A One-Dimensional Polymeric Form of the Polycation Te₈²⁺ in the Structure of Te₈[Bi₄Cl₁₄]

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Z. Naturforsch. 56 b, 453–457 (2001); received March 9, 2001

catena-Octatellurium(2+), Main Group Element Clusters, Chalcogen Polycations

The reaction of Te, TeCl₄ and BiCl₃ in a sealed evacuated glass ampoule in a temperature gradient 160 to 90 °C yields Te₈[Bi₄Cl₁₄] as black platelike crystals with a golden lustre which are deposited in the temperature zone 150 to 130 °C. The best yield is obtained with a Te/TeCl₄/BiCl₃ molar ratio of 15/3/4. The crystal structure determination (orthorhombic, P2₁2₁2₁, \(a = 879.9(3)\), \(b = 1642.3(4)\), \(c = 2267.3(8)\) pm, \(Z = 4\)) shows that Te₈[Bi₄Cl₁₄] consists of a novel one-dimensional (Te₈²⁺)ₙ polycation and a two-dimensional chlorobismutate anion Bi₄Cl₁₄²⁻. The structure of the cation consists of boat shaped Te₆ rings which are connected in the 1,4-positions by Te₂ groups to a one-dimensional polymeric strand. The structure is substantially different from the previously reported Te₈²⁺ polycations in Te₈[WCl₆]²⁺ and Te₈[MCl₆] (M = Zr, Hf, Re) where discrete bicyclic clusters with only weak interionic interactions are present. The Bi₄Cl₁₄²⁻ ion can be described as built up of BiCl₃ molecules which are connected by Cl⁻ ions to a two-dimensional network [(BiCl₃)₄(Cl⁻)₂]ₙ.