

CRYSTAL STRUCTURES OF BINUCLEAR Bi(III) CHLORIDE AND BROMIDE COMPLEXES WITH SOME CATIONS – ALKYLATED PYRIDINE DERIVATIVES

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By a reaction of $[\text{BiX}_6]^{3-}$ with salts of various N-alkylated pyridine derivatives in 2M HX (X = Cl, Br), (N-BzPy)₄[Bi₂X₁₀] complexes (X = Cl (**1**), Br (**2**), (4-MePyH)₄[Bi₂Cl₁₀] (**3**)) are obtained and structurally characterized.

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One of the key problems in the chemistry of polynuclear halide complexes of bismuth(III) (polyhalide bismuthates, PHBs) remains the establishment of the relationship between synthesis conditions, the composition and structure of the anionic part of these compounds [1-3]. This is due to an important feature of PHBs, which consists in their high lability because of a relatively low binding energy of Bi(III)-X (X = Cl, Br, I) and a rapid kinetics of ligand substitution in the Bi(III) coordination sphere. During crystallization, complex $[\text{BiX}_6]^{3-}$ anions existing in the solution can transform into PHBs with diverse geometries and nuclearities (from 1 to 8) [4-15]. It has previously been noted [1-3] that the nature of a solvent and a cation used to extract PHB are the most significant factors affecting the product structure. Taking into account that single crystal and powder XRD are the main methods for identifying PHB complexes (the use of other physical methods is very limited because of low information content), it is an essential task to obtain new data on their crystal structure.

In this work, three new complexes are structurally characterized: (N-BzPy)₄[Bi₂X₁₀] (X = Cl (**1**), Br (**2**), and (4-MePyH)₄[Bi₂Cl₁₀] (**3**).

EXPERIMENTAL

Synthesis was carried out in the air. Precursors (HBr, HCl, BiCl₃, BiOBr, pyridine, 4-methylpyridine (4-picoline), and benzyl bromide) were purchased and used as received. N-benzylpyridinium bromide (N-BzPyBr) was obtained by a reaction of benzyl bromide and pyridine (1:1:1) in a benzene:acetone (1:1) mixture at room temperature [16] and identified by the ¹H NMR spectrum.

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