The Bicyclic Polyselenium Cation Se₁₀²⁺ in the Structure of Se₁₀[Bi₄Cl₁₄] Johannes Beck^{*[a]} and Steffen J. Eck^[a]

Keywords: Selenium; Clusters; Polycations; Chloridobismutates; Bismuth

Abstract. In the ternary system Se/Bi/Cl a new polycation containing phase besides the already known Se₄[Bi₄Cl₁₄], Se₈[Bi₄Cl₁₄], and Se₁₀[Bi₅Cl₁₇] was discovered. Red, transparent, plate shaped crystals of Se₁₀[Bi₄Cl₁₄] were formed by reaction of Se/SeCl₄/BiCl₃ in 15:1:8 molar ratio in evacuated glass ampoules applying a temperature gradient from 90 to 80 °C. The crystal structure consists of bicyclic Se₁₀²⁺ cations and of layered chloridobismutate anions with the cations located between the anionic planes. The atoms of the cation form a six

Introduction

Bismuth trichloride is a strong Lewis acid. It reacts with chloride ion donors with formation of chloridobismutates. $[BiCl_4]^-$ is formally the first product, but since Bi^{3+} ions prefer higher coordination numbers between six and eight, it is generally observed that variable amounts of BiCl₃ associate with tetrachloridobismutate with formation of chloridobismutates of higher nuclearity. The weak donor strength of these chloridobismutates is obvious in their ability to stabilise "naked" polycationic clusters of the elements of the chalcogens [1]. In the ternary system Se/Bi/Cl three compounds containing polycationic clusters were already discovered: Se₄[Bi₄Cl₁₄], containing the square planar Se₄²⁺ ion [2], Se₈[Bi₄Cl₁₇] with the bicyclic Se₁₀²⁺ cluster ion [3]. We discovered a fourth phase in this system and report on the synthesis and structure of Se₁₀[Bi₄Cl₁₄].

Experimental Section

Bismuth and selenium were used as commercial products. Bismuth was purified by melting under argon protecting gas and decanting the melt from the black residue. SeCl₄ and BiCl₃ were prepared by reaction of the elements with Cl₂. The chlorine gas was purified by condensing to the liquid state at -75 °C in a U-shaped vessel. The Cl₂ gas stream for the chlorination reaction was established by bubbling argon gas through the cold, liquid chlorine. SeCl₄ and BiCl₃ were both sublimated in the Cl₂/Ar stream. All further manipulations like charging and opening of the reaction ampoules were performed in an argon filled glove box.

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membered ring with a Se₄ chain bridging over the 1,4 positions of the Se₆ ring. The anions are made up of BiCl₇ polyhedra connected by common edges to layers $\frac{2}{\alpha}$ [Bi₄Cl₁₄^{2–}]. Se₄[Bi₄Cl₁₄], Se₈[Bi₄Cl₁₄], Se₁₀[Bi₄Cl₁₄], and Te₈[Bi₄Cl₁₄] all contain an anion of identical formula and two-dimensional connectivity, but these polymeric chloridobismutates are not isostructural. The structural differences are discussed on basis of the different topologies of the nets made up by the bismuth atoms.

Glass ampoules of 12 cm length and 1.4 cm diameter were filled with selenium, SeCl₄, and BiCl₃ in the molar ratio 15:1:8 in a total amount of 300 mg. The ampoules were evacuated, sealed and placed in a horizontal tube furnace. After keeping at 80 °C for 4 hours, a temperature gradient 90 to 80 °C was applied along the ampoule for 36 hours. Besides the main products Se₄[Bi₄Cl₁₄] and Se₁₀[Bi₅Cl₁₇], red transparent plate shaped crystals were deposited along the walls of the reaction ampoule.

Crystals were isolated by immersing in cold perfluorinated oil. Diffraction data were recorded with a Bruker Nonius CCD diffractometer at low temperature generated with a cold nitrogen stream. The space group was derived from the reciprocal lattice extinctions as $P2_12_12_1$ and the non-centrosymmetry was confirmed during the refinements. The structure was solved by direct methods [4] and refined with anisotropic displacement parameters for all atoms [5]. A Flack *x* parameter of -0.042(4) showed the absence of inversion twinning [6]. An empirical absorption correction was applied to the data [7]. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421619 [8]. For the graphical representations the program DIAMOND was used [9].

Results and Discussion

 $Se_{10}[Bi_4Cl_{14}]$ is formed in the reaction of selenium, $SeCl_4$, and $BiCl_3$ besides the related phases $Se_4[Bi_4Cl_{14}]$, $Se_{10}[Bi_5Cl_{17}]$, and $Se_8[Bi_4Cl_{14}]$. Small differences in the reaction conditions favour the formation of one of the different compounds. For the synthesis of $Se_{10}[Bi_4Cl_{14}]$, the reaction conditions were found to be optimal at a Se/SeCl_4/Bi ratio of 15:1:8 and a temperature of 90 °C. The crystals are deposited from the gas phase and can be distinguished visually by their thin platy shape from the neighbouring phases.

The crystal structure consists of discrete Se_{10}^{2+} cations and of polymeric chloridobismutate anions $\frac{2}{\infty}[\text{Bi}_4\text{Cl}_{14}^{2-}]$. The cation

(Figure 1) is built of a six-membered ring in boat conformation bearing a Se₄ chain bridging over the 1,4 positions of the Se₆ ring. The Se–Se bonds show the typical separation in short bonds around 2.29 Å at the dicoordinate selenium atoms and long bonds around 2.43 Å at the tricoordinate selenium atoms. The Se–Se–Se angles are almost equalised in the narrow range between 99.73(4) and 102.68(4) °. The structure of the cation is thus analogous to the ions found in the structures of Se₁₀[SbF₆]₂ [10], Se₁₀[AlCl₄]₂ [10], Se₁₀[SO₃F]₂ [11], and Se₁₀[Bi₅Cl₁₇] [3]. The crystal structure is acentric. Since the structure of the Se₁₀²⁺ ion allows only for a twofold axis as the only symmetry operation, which is approximately fulfilled in the presented structure, the ion is enantiomorphic.



Figure 1. The Se_{10}^{2+} cationic cluster in the structure of $Se_{10}[Bi_4Cl_{14}]$. The thermal ellipsoids represent a probability level of 50 %. Bond lengths /Å: Se(1)–Se(2) 2.421(2), Se(1)–Se(6) 2.423(2), Se(1)–Se(7) 2.447(2), Se(2)–Se(3) 2.261(2), Se(3)–Se(4) 2.457(2), Se(4)–Se(5) 2.392(2), Se(4)–Se(10) 2.437(2), Se(5)–Se(6) 2.269(2), Se(7)–Se(8) 2.285(2), Se(8)– Se(9) 2.361(2), Se(9)–Se(10) 2.277(2).

The Bi–Cl bonds in the chloridobismutate anion are spread over a wide range beginning from 2.490(2) Å (Bi(1)–Cl(1)). A first large gap in the bond lengths is present after Bi(3)–Cl(2)^{IV} = 3.379(2) Å (Figure 2). If all Bi–Cl distances up to this limit are taken into account, all four independent bismuth atoms obtain coordination polyhedra with coordination number seven. These polyhedra are connected via common edges to layers spread out in the crystallographic *ab* plane. The Se₁₀²⁺ cations are embedded between the layers of the polymeric anions (Figure 3).

Four compounds are now known, which all contain the $[Bi_4Cl_{14}]^{2-}$ anion, $Se_4[Bi_4Cl_{14}]$ $Se_8[Bi_4Cl_{14}]$, $Se_{10}[Bi_4Cl_{14}]$, and Te₈[Bi₄Cl₁₄] [12]. It is remarkable that the anions in all four structures are not isostructural, despite the identical formula and the shared structural feature of forming two-dimensional arrangements. The differences between the anions, but also their relationship, can be understood if, for simplification, only the arrangement of the bismuth atoms is considered. The respective nets of the bismuth atoms are depicted in Figure 4. The nets present in the structures of the selenium containing compounds $Se_8[Bi_4Cl_{14}]$ (a), $Se_{10}[Bi_4Cl_{14}]$ (b), and $Se_4[Bi_4Cl_{14}]$ (c) are closely related. They show an arrangement of the bismuth atoms analogous to the motif of the oxide ions in the rutile structure. This is in line with the tetragonal sym-



Figure 2. The four independent bismuth atoms in the structure of $Se_{10}[Bi_4Cl_{14}]$ and their coordination by surrounding chlorine atoms with Bi–Cl distances up to 3.4 Å. The thermal ellipsoids represent a probability level of 50 %. Symmetry operations: $I = -\frac{1}{2}+x$, $-\frac{1}{2}-y$, -z; II = -1+x, *y*, *z*; $III = -\frac{1}{2}+x$, $\frac{1}{2}-y$, -z; IV = 1+x, *y*, *z*; $V = \frac{1}{2}+x$, $\frac{1}{2}-y$, -z. The inset on the bottom shows the distribution of the Bi–Cl bond lengths in form of a histogram. The arrow indicates the upper limit of Bi–Cl bonds at 3.4 Å taken into account.



Figure 3. The unit cell of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ in a view along the crystallographic *c* axis. Shown is one layer of the $\frac{2}{\infty}$ [Bi}4Cli4²⁻] anion and the directly neighboured Se_{10}^{2+} cations. The thermal ellipsoids represent a probability level of 50 %.

metry of Se₄[Bi₄Cl₁₄] as the representative with the highest symmetry. Orthorhombic Se₁₀[Bi₄Cl₁₄] and triclinic Se₈[Bi₄Cl₁₄] are distorted variants. The three nets share the same connection type, expressed by the Schläfli symbol $3^{3}4^{2}$ [13]. The arrangement of triangles and quadrangles is different in the net belonging to the structure of Te₈[Bi₄Cl₁₄] (d), but the connection type $3^{3}4^{2}$ is also valid for this arrangement.

SHORT COMMUNICATION



Figure 4. The nets of bismuth atoms in a layer of the $[Bi_4Cl_{14}]^{2-}$ anions in the structures of $Se_8[Bi_4Cl_{14}]$ (a), $Se_{10}[Bi_4Cl_{14}]$ (b), $Se_4[Bi_4Cl_{14}]$ (c), $Te_8[Bi_4Cl_{14}]$ (d), all in a view perpendicular to the plane of the nets. All Bi–Bi distances up to 5.3 Å have been taken into account. The unit cell edges are given with thin lines. The nets are not planar since the height differences of the bismuth atoms perpendicular to the viewing direction amount between 3 and 3.5 Å.

Acknowledgement

The authors thank *Dr. Jörg Daniels*, Inorganic Chemistry Institute of University of Bonn, for encouraging help with the isolation of suitable crystals and for the recording of the diffraction data set.

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- [6] Formula Bi₄Cl₁₄Se₁₀; orthorhombic; space group P2₁2₁2₁; lattice constants a = 11.8457(4), b = 11.9888(4), c = 21.9953(7) Å; unit cell volume 3123.6(1) Å³; temperature 123(2) K; number of formula units Z = 4, calculated density 4.512 g·cm⁻³; Mo-K_α radiation (λ = 0.71073 Å); crystal dimensions 0.12 × 0.065 × 0.006 mm; range of data collection 5.8 ≤ 2θ ≤ 59.2°; range of indices h ± 16, k ± 16, l ± 30; 68190 measured reflections; 8322 independent reflections; R_{int} for averaging data 0.065, absorption coefficient μ = 35.32 mm⁻¹; 254 refined parameters, ratio reflections/parameters = 14.6; reliability factors of refinement R(|F|) for all data = 0.040, R(|F|) for 7443 (F₀)=4σ(F₀) = 0.029, wR(F²) = 0.054; Flack x parameter -0.042(4); max. /min. residual density +1.61 / -1.80 e·Å⁻³.
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Received: April 10, 2010 Published Online: June 17, 2010