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Bromobismuthates: Cation-induced structural diversity and Hirshfeld surface analysis of cation–anion contacts

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ABSTRACT

Reactions of $[BiBr_6]^{3-}$ and bromide salts of various substituted pyridinium cations in excess of HBr result in a series of bromobismuthate anionic complexes of various geometry and nuclearity: $[\{BiBr_4\}_n]^{n-}$, $[Bi_2Br_9]^{3-}$ and $[Bi_2Br_{10}]^{4-}$. Hirshfeld surface analysis for 19 crystal structure was performed; impact of various X-Br contacts on the crystal structures is discussed.

1. Introduction

Although halide complexes of late transition and p-block metals are known for over 100 years, the interest on this class of coordination compounds is persistent. Within the last decade, it is mostly focused on their numerous applications in materials science, particularly, for development of hybrid solar cells [1–7], ferroelectric and ferroelastic materials [8–10], photocatalysts [11–14] etc. From simplistic point of view the halometalates may be regarded as trivial objects for preparative chemist. Indeed, their preparation protocols are straightforward [15], and usually result in crystalline solids suitable for XRD. On the other hand, the price for the simplicity is extreme difficulty (or even impossibility) of making any reliable predictions about the structure of a particular complex forming under certain conditions. Depending on the nature of metal, p-block elements form discrete polynuclear halide complexes of different nuclearity (up to 8 for Bi(III) [16–18] or 18 for Pb(II) [19]), as well as one-, two- or three-dimensional polymers [15,20–24]. Usually, such reactions cannot be reliably controlled stoichiometrically; the key factors governing the structure and composition of resulting halometalates are the nature and geometry of counter cations and, in some cases, the solvent.[15] In particular, Benetollo et al. have shown [25] that reaction between Bi_2O_3 and N-heterocyclic bases in HCl solutions may result both in $[BiCl_6]^{3-}$ and binuclear $[Bi_2Cl_{10}]^{4-}$ in the case of 8-hydroxyquinolinium and quinolinium or isoquinolinium, respectively [25]. Similar observations were made by Junk et al. for the heteroligand Bi(III) halide complexes [26–29]. It must be noted, however, that although there are a great number of polyclear halobismuthates reported to date, only in a few cases the role of cation was systematically analysed. Recently, Mercier et al. presented a very interesting highlights paper [30] on the structural diversity of iodometalates, stating: "Unfortunately, metal halide complexes are involved in fast dissociation and association processes due to the labile halide ligands in solution, which means that the concept of pre-defined subunits cannot be applied to these systems" [30]. In this article, authors tried to find some cation–anion correlations in the compounds reported earlier. However, any general rules allowing the directed synthesis of halometalates are still lacking. We proposed that one of strategies that could make the search of such correlations possible, is to prepare a series of certain halide complexes, e.g. bromobismuthates (III), using a kit of closely related cations under identical conditions. For this purpose, we have chosen substituted pyridines, since this class of compounds

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