

Synthesis and structure of bismuth complexes $[\text{Bu}_4\text{P}]^+{}_2[\text{Bi}_2\text{I}_8\cdot 2\text{Me}_2\text{S}=\text{O}]^{2-}$, $[(\text{Me}_2\text{S}=\text{O})_8\text{Bi}]^{3+}[\text{Bi}_2\text{I}_9]^{3-}$

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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 $[\text{Bu}_4\text{P}]^+{}_2[\text{Bi}_2\text{I}_8(\text{Me}_2\text{S}=\text{O})_2]^{2-}$ (**I**) in dimethylsulfoxide. The second reaction product is the complex $[(\text{Me}_2\text{S}=\text{O})_8\text{Bi}]^{3+}[\text{Bi}_2\text{I}_9]^{3-}$ (**II**) (tetrabutylphosphonium iodide, bismuth triiodide: 1:2 mol.) In cationic complexes **I** P atoms have distorted tetrahedral coordination (CPC angles are 104.1(1)°-112.6(1)°). In dinuclear centrosymmetric anions complex **I** hexacoordinative bismuth atoms linked by two bridging iodine atoms (Bi-I_{br} 3.260(1) and 3.315(1) Å), the terminal iodine atoms atom form stronger bonds bismuth (Bi-I_{term} 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)°-98.9(3)°, the length of the Bi-O bonds constitute 2.381(4)-2.476(4) Å). In the anion $[\text{Bi}_2\text{I}_9]^{3-}$ of complex **II** Bi atoms have octahedral coordination; BiI₃ groups linked to each other through a three bridging atoms of iodine (Bi-I_{br} 3.156(1)-3.343(1) Å, Bi-I_{term} 2.910(1)- 3.021(1) Å).