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Synthesis and structure of bismuth complexes $[Bu_4P]^+_2[Bi_2I_8\cdot 2Me_2S=O]^{2^-}$, $[(Me_2S=O)_8Bi]^{3^+}[Bi_2I_9]^{3^-}$

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Abstract

By the reaction of tetrabutylphosphonium iodide with bismuth triiodide (2:1, 1:1, 1:2 mol) we synthesized the complex $[Bu_4P]^+_2[Bi_2I_8(Me_2S=O)_2]^{2-}$ (I) in dimethylsulfoxide. The second reaction product is the complex $[(Me_2S=O)_8Bi]^{3+}[Bi_2I_9]^{3-}$ (II) (tetrabutylphosphonium iodide, bismuth triiodide: 1:2 mol.) In cationic complexes I P atoms have distorted tetrahedral coordination (CPC angles are $104.1(1)^\circ-112.6(1)^\circ$). In dinuclear centrosymmetric anions complex I hexacoordinative bismuth atoms linked by two bridging iodine atoms (Bi-Ibr 3.260(1) and 3.315(1) Å), the terminal iodine atoms atom form stronger bonds bismuth (Bi-Iterm 2.926(1)-3.031(1) Å), the bond length Bi-O 2.436(1) Å. In the cation complex II eight molecules of dimethyl sulfoxide on the bismuth atom is coordinated via oxygen atoms (angles OBiO $69.9(2)^\circ-98.9(3)^\circ$, the length of the Bi-O bonds constitute 2.381(4)-2.476(4) Å). In the anion +[Bi2I9]3- of complex II Bi atoms have octahedral coordination; BiI3 groups linked to each other through a three bridging atoms of iodine (Bi-Ibr 3.156(1)-3.343(1) Å, Bi-Iterm 2.910(1)-3.021(1) Å).

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