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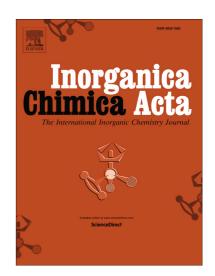
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ACCEPTED MANUSCRIPT

Halobismuthates with bis(pyridinium)alkane cations: correlations in crystal structures and optical properties

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Abstract: A series of four chloro- and bromobismuthates with bis(pyridinium)alkane cations $(Py(CH_2)_nPy)^{2+}$ (C_n) and $(4-PyH)(CH_2)_n(4-PyH)^{2+}$ (H₂C_n) were synthesized and characterized. Analysis of their crystal structures, as well as previously reported data, results in establishment of correlations between the type of halobismuthate anion and the nature of cation. Luminescent properties of obtained compounds are reported and discussed.

Keywords: halometalate / halide complexes / bismuth / luminescence / crystal structure

Introduction

Halide complexes of late transition and post-transition metals (in particular, bismuth) evoke a significant interest due to a number of promising physical properties, ^{1,2} including ferroelectricity and ferroelasticity, ³⁻⁹ thermochromism, ^{10,11} luminescence, ¹²⁻¹⁵ photochromism¹⁶⁻¹⁹ and photocatalytic activity. ²⁰⁻²⁴ From the point of view of coordination chemistry, an attractive feature of this class of compounds is their remarkable structural diversity. ¹⁻² Due to the oligomerization via bridging halide ligands, halobismuthates can reach nuclearity of up to 8 Bi (for discrete anions), ²⁴⁻³³ as well as form various, predominantly 1D, polymers ^{25,34-36} and heterometallic complexes. ³⁷⁻³⁹ However, synthesis of such complexes cannot be always controlled in a straightforward, i.a. stoichiometric, way: even when well defined amounts of all reagents are used, the final X/metal ratio and the structure of forming halobismuthate will vary and cannot be precisely predicted. It was noted ^{2,40} that one of the

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