

Review

Polyhalide-bonded metal complexes: Structural diversity in an eclectic class of compounds



Sergey A. Adonin^{a,b,*}, Maxim N. Sokolov^{a,b}, Vladimir P. Fedin^{a,b}

^a Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Lavrentieva St. 3, Novosibirsk, Russia

^b Novosibirsk State University, 630090, Pirogova St. 2, Novosibirsk, Russia

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ABSTRACT

This review is focused on a special class of metal complexes where polyhalide units are either coordinated to metal (“true polyhalide complexes”) or form specific associates with metal center via halogen-halogen contacts. Diversity of structural types, as well as main characterization features, is discussed for all d-elements and p-block metals and metalloids, providing a concentrated source of information on this eclectic class of compounds.

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* Corresponding author at: Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Lavrentieva St. 3, Novosibirsk, Russia.

E-mail address: adonin@niic.nsc.ru (S.A. Adonin).

1. Introduction

The history of polyhalides began almost 200 years ago, when existence of the simplest representative of this class – triiodide – was discovered [1]. To date, these compounds constitute a great and important area which, although belonging to the classics of inorganic chemistry commonly mentioned in textbooks, still provide enough “free space” for further research and novel discoveries. Among those made in recent years, there are, for example, structural and theoretical studies of polychlorides [2,3], preparation of three-dimensional polybromide networks [4,5] and new polybromides of lower nuclearity which “fill the gap” in Br_x family (i.e. $[\text{Br}_6]^{2-}$) [6] etc. [7–11]. Advances in this field were recently summarized in an excellent review presented by Riedel et al. [12] which may be regarded as a most comprehensive to date.

However, despite overall progress in this area, it can be seen that one important part of this chemistry remains overlooked. There exists a class of metal complexes where polyhalides are either coordinated to metal center or, and this is even more common situation, “trapped” in crystal structure via specific non-covalent interactions with metal complex units. Even though first examples of such compounds were reported many decades ago (for instance, bromoantimonates (III) and (V) with $\{\text{Br}_2\}$ or $\{\text{Br}_3\}$ fragments incorporated in solid state were structurally characterized by Lawton and Jacobson et al. in 1960s and 1970s [13–15]), but data on these complexes remain very sporadic and, to our best knowledge, no attempts of systematization were undertaken yet.

The main goal of this review is to create a concentrated source of information about **metal complexes** containing polyhalide units in solid state. The main focus is on structural diversity; however, relevant synthetic methodologies and characterization aspects are briefly discussed as well. The main sources were the Cambridge Structural Database (CSD) and, to a lesser extent, the Inorganic Crystal Structure Database (ICSD). The entries are classified by: 1) metal, 2) halogen the polyhalide fragments are built of; both homo- and heteroligand complexes are considered. In the cases where atoms of different metals are present in the same crystal structure, those are mentioned in a section corresponding to the metal that participates in the formation of halogen...halogen supramolecular networks via halide ligands. Our criterion for recognition of such interactions is the sum of the van der Waals radii (1.75 for Cl, 1.83 for Br and 1.98 for I [16]). Examples where two or more metals contribute in such interactions comparably are mentioned in a section discussing the metal with lower atomic weight. In all figures, Cl atoms are shown in light green, Br olive green and I in purple; halogen...halogen interactions are dashed. Organic ligands are generally shown in wire-and-stick representation or simply omitted.

We use the term “polyhalide-bound metal complex” (PBMC) throughout for all compounds where polyhalide units are either coordinated to metal (“true polyhalide complexes”) or form associates with metal center of the abovementioned nature

(“supramolecular PBMCs”). Although we understand that this term is artificial, we make this assumption in order to discard the cases where “free” polyhalide anions acting as counter anions, revealing absence of $\text{M-X}\cdots\{\text{X}_n\}$ contacts. Those, although numerous, are generally excluded from our consideration or mentioned briefly. The more general term “halogen-rich complexes”, which appeared in several relevant publications, was not used for this reason.

2. Structural overview

2.1. Transition metals

2.1.1. Elements of Groups 3–5

There are no PBMCs containing polybromide or any mixed polyhalide and Sc, Y or La in the same crystal structure. Several homometallic heteroligand complexes of Y [17] and La [18,19] contain triiodide anions; however, in all cases $\text{I}\cdots\text{I}$ distances do not allow to expect any reasonable interaction of the polyiodide with metal. The same applies for lanthanides and actinides.

For Ti(IV), there is a single example of a polybromide-based supramolecular network; it is based on a brominated fullerene (C_{60}Br_8), TiBr_4 and Br_2 [20]. Both tetrahedral TiBr_4 and dibromine units are disordered over two positions (50:50 for $\{\text{Br}_2\}$); each of the latter plays the role of a linker between the Br atoms of fullerene and $\{\text{TiBr}_4\}$ ($\text{Br}\cdots\text{Br} = 3.29$ and 3.06 Å, respectively). Therefore, there is a pseudo-one-dimensional structure (Fig. 1). PBMCs of Zr and Hf are unknown.

In a set of crystal structures reported by Troyanov et al. [21–24], different polychlorinated fullerenes are accompanied by V oxochloride anions and Cl_2 . Unfortunately, in all cases the $\{\text{VOCl}_n\}$ and $\{\text{Cl}_2\}$ units have only partial occupancy; therefore, estimation of possible $\text{Cl}\cdots\text{Cl}$ interactions is problematic.

2.1.2. Cr, Mo, W

Bromine. For tungsten, existence of polybromide PBMCs was described 50 years ago by von Schnering et al. [25]. Interestingly, the only reported example is based on low-valent cluster $\{\text{W}_6\text{Br}_8\}^{5+}$; those are linked via $\{\text{Br}_4\}^{2-}$ units (Fig. 2, 3.56 Å).

Iodine. Polyiodide PBMCs are known for all three elements. For Cr, those are relatively rare (there are only three examples, all heteroligand). In pentamethylcyclopentadienyl derivatives of Cr (III) [26,27], the $\{\text{I}_2\}$ units bind metal centers via contacts with iodide ligands into 1D *catena*-polymeric structure (Fig. 3) ($\text{I}\cdots\text{I} = 3.34$ – 3.54 Å [27]). Similar connectivity mode was found in iodide-phthalocyanine complex [28]: each $\{\text{Cr}(\text{Fc})\text{I}_2\}$ (Fc = phthalocyanine) unit interacts with two $\{\text{I}_2\}$ fragments via opposite iodide ligands in a symmetric manner ($\text{I}\cdots\text{I} = 3.50$ Å).

For Mo, coordination of one $\{\text{I}_3\}$ ligand was observed in carbonyl [29] and isocyanide [30] complexes. The Mo–I bond lengths are such as expected for the iodide complexes (2.88 and 2.76, respectively). The I–I distances in the triiodide unit are not equal; in both cases, the bond between central I and one coordinated to Mo is

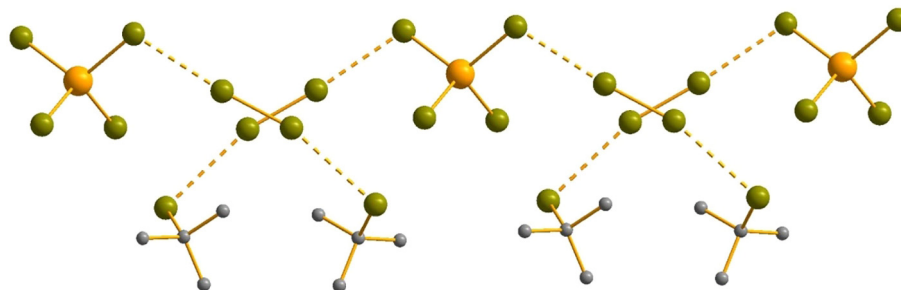


Fig. 1. Pseudo-1D structure in a fullerene- TiBr_4 - Br_2 hybrid [20]. Here and below transition metal atoms are shown in orange. Most of fullerene units are omitted for clarity.

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