

Tris(ethyldimethylphenylammonium) nonahalogenodibismuthates(III)

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Dedicated to Prof. Dr. Bernt Krebs on the occasion of his 60th birthday

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Bismuth, Tris(ethyldimethylphenylammonium) nonachlorodibismuthate, Tris(ethyldimethylphenylammonium) nonabromodibismuthate, Tris(ethyldimethylphenylammonium) nonaiododibismuthate, Enthalpy of Transition

The halogenobismuthates $Q_3Bi_2X_9$ ($Q = EtMe_2PhN$; $X = Cl, Br, I$) were prepared by reaction of BiX_3 with $EtMe_2PhNX$ in ethanol. Single crystal structure determinations yielded: $[EtMe_2PhN]_3[Bi_2Cl_9]$, S. G. $P2_12_12_1$, Nr. 19, $a = 952.5(3)$, $b = 1184.1(4)$, $c = 3726.4(9)$ pm, $Z = 2$; $[EtMe_2PhN]_3[Bi_2Br_9]$ S. G. $P2_1/c$, No. 14, $a = 1839.4(4)$, $b = 1329.5(3)$, $c = 1817.3(6)$ pm, $\beta = 92.68(3)^\circ$, $Z = 4$, $[EtMe_2PhN]_3[Bi_2I_9]$, S. G. $P2_1/c$, No. 14, $a = 1915.3(2)$, $b = 1379.0(3)$, $c = 1890.9(5)$ pm, $\beta = 92.48(1)^\circ$, $Z = 4$. The thermal behaviour was investigated with the aid of DSC measurements and temperature dependent X-ray powder diffraction. All compounds undergo a transition into a high temperature modification which could be obtained in case of $[EtMe_2PhN]_3[Bi_2Br_{9-x}I_x]$ in form of single crystals: S. G. $P2_1/c$, Nr. 14, $a = 1002.7(5)$, $b = 1278.7(8)$, $c = 3584.3(5)$ pm, $\beta = 90.12(2)^\circ$, $Z = 4$. Surprisingly in this compound the iodine atoms are not statistically distributed over all possible bromine positions, but occupy only one position. Lattice parameters of the other high temperature modifications and enthalpies of transition of the compounds are given. In addition a second iodobismuthate was isolated: $[EtMe_2PhN]_4[Bi_6I_{22}]$, S. G. $P\bar{1}$, Nr. 2, with lattice parameters of $a = 1343.4(3)$, $b = 1554.3(3)$, $c = 2262.5(6)$ pm, $\alpha = 100.89(3)^\circ$, $\beta = 96.63(1)^\circ$, $\gamma = 98.94(2)^\circ$ and $Z = 2$.

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