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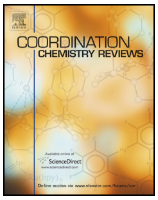

Review

Polynuclear halide complexes of Bi(III): From structural diversity to the new properties

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ABSTRACT

This review is focused on the chemistry of polynuclear halide complexes of Bi(III) (polyhalidebismuthates, or PHBs). It consists of three parts. The first one is dedicated to the known structural types of PHBs (discrete Bi(III) complexes, coordination polymers and heterometallic compounds), their features and occurrence. The second chapter briefly describes what can be called chemistry of PHBs (synthetic approaches by which they can be obtained, and some reactions they can be involved in). The final, third part is focused on the physical properties of PHBs reported recently, which would be of a special interest for the chemical community.

1. Introduction

Over the last 20 years, the chemistry of polynuclear halide anionic complexes of Bi(III) (polyhalidebismuthates or PHBs), has been attracting growing attention [1,2]. This interest is inspired by two main reasons. The first one is related to numerous promising physical (in particular optical) properties demonstrated by the members of this class of compounds, for example, semiconductivity [3,4], photochromism [5–7] and luminescence in organic–inorganic hybride salts [8,9], thermochromism [10,11], etc. These features account for the increasing involvement of PHBs in the advanced materials science studies.

The second point is related to more fundamental aspects of inorganic chemistry. It is known that PHBs, like many other post-transition metal halides, are very labile due to the favorable kinetics and low energy of M—X bonding. In solution, these complexes undergo fast dissociation/association processes [2]; it is usually assumed that they exist as $[BiX_6]^{3-}$ and form the polynuclear motifs only in the solid state, so that the "building block concept", workable for many other complicated inorganic systems, seems to be inapplicable in this case. Therefore, there arises principal question: is it possible to manage the structure or, at least, nuclearity and composition of complexes varying the reaction conditions, stoichiometry and the nature of cation used in the synthesis? Are there any rules and laws which govern the molecular design of such compounds – or this area chemistry is completely stochastic and the synthesis of a complex with interesting structure and useful properties will always remain the matter of serendipity? This fundamental problem inspires further research in this field, both experimental and theoretical [2].

Although the significant progress in the chemistry of PHBs – in terms of both new structural types and emergent properties – has been achieved in the last decades, an overview of more recent publications in this area is lacking. In 1994, Fisher and Norman published a comprehensive review focused on the structural types found for the group 15 halide complexes in general, including those of Bi(III) [12]. Since then many new structures of PHBs were reported, and the necessity of an updated review is becoming evident. In 2009, review by Wu et al., dedicated to iodoplumbates and iodobismutates, was published [1]. Finally, in the same year Mercier et al. presented a very interesting highlight paper where the possibility of prediction of PHB molecular structure in certain cases was discussed [2]. To our best knowledge, neither chloride nor bromide complexes of Bi have been comprehensively reviewed at all.

Thus, the main goal of this review is the filling of the existing gap in this field, providing the chemical community with a concentrated data source about the chemistry and structural types of PHBs, as well as their relevant physical properties worth of consideration from the point of view of advanced materials development. We set only a few restrictions on the scope of the review. First, it is focused exclusively on the complexes where Bi has 3+ oxidation state. For information about the low-valence, i.a. Bi subhalides, we recommend the recent reviews by Ruck et al. [13,14]. Second, we do not mention mixed-ligand complexes except in few special cases. This restriction concerns heterometallic compounds, because there is a large family of Bi(III) arene derivatives sharing the halide ligands with an atom of other main group element, e.g. Al – so-called Menshutkin complexes. There exists an excellent review on this topic [15].

The present review consists of three main parts. The first one is dedicated to the known structural types of PHBs (discrete Bi(III) complexes, coordination polymers and heterometallic compounds), their features and occurrence. The second chapter briefly describes what can be called chemistry of PHBs (synthetic approaches by which they can be obtained, and some reactions they can be involved in). The final, third part is focused on the physical properties of PHBs reported recently, which would be of a special interest for the chemical community.

2. Structural diversity of polyhalidebismuthates

As mentioned above, the last comprehensive review dedicated to the structures of polynuclear anions occurring in the group 15 element (III) halides was published in 1994 [12]. For this reason, we have decided to highlight the results (including the discovery of brand new structural types) only within the last 20 years. The earlier reports are cited only in a few cases, when no new examples of PHB anions have been added since 1994. Besides, we do not specifically mention the polymeric moieties encountered in the structures of low-valent Bi halides which often contain $\{Bi_x\}^{y+}$ cations together with the anionic Bi(III) part [16–18]. The classification used in this part of the review is based on the nuclearity of PHBs (for discrete anions) or on the type of structural motif (for polymers).

2.1. Discrete anions

2.1.1. Binuclear complexes

This is one of the most widespread subclasses of the Bi(III) halide complexes. It often happens when PHBs are isolated from acidic (HCl, HBr, HI) media (see Section 3). There are four different structural types known, depending on the number of halide ligands and the motif of dimerization: $[Bi_2X_8]^{2-}$, $[Bi_2X_9]^{3-}$, $[Bi_2X_{10}]^{4-}$ and $[Bi_2X_{11}]^{5-}$. The $[Bi_2X_8]^{2-}$ anion consists of two Bi atoms surrounded by 5 X (square pyramidal coordination environment), connected via a common edge (Fig. 1). In all cases, the length of Bi—X(term) bond may vary (2.51–2.70, 2.68–2.71 and 2.82–2.98 Å for X = Cl, Br and I), but it is always shorter than that of Bi-μ_2-X (2.87, 3.06 and 3.10 Å, respectively). This is the rarest type among the dimers (one example for Cl [19] and Br [20], two for I [21,22]).

All the other binuclear PHBs are built of octahedral units. In $[Bi_2X_9]^{3-}$, two $\{BiX_6\}$ fragments share a common face with three binding X ligands (Fig. 1). This is the most common type of the dimeric anions, especially for iodides (see Fig. 3 for statistics). The ranges of bond lengths are: 2.51–2.66, 2.68–2.77, 2.88–3.05 Å