

Octachalcogen Cations Te_8^{2+} , Se_8^{2+} , and Mixed $(\text{Te}_{8-x}\text{Se}_x)_8^{2+}$ Stabilized by Chlorometallates of Bi, Zr, and Hf: Synthesis and Crystal Structures of $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ and $\text{E}_8[\text{MCl}_6]$ (E = Se, Te; M = Zr, Hf)

A. Baumann, J. Beck*, and T. Hilbert

Institut für Anorganische Chemie der Universität Bonn,
Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

* Reprint requests to Professor J. Beck. Fax: (49) 228 73 56 60. E-mail: j.beck@uni-bonn.de

Z. Naturforsch. **54 b**, 1253–1259 (1999); received July 15, 1999

Octaselenium(2+), Octatellurium(2+), Chalcogen Polycations, Halogenobismutates(III),
Crystal Structure

The title compounds were obtained by the reaction of elemental chalcogens E (E = Se, Te) with the respective tetrachlorides ECl_4 and the Lewis acidic metal halides ZrCl_4 , HfCl_4 , and BiCl_3 . An alternative way, particularly for the preparation of mixed Se/Te-species, is the enlargement of smaller cationic rings in $\text{E}_4[\text{MCl}_6]$ (M = Zr, Hf) by adding the respective complementary chalcogen. All reactions were carried out in sealed, evacuated glass ampoules at temperatures between 120 °C and 220 °C, and yielded black crystals of $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, $(\text{Te}_{5.0}\text{Se}_{3.0})[\text{HfCl}_6]$, $(\text{Te}_{5.3}\text{Se}_{2.7})[\text{ZrCl}_6]$, $(\text{Te}_{6.5}\text{Se}_{1.5})[\text{ZrCl}_6]$ and $\text{Te}_8[\text{HfCl}_6]$, which have been identified by crystal structure analyses. All five compounds contain eight-membered chalcogen rings in an endo-exo-conformation which are isostructural to the known octachalcogen dicationic E_8^{2+} (E = S, Se, Te). While in $(\text{Te}_{5.0}\text{Se}_{3.0})[\text{HfCl}_6]$, $(\text{Te}_{5.3}\text{Se}_{2.7})[\text{ZrCl}_6]$, $(\text{Te}_{6.5}\text{Se}_{1.5})[\text{ZrCl}_6]$ and $\text{Te}_8[\text{HfCl}_6]$ the molecular polycations are surrounded by discrete, octahedral $[\text{MCl}_6]^{2-}$ counterions, $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ contains a two-dimensional polymeric anion $([\text{Bi}_4\text{Cl}_{14}]^{2-})_n$ built of a variety of vertex and edge-sharing BiCl_x -polyhedra ($x = 6, 7$). The Bi-Cl bond lengths are spread over a wide range between 250 and 350 pm.