

Review

# Recent Progress in the Theoretical Studies of the Noncovalent Interactions of Supramolecular Complexes with Polyhalides and Halometalates

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**Abstract:** Despite the fact that first polyhalides and halometalates have been discovered decades ago, this subject of chemical science has been progressing, and many supramolecular associates with these compounds exhibiting promising properties were reported. In this mini-review, I would like to highlight recent progress in theoretical studies of noncovalent interactions in supramolecular complexes with polyhalides and halometalates from our research group.

**Keywords:** supramolecular associates; noncovalent interactions; halometalates; polyhalides; theoretical studies

## 1. Introduction

The first polyhalides and halometalates were synthesized decades ago, but this direction of chemistry and material science has been progressing (Figures 1–4), resulting in a huge variety of substances that quite often have interesting chemical and physical properties (e.g., unusual coloring, ferroelectricity and ferroelasticity, photocatalytic properties, photo/thermochromism, and strong photoconductivity effects), featuring multiple potential applications in electronics and photovoltaics. An attractive feature of these compounds from the coordination chemistry point of view is the great variety of structural types. The most recent progress was observed in the area of noniodide polyhalides (i.e., polybromide frameworks and polychlorides), and there was clearly a trend of decreasing abilities to form polyhalides in the  $I > Br > Cl \gg F$  row. However, despite the general progress in this field, it can be noted that the polyhalide metal complexes remain incomparably explored. In addition to the well-established halide complexes of various metals, commonly referred to as halometalates, there exists a huge family of polyhalide–halometalate hybrids: in these complexes, the polyhalide units are either coordinated directly to the metal center or, more commonly, are connected to the halide ligands via specific halogen···halogen interactions, which are sometimes considered to be a specific case of halogen bonding. In this minireview, I highlighted the recent progress in the theoretical studies of the noncovalent interactions of supramolecular complexes with polyhalides and halometalates of our research group, which may be of interest both in terms of fundamental inorganic chemistry and material science for the design of novel Pb-free Sb-based solar cells in particular.



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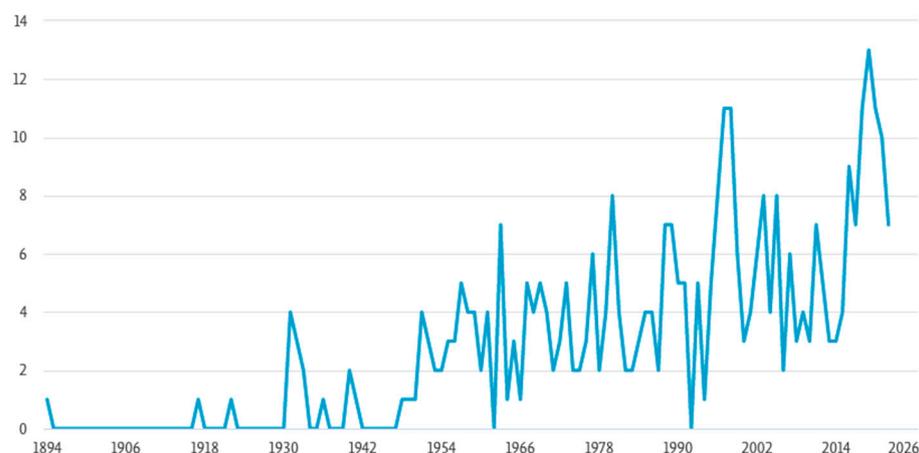
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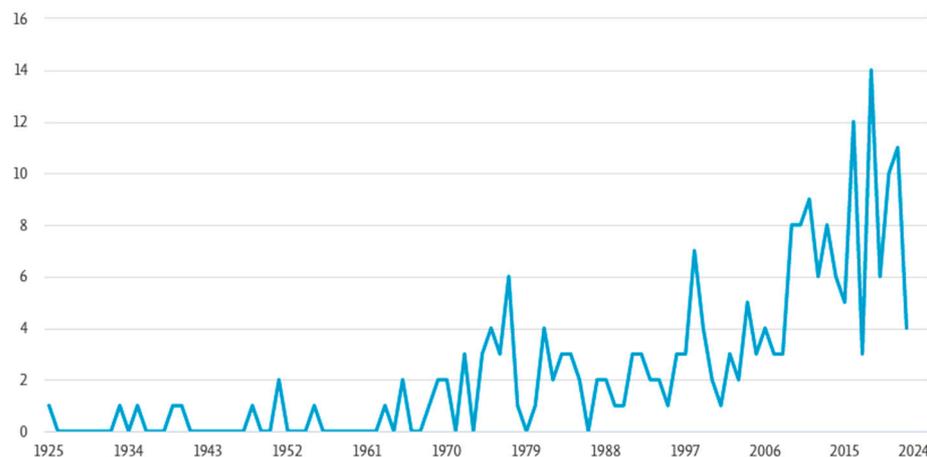
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**Figure 1.** Number of publications per year (ordinate and abscissa axes, respectively) devoted to polyhalides (19 December 2022; Scopus database, search TITLE-ABS-KEY (polyhalide \*)—355 examples).



**Figure 2.** Number of publications per year (ordinate and abscissa axes, respectively) devoted to polychlorides (19 December 2022; Scopus database, search TITLE-ABS-KEY (polychloride \*)—222 examples).



**Figure 3.** Number of publications per year (ordinate and abscissa axes, respectively) devoted to polybromides (19 December 2022; Scopus database, search TITLE-ABS-KEY (polybromide \*)—177 examples).



**Figure 4.** Number of publications per year (ordinate and abscissa axes, respectively) devoted to polyiodides (19 December 2022; Scopus database, search TITLE-ABS-KEY (polyiodide\*)—864 examples).

## 2. Our Works

In [1], the reported reactions of  $\text{TeO}_2$  and  $\text{Br}_2$  in concentrated  $\text{HBr}$  in the presence of various organic cations resulted in the formation of one-dimensional supramolecular polymers with the structure cation  $2\{[\text{TeBr}_6](\text{Br}_2)\}$ . In the crystal structures, the  $\text{Br}_2$  units were connected to the  $[\text{TeBr}_6]^{2-}$  octahedra via halogen...halogen contacts, building symmetrical linear chains of two different geometries. The nature of the  $\text{Br}\cdots\text{Br}$ ,  $\text{Br}\cdots\text{Cl}$ , and  $\text{Cl}\cdots\text{Cl}$  contacts in the present and previously reported complexes of this family was investigated through theoretical methods (DFT calculations and QTAIM analyses), allowing the estimation of their energies ( $0.9\text{--}3.8\text{ kcal}\cdot\text{mol}^{-1}$ ).

In [2], we observed that a yellow bromobismuthate  $\{(2\text{-BrPy})_2\text{H}\}[\text{BiBr}_4]$  transformed into the unusually deeply colored cherry-red  $(2\text{-BrPyH})_2[\text{BiBr}_5]$ . A combination of structural studies and theoretical calculations (including QTAIM analysis) confirmed that the appearance of short noncovalent  $\text{Br}\cdots\text{Br}$  interactions ( $\sim 3.3\text{ \AA}$ ) in  $(2\text{-BrPyH})_2[\text{BiBr}_5]$  was responsible for the anion-to-cation charge transfer ( $\text{LP}(\text{Br}_{\text{ligand}}) \rightarrow \sigma^*(\text{Br}\text{--}\text{C}))$ , yielding dramatic changes in optical behavior. This effect opened the way towards novel halogen-bonding-templated halometalate-based hybrid materials with enhanced optical properties.

In [3], the reported reactions between the  $\text{BiCl}_3$ ,  $\text{Br}_2$ , and chlorides of pyridinium, 4,4'-propylenedipyridinium, and trimethylphenylammonium in aqueous  $\text{HCl}$  led to the formation of chlorobismuthate complexes, trapping  $\{\text{Br}_2\}$  in the solid state in two-dimensional symmetrical polyhalide supramolecular networks. The nature of the noncovalent  $\text{Br}\cdots\text{Cl}$  interactions in these supramolecular complexes were studied through theoretical methods (DFT calculations and QTAIM analyses); the estimated energies of these contacts were  $1.9\text{--}6.0\text{ kcal}\cdot\text{mol}^{-1}$ .

In [4], the reactions of the  $[\text{BiBr}_6]_3$  and bromide salts of various substituted pyridinium cations in excess of  $\text{HBr}$  were discussed. These reactions resulted in a series of bromobismuthate anionic complexes of various geometries and nuclearities (including a symmetrical one):  $[\{\text{BiBr}_4\}_n]_n$ ,  $[\text{Bi}_2\text{Br}_9]_3$ , and  $[\text{Bi}_2\text{Br}_{10}]_4$ . Hirshfeld surface analyses for 19 crystal structures were performed, and the impact of various  $\text{X}\cdots\text{Br}$  contacts on the crystal structures was discussed.

In [5], three novel polybromide complexes of bismuth(III)— $(2,6\text{-MePyH})_3[\text{BiBr}_5(\text{Br}_3)]$ ,  $(\text{H}_2\text{bpp})\{[\text{BiBr}_5](\text{Br}_2)\}$ , and  $(3\text{-ClPyH})_2\{[\text{BiBr}_5](\text{Br}_2)\}$ —were synthesized. The results of an extended screening involving a set of organic cations leading to the formation/nonformation of the Bi(III) polybromides were presented and discussed. The nature of the  $\text{Br}\cdots\text{Br}$  interactions in the Bi(III) polybromides was investigated through theoretical methods (DFT calculations and QTAIM analyses), enabling the estimation of their energies (they varied in the range of  $2.2\text{--}5.4\text{ kcal}\cdot\text{mol}^{-1}$ ).

In [6], the reported cation-dependent reactions “[SbBr<sub>6</sub>]<sup>3-</sup> + Br<sub>2</sub> + HBr + CationBr<sub>x</sub>” resulted in the formation of bromide/polybromide complexes with zero-, one-, two-, or three-dimensional supramolecular symmetrical frameworks and different Br/Sb ratios (up to 11). Seven new compounds representing six structural types were characterized through X-ray diffraction and thermogravimetric analyses, and DFT calculations following the QTAIM analyses enabled the estimation of the energies of the Br⋯Br contacts (1.1–4.6 kcal·mol<sup>-1</sup>).

In [7], three novel polybromotellurates(IV) were obtained through the reactions of TeO<sub>2</sub> in concentrated HBr with Br<sub>2</sub> and tri- or tetraalkylammonium salts. They contained [TeBr<sub>6</sub>]<sup>2-</sup> octahedra connected by the {Br<sub>2</sub>} linkers in one- or pseudo-two-dimensional symmetrical networks. The thermal stability of the products was investigated through thermogravimetric analyses; additionally, all the compounds were characterized through Raman spectroscopy. The energies of the Br⋯Br interactions were estimated through DFT calculations and QTAIM analyses (they varied from 1.3 to 5.4 kcal·mol<sup>-1</sup>).

In [8], we observed that, in the presence of different cations, the reactions of [SbBr<sub>6</sub>]<sup>3-</sup> and I<sub>2</sub> resulted in a new family of diverse supramolecular 1D polyiodide-bromoantimonate networks. The coordination number of Sb as well as the geometry of assembling {I<sub>x</sub>}<sup>n-</sup> polyhalide units could vary, resulting in unprecedented structural types (including a symmetrical one). The nature of the I⋯Br interactions was studied through DFT calculations and QTAIM analyses; the estimated energy values were 1.6–6.9 kcal·mol<sup>-1</sup>. Some of the compounds showed strong photoconductivity in thin films, suggesting multiple feasible applications in optoelectronics and solar energy conversion.

In [9], we showed that reaction between [BiBr<sub>6</sub>]<sup>3-</sup> and Br<sub>2</sub> in HBr in presence of trimethylammonium bromide resulted in the self-assembly of a supramolecular halometalate-polybromide derivative (Me<sub>3</sub>NH)<sub>3</sub>{[Bi<sub>2</sub>Br<sub>9</sub>](Br<sub>2</sub>)} belonging to a novel structural type. DFT calculations and QTAIM analyses allowed the estimation of the Br⋯Br contact energies (1.3–4.4 kcal·mol<sup>-1</sup>).

In [10], a series of chloro- and bromobismuthate complexes with bromopyridinium cations was prepared and characterized through X-ray diffraction analyses and diffuse reflectance spectroscopy. In one case, the short Cl⋯Br contacts between the 2-BrPyH<sup>+</sup> and chlorobismuthate units in a solid state resulted in a notable charge transfer and the appearance of unusual coloring. The nature of the halogen⋯halogen interactions, which can be regarded as halogen bonding, in the obtained complexes was studied through DFT calculations and QTAIM analyses, and their energies were estimated (1.3–3.6 kcal·mol<sup>-1</sup>) and compared with those in related bromo- and iodoplumbates(II). It was concluded that the presence of halogen bonding was not the single factor affecting the optical properties.

In [11], four novel polybromide salts containing pyridinium-type and quinolinium-type cations, {(2-Br-5-MePy)<sub>2</sub>H}Br<sub>3</sub>, (1,3,5-MePy){(Br<sub>3</sub>)(Br<sub>2</sub>)}, (1-Et-2,6-MePy){(Br<sub>3</sub>)(Br<sub>2</sub>)<sub>0.5</sub>}, and (N-MeIsoquin){(Br<sub>3</sub>)(Br<sub>2</sub>)<sub>0.5</sub>}, were isolated from HBr/Br<sub>2</sub> solutions. The Hirshfeld surface analyses of the organic parts of X-ray structures and a set of related compounds reported earlier revealed that, in all cases, crystal packing was determined primarily by the intermolecular contacts Br⋯H, H⋯H, C⋯H, Br⋯Br, and Br⋯C. DFT calculations and QTAIM analyses allowed the estimation of the Br⋯Br halogen bonding energies (0.9–7.5 kcal·mol<sup>-1</sup>).

In [12], a series of nine bromobismuthate complexes containing Py-derived cations—(cat)<sub>3</sub>[Bi<sub>2</sub>Br<sub>9</sub>] (cat = 1-*i*-PrPy; 3,5-MePyH; 1,2-MePy; 1,3-MePy; 1-Et-3-MePy; 1-Et-4-MePy; and 1,2,4,6-MePy), (2-MePyH){[BiBr<sub>4</sub>]}, and (1-Bz-4-MePy)<sub>4</sub>[Bi<sub>2</sub>Br<sub>10</sub>]—were prepared and characterized through X-ray diffractometry. The thermal stability was studied for the synthesized compounds as well as for the related complexes reported earlier. The Hirshfeld surface analyses revealed that the H⋯Br contacts gave the largest contributions to crystal packing (over 86% in all cases).

In [13], we found that, in the reactions between the mononuclear [SbBr<sub>6</sub>]<sup>3-</sup> species, Br<sub>2</sub>, and various {cationBr} salts, Sb(III) was commonly oxidized to Sb(V), and the cations played a key role in the formation of the particular bromoantimonate or polybromide-

bromoantimonate frameworks of different dimensionalities (1D, 2D, or even 3D). Screening this system yielded eleven novel compounds belonging to both the known and the novel structural types (including a symmetrical one). The role of Br⋯Br halogen bonding was studied through DFT calculations and QTAIM analyses, resulting in the estimation of its bond energy (1.1–2.9 kcal·mol<sup>-1</sup>).

In [14], we found that the reactions of 3-iodopyridine with [BiX<sub>6</sub>]<sup>3-</sup> solutions in HX (X = Cl, Br) resulted in the chloro- and bromobismuthate complexes (3-IPyH)<sub>2</sub>{[BiCl<sub>5</sub>]}·H<sub>2</sub>O and (3-IPyH)<sub>4</sub>[Bi<sub>2</sub>Br<sub>10</sub>]·2H<sub>2</sub>O. In both cases, the symmetrical halogen⋯halogen contacts played important roles in the formation of crystal packing; the energies of these interactions were estimated through DFT calculations and QTAIM analyses (they varied from 2.4 to 4.6 kcal·mol<sup>-1</sup>).

In [15], the supramolecular hybrid (2-CIPy)<sub>2</sub>{[TeBr<sub>6</sub>](Br<sub>2</sub>)} was prepared through the reaction of TeO<sub>2</sub>, Br<sub>2</sub>, and 2-chloropyridinium in HBr. In its structure, the mononuclear [TeBr<sub>6</sub>]<sup>2-</sup> units were connected by {Br<sub>2</sub>} linkers in 1D symmetrical zigzag-shaped infinite chains. The energies of halogen bonding were estimated through DFT calculations and QTAIM analyses (1.3–3.3 kcal·mol<sup>-1</sup>).

In [16], we found that the reactions of [SbBr<sub>6</sub>]<sup>3-</sup> with Br<sub>2</sub> in HBr in the presence of N-substituted quinolinium or isoquinolinium cations resulted in new complexes of the hexabromidoantimonates of Sb<sup>V</sup> and their polybromide adducts: (N-MeQuin)<sub>2</sub>{[SbBr<sub>6</sub>](Br<sub>3</sub>)}, (N-MeIsoquin)<sub>2</sub>{[SbBr<sub>6</sub>](Br<sub>3</sub>)}, and (N-EtQuin)[SbBr<sub>6</sub>]. The thermal stability of these compounds was studied, and the energies of the supramolecular symmetrical Br⋯Br interactions were estimated using DFT calculations and QTAIM analyses (1.3–2.1 kcal·mol<sup>-1</sup>).

In [17], we reported that the reactions of Sb<sub>2</sub>O<sub>3</sub> solutions in HBr in the presence of Br<sub>2</sub> with a series of pyridinium-type cation salts resulted in the formation of Cat[SbBr<sub>6</sub>] (Cat = 1,3,4-MePy<sup>+</sup> and 1,4-MePy<sup>+</sup>) and Cat<sub>2</sub>{[SbBr<sub>6</sub>](Br<sub>3</sub>)} (Cat = 1,2-MePy<sup>+</sup>, 1-Et-2-MePy<sup>+</sup>, and 1-Et-4-MePy<sup>+</sup>) complexes which were characterized through X-ray diffractometry. For all the compounds, the thermal stability was investigated through the thermogravimetric analysis method; the energies of the symmetrical noncovalent Br⋯Br interactions were estimated through DFT calculations and QTAIM analyses (1.3–2.2 kcal·mol<sup>-1</sup>).

In [18], we observed that the reactions of the BiI<sub>3</sub>, I<sub>2</sub>, and iodide salts of two different pyridinium cations resulted in the formation of the novel iodine-rich iodobismuthates(III) (1,3-MePy)<sub>4</sub>{[Bi<sub>4</sub>I<sub>16</sub>](I<sub>2</sub>)} and (1-MePy){[BiI<sub>4</sub>](I<sub>2</sub>)<sub>0.5</sub>}, where the halometalate anions were connected by diiodine linkers in one- or two-dimensional symmetrical supramolecular structures. Both complexes revealed narrow optical band gaps and a fairly high thermal stability, favoring their potential use in photovoltaic devices. The energies of the noncovalent I⋯I interactions responsible for the supramolecular organization in the solid state were estimated through DFT calculations and QTAIM analyses (1.6–3.8 kcal·mol<sup>-1</sup>).

In [19], the reported reactions of chlorotellurates(IV) and Br<sub>2</sub> afforded the formation of the one-dimensional supramolecular complexes of the general formula Cat<sub>2</sub>{[TeCl<sub>6</sub>](Br<sub>2</sub>)} (Cat = Me<sub>3</sub>N<sup>+</sup>, PyH<sup>+</sup>, 4-MePyH<sup>+</sup>, and 1-MePy<sup>+</sup>), where dibromine fragments were “trapped” by [TeCl<sub>6</sub>]<sup>3-</sup> via specific symmetrical Br⋯Cl interactions (halogen bonding). The energies of the latter were estimated through DFT calculations and QTAIM analyses (up to 5.7 kcal·mol<sup>-1</sup>).

In [20], we reported the preparation and investigation of the complexes of Cat<sub>2</sub>{[TeCl<sub>6</sub>](Cl<sub>2</sub>)} (Cat = 1-methylpyridinium and tetramethylammonium), where the dichlorine units were “trapped” by chlorotellurate(IV) anions via a system of symmetrical noncovalent Cl⋯Cl interactions which were studied theoretically through DFT calculations and QTAIM analyses (their estimated strengths varied from 2.2 to 2.7 kcal·mol<sup>-1</sup>). These complexes revealed a record thermal stability (>100 °C) for inclusion compounds with Cl<sub>2</sub>, indications that such compounds could be used as a solid Cl<sub>2</sub> source.

In [21], the novel hybrid chlorobismuthate(III) with “captured” dibromine, (1-MePy)<sub>3</sub>{[Bi<sub>2</sub>Cl<sub>9</sub>](Br<sub>2</sub>)}, was isolated and characterized through X-ray diffractometry, thermogravimetric analyses, and Raman spectroscopy. The features of symmetrical noncovalent Br⋯Cl

interactions in the solid state were investigated through theoretical methods (DFT calculations and QTAIM analyses; their estimated strengths varied from 2.9 to 3.6 kcal·mol<sup>-1</sup>).

In [22], the supramolecular decabromide anion {Br<sub>10</sub>}<sup>2-</sup> was found in the structure of the polybromide-bromoantimonate complex (4-MePyC<sub>3</sub>)<sub>2</sub>{[SbBr<sub>6</sub>]<sub>2</sub>{Br<sub>10</sub>}} (4-MePyC<sub>3</sub> = 1,1'-(propane-1,3-diyl)-bis(4-methylpyridin)-1-ium dication). The {Br<sub>10</sub>}<sup>2-</sup> was a Z-shaped dimer of the pentabromide Br<sub>5</sub><sup>5-</sup> units connected via the terminal Br atoms. Each {Br<sub>5</sub>} formed halogen bonding with one [SbBr<sub>6</sub>]<sup>-</sup> anion. These symmetrical noncovalent interactions were studied theoretically through DFT calculations and QTAIM analyses, and their estimated strengths varied from 2.2 to 3.6 kcal·mol<sup>-1</sup>.

In [23], the highlighted one-dimensional iodine-rich iodobismuthates(III), Cat<sub>3</sub>{[Bi<sub>2</sub>I<sub>9</sub>](I<sub>2</sub>)<sub>3</sub>} (Cat = 1,4-MePy and 1-EtBMA), featured the highest amount of “trapped” diiodine units in the polyhalogen–halometalates of the p-block elements. Both complexes had narrow optical band gaps (1.55 and 1.63 eV, respectively) and a moderate thermal stability. The features of the symmetrical noncovalent I··I interactions in the solid state responsible for the supramolecular organization were investigated through theoretical methods (DFT calculations and QTAIM analyses; the estimated strengths varied from 4.2 to 8.1 kcal·mol<sup>-1</sup>).

In [24], we observed that in the supramolecular complex (1-EtPy)<sub>3</sub>{[Bi<sub>2</sub>I<sub>9</sub>](I<sub>2</sub>)<sub>0.75</sub>}, diiodine fragments were “captured” by iodobismuthate anions via the system of the symmetrical noncovalent I··I interactions (halogen bonding). The energies of the latter were estimated through theoretical methods (DFT calculations and QTAIM analyses, 3.2–6.0 kcal·mol<sup>-1</sup>); the optical features and Raman spectrum were discussed.

In [25], we found that the reactions of [SbBr<sub>6</sub>]<sup>3-</sup> containing HBr solutions with the bromide salts of 1,1'-(1,2-ethanediyl)bis(pyridine) (PyC<sub>2</sub><sup>2+</sup>) or 1,1'-(1,2-ethanediyl)bis(3,5-dimethylpyridine) (3,5-MePyC<sub>2</sub><sup>2+</sup>) initially resulted in the formation of the deep-orange complexes of Cat[SbBr<sub>5</sub>] (“A” and “B”), featuring unusual Sb··Br interactions in the solid state. In the mother liquor, “A” transformed into discrete binuclear (C<sub>2</sub>Py)<sub>2</sub>[Sb<sub>2</sub>Br<sub>10</sub>], which demonstrated polymorphisms (triclinic and monoclinic), while “B” transformed into polymeric (3,5-MePy){[SbBr<sub>4</sub>]}. DFT calculations and QTAIM analyses revealed that the system of the noncovalent Sb··Br contacts may be responsible for the appearance of the observed optical properties (unusual deep-orange coloring).

In [26], the supramolecular derivatives of chlorostannate(IV) and chloroplumbate(IV) with {Cl<sub>2</sub>} units, Cat<sub>2</sub>{[MCl<sub>6</sub>](Cl<sub>2</sub>)<sub>x</sub>} (M = Sn and Pb; Cat = 1-methylpyridinium (1-MePy) and tetramethylammonium (TMA)), were prepared and characterized through X-ray diffractometry and Raman spectroscopy. In particular, the TMA-containing complexes demonstrated a remarkable thermal stability, releasing Cl<sub>2</sub> only at elevated temperatures. The features of the noncovalent Cl··Cl interactions in the solid state responsible for the supramolecular symmetrical organization were investigated through theoretical methods (DFT calculations and QTAIM analyses; the estimated strengths varied from 1.9 to 2.7 kcal·mol<sup>-1</sup>).

In [27], dihalogen-halorhenates(IV) (Me<sub>4</sub>N)<sub>2</sub>{[ReX<sub>6</sub>](X<sub>2</sub>)} (X = Cl, Br) were prepared and structurally characterized, featuring the first examples of rhenium/dihalogen supramolecular complexes. These compounds revealed pseudo-3D structures; both compounds demonstrated a high thermal stability, releasing Cl<sub>2</sub> or Br<sub>2</sub> only at elevated temperatures (over 90 and 150 °C, respectively). The energies of the halogen··halogen noncovalent interactions were estimated to be as high as 2.5 and 5.1 kcal·mol<sup>-1</sup>, respectively. Hirshfeld surface analyses were performed for both structures, allowing the estimation of the contributions of different noncovalent interactions to crystal packing.

In [28], we reported that the reactions between the SnBr<sub>2</sub>, HBr, Br<sub>2</sub>, and bromides of different organic cations yielded the formation of supramolecular bromostannate(IV) complexes, where polybromide fragments were “trapped” in the solid state by Br··Br noncovalent interactions. The five compounds of this family—Cat<sub>2</sub>{[SnBr<sub>6</sub>](Br<sub>2</sub>)} (cat = Me<sub>4</sub>N<sup>+</sup>, 1-MePy<sup>+</sup>, Me<sub>3</sub>NH<sup>+</sup>, and 2-MePyH<sup>+</sup>) and (4-MePyH)<sub>3</sub>{[SnBr<sub>6</sub>](Br<sub>5</sub>)}—were prepared and characterized through X-ray diffractometry and Raman spectroscopy. Using DFT calcula-

tions and QTAIM analyses, we proved the existence of Br $\cdots$ Br noncovalent interactions in the obtained X-ray structures.

In [29], the first heteroleptic pentaiodobenzoate (PIBA) metal complexes, [Cu(PIBA)<sub>2</sub>L<sub>2</sub>] (L = Py; 3,5-MePy; and 2,6-MePy) and [Cu(PIBA)<sub>2</sub>(4-MePy)(DMF)<sub>1.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>] $\cdot$ 2DMF, were prepared and characterized. In most cases, there were multiple strong halogen bonds and type I halogen $\cdots$ halogen interactions in their structures; the energies of these contacts were estimated through theoretical methods, and the thermal stability was studied through thermogravimetric analyses.

In [30], we reported that the reactions of CuCl<sub>2</sub> $\cdot$ 2H<sub>2</sub>O or Cu(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O with 3,5-diiodosalicylic acid (DISA) in the presence of trialkylamines resulted in structurally diverse products. Depending on the ratio of the reagents and the Cu source, they isolated either the mononuclear complexes of (R<sub>3</sub>NH)<sub>2</sub>[Cu(DISA)<sub>2</sub>] (R = Et, *n*-Pr, and *n*-Bu), where fully deprotonated DISA formed 5-membered chelate rings, or the binuclear paddlewheel-type (R<sub>3</sub>NH)<sub>2</sub>[Cu<sub>2</sub>(DISA)<sub>4</sub>Cl<sub>2</sub>] (R = *n*-Pr). The general feature of these complexes was their ability to form halogen bonding in the solid state; the energies of halogen bonds were estimated based on the QTAIM analysis results (DFT calculations were used to obtain the electron densities, and then topological analyses were used to estimate the energies via empirical correlations between the interaction energy and the potential or kinetic energy density of the electrons at the bonds' critical points (3, -1)).

In [31], we reported that the reactions between Zn(II) dihalides and 2-halogen-substituted pyridines 2-XPY resulted in a series of the heteroleptic molecular complexes of [(2-XPY)<sub>2</sub>ZnY<sub>2</sub>] (Y = Cl, and X = Cl, Br, and I; Y = Br, and X = Cl, Br, and I; Y = I, and X = Cl, Br, and I). In all cases, halogen bonding played an important role in the formation of crystal packing. Moreover, some of these compounds demonstrated luminescence in the solid state; for the best emitting complexes, the quantum yield exceeded 21%.

In [32], we discussed the outcomes of the reactions of Cu(II) salts with 2-iodobenzoic acid (2-IBA) in acetonitrile in the presence of different substituted pyridines (Py; 4-MePy; 4-EtPy; 3,4-MePy; 2,6-MePy; 2,4,6-MePy; and 2,6-BrPy) (L) depending on the nature of the Cu-containing precursors and L, resulting in [Cu<sub>2</sub>(2-IBA)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>], [Cu<sub>2</sub>(2-IBA)<sub>4</sub>L<sub>2</sub>] or [Cu<sub>2</sub>L<sub>4</sub>(2-IBA)<sub>2</sub>Cl<sub>2</sub>] complexes. In total, seven complexes were prepared and characterized through X-ray diffractometry. The role of halogen bonding in the structures was examined through theoretical methods.

In [33], we reported that the reaction of SeO<sub>2</sub>, tetramethylammonium (TMA) chloride, aqueous HCl, and Cl<sub>2</sub> yielded oxochloroselenate with incorporated Cl<sub>2</sub> units, TMA<sub>3</sub>{[Se<sub>2</sub>O<sub>2</sub>Cl<sub>7</sub>](Cl<sub>2</sub>)}. The main feature of this compound was the strong (up to 3.5 kcal $\cdot$ mol<sup>-1</sup> according to DFT calculations) Cl $\cdots$ Cl bonding, which was also detected through Raman spectroscopy.

In [34], we showed that the bromoantimonate(III) species, which can be generated in solution through the reaction of Sb<sub>2</sub>O<sub>3</sub> and HBr, could be oxidized by Br<sub>2</sub> into mixed-valence complexes or bromoantimonates(V). The outcome of these reactions governed, by the nature of cations, which salt was used for the isolation of the solid complexes. Using the bromides of three 1,*n*-bis(pyridinium)alkane cations (PyC<sub>*n*</sub>, where *n* = 2, 3, and 4), we isolated three complexes: (PyC<sub>2</sub>)<sub>2</sub>{[SbBr<sub>6</sub>](Br<sub>3</sub>)}, (PyC<sub>3</sub>)<sub>2</sub>[Sb<sub>2</sub>Br<sub>9</sub>][SbBr<sub>6</sub>], and (PyC<sub>4</sub>)<sub>2</sub>{[SbBr<sub>6</sub>](Br<sub>3</sub>)}, respectively. Their structures were determined through X-ray diffractometry, and the energies of the noncovalent interactions between the tribromide units and [SbBr<sub>6</sub>]<sup>-</sup> were estimated using DFT calculations.

In [35], we highlighted that both the Cambridge Crystallographic Data Centre (CCDC) and the Protein Data Bank (PDB) provided unique opportunities for finding information about the structures of the chemical and biochemical compounds in the solid state. IsoStar—a knowledge-based library of intermolecular interactions—is a very powerful tool for the automatic analysis of a large amount of data from these databases. The IsoStar program suite could help chemists understand the probability of occurrence (frequencies) and the spatial characteristics (directionalities) of the noncovalent contacts (including hydrogen, halogen, and chalcogen bonds as well as interactions involving  $\pi$ -systems) between the pairs of chemical functional groups; this web application may also be useful for crystal engi-

neers, crystallographers, medicinal chemists, and researchers in the fields of computational chemistry and molecular modeling.

Finally, in [36], we highlighted and briefly discussed the most popular modern programs for quantum chemical and molecular dynamics (classical, *ab initio*, and QM/MM) calculations which are relevant for the investigation of the nature and various properties (including noncovalent interactions) of different molecules and periodic chemical systems, such as nanotubes, surfaces and films, polymers, and crystalline solids.

### 3. Works from Other Researchers

Also, several recent publications devoted to various noncovalent interactions in supramolecular complexes with polyhalides and halometalates from other authors could be mentioned. In [37], the authors discussed the controlled synthesis of the polyions of the heavy main-group elements in ionic liquids (ranging from the polyhalides of carbonyl complexes and selenidostannates to homo and heteropolycations). In [38], the reaction of the complex  $[\text{Au}(\text{phen})\text{Br}_2](\text{PF}_6)$  (phen = 1,10-phenanthroline) with molecular dibromine afforded  $\{[\text{Au}(\text{phen})\text{Br}_2](\text{Br}_3)\}_\infty$ . Single-crystal diffraction analyses showed that the  $[\text{Au}(\text{phen})\text{Br}_2]^+$  complex cations were bridged with asymmetric tribromide anions to form infinite zig-zag chains featuring the motif  $\cdots\text{Au}-\text{Br}\cdots\text{Br}-\text{Br}\cdots\text{Au}-\text{Br}\cdots\text{Br}-\text{Br}\cdots$ . The complex cation played an unprecedented halogen bonding donor role, engaging type-I and type-II noncovalent interactions of comparable strengths with symmetry-related  $[\text{Br}_3]^-$  anions. A network of hydrogen bonds connected the parallel chains in an infinite 2D network, contributing to the layered supramolecular architecture. In [39], antimicrobial V-shaped pentaiodide  $[\text{Cu}(12\text{-crown-}4)_2]\text{I}_5$  was investigated. The chain-like pentaiodide structure was V-shaped and consisted of iodine molecules with very short covalent bonds connected to triiodides through halogen bonding. The single crystal structure was arranged across the lattice fringes in the form of ribbons or honeycombs. The susceptibility of microorganisms towards the polyiodides depended on the polyiodide bonding patterns with halogen, covalent, and noncovalent bonding. Also, the phenomenon of bidimensional polyiodide netting stabilization with Cu(II) macrocyclic complexes was discussed in [40]. In [41], the authors demonstrated that a three-component hybrid  $\{[(\text{BiI}_6)\text{I}_{13}]\cdot 2\text{I}_3\cdot (\text{H-BPA})_4\}_n$  could be utilized in dye degradation in seawater. The highly interesting feature of this compound lay in its unique 1D Z-shape  $[(\text{BiI}_6)\text{I}_{13}]_n^{6-}$  infinite chain constructed from the  $\text{I}\cdots\text{I}$  contacts between the mononuclear  $(\text{BiI}_6)^{3-}$  anions and  $\text{I}_{13}^{3-}$  polyiodide anions. Simultaneously, the hydrogen bonds between the  $[(\text{BiI}_6)\text{I}_{13}]_n^{6-}$  polyanions and the  $\text{H-BPA}^{2+}$  cations contributed to the formation a quasi-3D network. In [42], an approach for assembling polyiodides and iodobismuthates using the template effect of a cyclic diammonium cation and the formation of a low-gap hybrid iodobismuthate with a high thermal stability was reported.

Thus, supramolecular associates involving polyhalides and halometalates is a large family of inorganic compounds featuring promising properties for material science, and further progress in this field is highly desirable.

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