terminal and μ_2 -bridging bromide ligands into

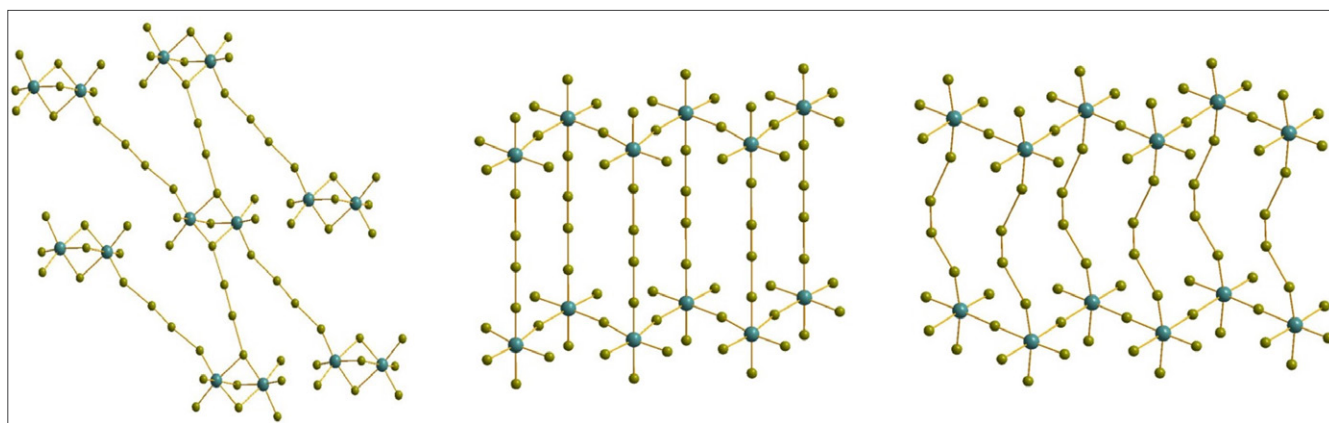


Fig. 2 - Structure of $\{[Bi_2Br_9](Br_2)_2\}$ (type 2, left) and $\{[BiBr_3](Br_2)\}$ (type 3, regular (middle) and distorted (right)). Bi turquoise, Br olive-green

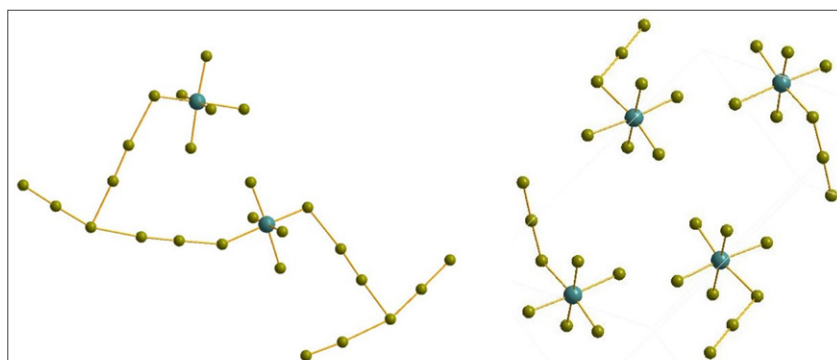


Fig. 3 - Structure of $[\text{BiBr}_5(\text{Br}_3)]^{3-}$ (left) and $\{[\text{BiBr}_5(\text{Br}_3)](\text{Br}_3)(\text{Br}_2)\}$ Bi turquoise, Br olive-green

two-dimensional layers. The same Br_2/Bi ratio was found in Type 3 (Fig. 2); this structure may be represented as a derivative of polymeric ziz-zag $\{[\text{BiBr}_5]^{2-}\}$ where the chains are connected with each other via terminal Br^- via $\{\text{Br}_2\}$ linkers. The $\{\text{Br}\cdots\text{Br}-\text{Br}\cdots\text{Br}\}$ units may be either linear or trapezoidal; in the latter case, the $\text{Br}\cdots\text{Br}$ distances become noticeably longer (3.33 vs 3.07 Å).

It should be emphasized that in all these structures the $\{\text{Br}_2\}$ units are “captured” by a system of supramolecular interactions. Our further efforts resulted in two compounds where polybromides are directly coordinated to Bi(III) (tribromide ligands). In the structurally simplest case, there are five bromide and one polybromide ligands giving mononuclear, zero-dimensional isolated $[\text{BiBr}_5(\text{Br}_3)]^{3-}$ complexes (Fig. 3) [7]. In the second complex involving more sophisticated polybromide moiety, the $[\text{BiBr}_5(\text{Br}_3)]^{3-}$ anion is accompanied by one $\{\text{Br}_3\}^-$ and one neutral $\{\text{Br}_2\}$ unit which form virtually planar supramolecular $\{\text{Br}_9\}^{4-}$ fragment (Fig. 3) [4].

With all these results, a question arises whether this straightforward synthetic approach can be applied for preparation of other polyhalide compounds, namely:

- with other halide ligands than bromide,
- with other polyhalide units (for example, polyiodide), and
- with other metals than bismuth?

Our experiments have shown that the answer is indeed positive for all three points. Indeed, once HBr is replaced by HCl, generating $[\text{BiCl}_6]^{3-}$ in

solution, there may be prepared complexes where chlorobismuthate units “trap” dibromine. These compounds are less stable than polybromobismuthates (decompose within minutes when kept outside the Br_2 -containing mother liquor). To date, only three complexes of this series were isolated. In two cases, the moieties resemble those found in polybromobismuthates (Fig. 4); surprisingly, with pyridinium cation, bromo- and chlorobismuthates give different structures (Type 1 and

distorted Type 3, respectively). The $\text{Cl}\cdots\text{Br}$ distances fall within the same range as $\text{Br}\cdots\text{Br}$ (2.92-3.39 Å) [8]. Similarly, polyhalide hybrids containing bromobismuthates and incorporated I_2 can be obtained (currently counting two examples) [7].

Polyhalide complexes of other metals deserve separate discussion. Digging deep into the relevant literature, we have found two very interesting series of articles. In the first one, presented over 40 years ago by Lawton *et al.* [9], the authors report their studies of reactions performed by the scheme very similar to the one we used ($\text{halometalate} + \text{Br}_2 + \text{CationBr}_x$), but with antimony instead of bismuth. The diversity of possible outcomes here is even greater because Sb(III), unlike Bi(III), can be partially or totally oxidized by Br_2 to Sb(V) and, depending on the cations, three sorts of complexes can be isolated: containing only Sb(III), mixed-valent Sb(III)/Sb(V), and only Sb(V). Additionally, polybromide units can enter the structure; therefore, even taking into account only oxidation state and presence/absence

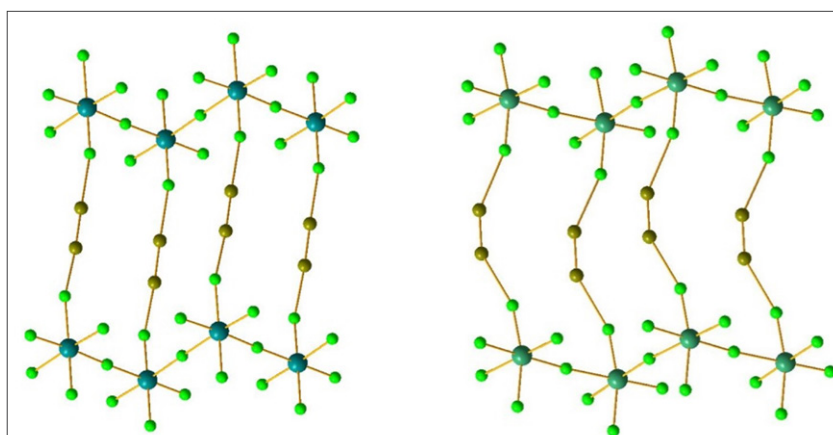


Fig. 4 - Structure of $\{[\text{BiCl}_5]_2(\text{Br}_2)\}$ Bi turquoise, Br olive-green, Cl light green

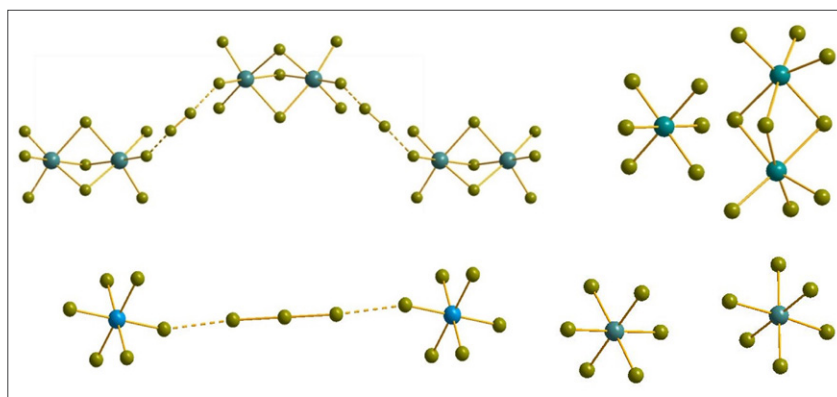


Fig. 5 - Structure of different moieties forming in reactions of "haloantimonate + Br₂ + CationBr_x" type. Sb turquoise, Br olive-green

of polyhalide, six distinct combinations are possible. The second group was published in Nineties by chemists from Bergen University; during their work with halotellurates (V), they have isolated two complexes containing binuclear {Te₂X₁₀} and {Br₂} units (both from acetonitrile) [10]. Unfortunately, although all these results seemed very inspiring, we could not trace any follow-up research in this field. Therefore, we decided to revive and update it, collecting an extended number of data and applying modern techniques for characterization and study of supramolecular interactions. Applying the same protocol "halometalate + Br₂ + CationBr_x", we isolated a set of 10 bromoantimonates. Surveying the whole list of these compounds (including earlier reports), we could note that the potential abundance of the products, which could be expected from the variety of oxidation states, is compensated by reluctance of Sb(V) to build polynuclear anions. Very often, the resulting complexes contain either trivial [Sb^VBr₆]⁻ or polymeric linear {[Sb^VBr₆](Br₃)₂]²⁻ units, both reported earlier. The only new structural type we found is a combination of [Sb^{III}₂Br₉]³⁻ and disordered [Sb^VBr₆]⁻. Interestingly, the TMA salt of

{[Sb^{III}₂Br₉](Br₂)} remains the only example where Sb(III) is accompanied by polybromide (Fig. 5) [7].

For Te(IV) complexes, the scheme "TeO₂ + HBr + X₂ + CationBr_x" (X = Br, I) works as well. In presence of greater excess of bromide, there form only mononuclear {TeBr₆} units connected by {X₂} linkers into one-dimensional polymers. Depending on the cation, the shape of 1D chain may be different; the most common is zig-zag (almost all polybromotellurates and all polyiodo-bromotellurates); "linear" chains were observed only once (Fig. 6).

Polybromide complexes are unstable, losing {Br₂} very rapidly when kept in air and giving corresponding cation₂[TeBr₆] complexes [11].

To conclude, several points can be highlighted. Solutions of dihalogens in hydrohalic acids represent virtual dynamic libraries of polyhalide species which can be "captured" by halometalates in presence of different cations, giving a diverse family of discrete complexes, one- and two-dimensional supramolecular frameworks with different structure and composition. This approach is applicable, at least, for bismuth, antimony and tellurium, and we expect that the range of elements is expandable. In our opinion, this class of compounds is of special interest for design of halometalate-based solar cells, since the presence of polyhalide (in particular, polyiodide) fragments may narrow band gaps. Besides, the system of halogen-halogen contacts makes the structures two- or even three-dimensional, which is favorable in terms of charge carrier mobility. Apart of this materials-related aspect, we believe that these studies can advance development of halogen bonding concept which remains in focus of modern su-

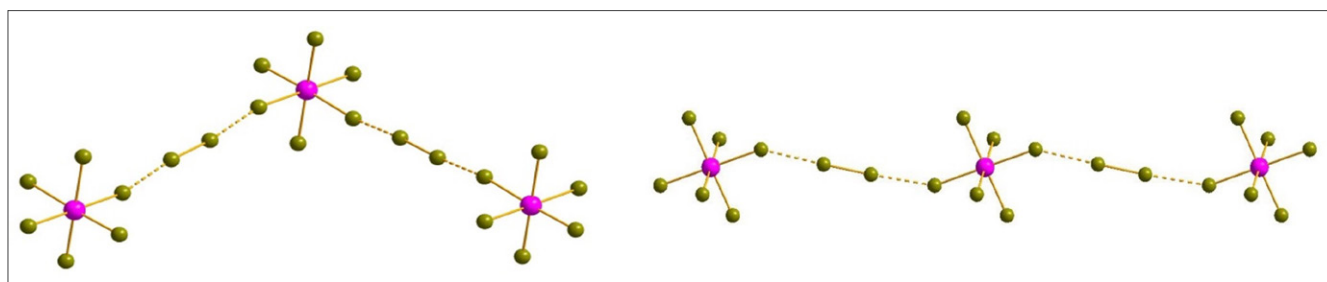


Fig. 6 - Structure of 1D polyhalotellurates (IV): zig-zag (left) and linear (right). Te purple, Br olive-green



pramolecular chemistry, and will contribute to our understanding of chemical bonding, which is the central pillar of chemical concepts.

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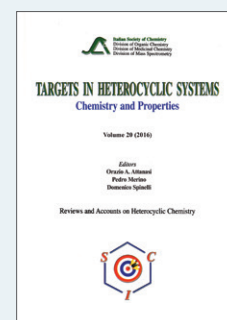
Complessi di polialogenuri di metalli post-transizione: un'interessante diversità dei tipi strutturali

Le soluzioni contenenti X_2 ($X = \text{Br}, \text{I}$) in acidi alogenidrici rappresentano una libreria dinamica virtuale di specie polialogenuriche. In presenza di $[\text{MX}_6]^{n-}$ ($M = \text{Sb}, \text{Bi}, \text{Te}$) e alogenuri di diversi cationi organici, può essere isolato un gran numero di complessi di alometallati contenenti unità polialogenuriche "intrappolate" allo stato solido. Qui, presentiamo una panoramica dei tipi strutturali e una discussione della potenziale applicabilità di questi composti nella scienza dei materiali.

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