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The Bicyclic Polyselenium Cation Se_{10}^{2+} in the Structure of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$

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Abstract. In the ternary system Se / Bi / Cl a new polycation containing phase besides the already known $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$, $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, and $\text{Se}_{10}[\text{Bi}_5\text{Cl}_{17}]$ was discovered. Red, transparent, plate shaped crystals of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ were formed by reaction of Se / SeCl_4 / BiCl_3 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 Se_{10}^{2+} cations and of layered chloridobismutate anions with the cations located between the anionic planes. The atoms of the cation form a six membered ring with a Se_4 chain bridging over the 1,4 positions of the Se_6 ring. The anions are made up of BiCl_7 polyhedra connected via common edges to layers $\infty [\text{Bi}_4\text{Cl}_{14}^{2-}]$. $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$, $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$, and $\text{Te}_8[\text{Bi}_4\text{Cl}_{14}]$ 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 Bi atoms.

Introduction

Bismuth trichloride is a strong Lewis acid. It reacts with chloride ion donors under formation of chloridobismutates. $[\text{BiCl}_4]^-$ 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 BiCl_3 associate with tetrachloridobismutate under formation of chloridobismutates of higher nuclearity. The weak donor strength of these chloridobismutates is obvious in their ability to stabilize “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: $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$, containing the square planar Se_4^{2+} ion [2], $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, containing the bicyclic Se_8^{2+} ion [2], and $\text{Se}_{10}[\text{Bi}_5\text{Cl}_{17}]$ with the bicyclic Se_{10}^{2+} cluster ion [3]. We discovered a fourth phase in this system and report on the synthesis and structure of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$.

Experimental

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. SeCl_4 and BiCl_3 were prepared by reaction of the elements with Cl_2 . The chlorine gas was purified by condensing to the liquid state at $-75\text{ }^\circ\text{C}$ in a U-shaped vessel. The Cl_2 gas stream for the chlorination reaction was established by bubbling argon gas through the cold, liquid chlorine. SeCl_4 and BiCl_3 were both sublimated in the Cl_2/Ar stream. All further manipulations like charging and opening of the reaction ampoules were performed in an argon filled glove box.

Glass ampoules of 12 cm length and 1.4 cm diameter were filled with Se, SeCl_4 , and BiCl_3 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 $80\text{ }^\circ\text{C}$ for 4 hours, a temperature gradient 90 to $80\text{ }^\circ\text{C}$ was applied along the ampoule for 36 hours. Besides the main products $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ and $\text{Se}_{10}[\text{Bi}_5\text{Cl}_{17}]$, 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

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3 absorption correction was applied to the data [7]. Further crystallographic data for the crystal
4 structure determination have been deposited with the *Fachinformationszentrum Karlsruhe*
5 under the deposit number CSD-421619 [8]. For the graphical representations the program
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7 DIAMOND was used [9].
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10 11 12 13 14 **Results and Discussion**

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17 $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ is formed in the reaction of Se, SeCl_4 , and BiCl_3 besides the related phases
18 $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$, $\text{Se}_{10}[\text{Bi}_5\text{Cl}_{17}]$ and $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$. Small differences in the reaction conditions
19 favour the formation of one of the different compounds. For the synthesis of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$, the
20 reaction conditions were found to be optimal at a Se / SeCl_4 / Bi ratio of 15 / 1 / 8 and a
21 temperature of 90 °C. The crystals are deposited from the gas phase and can be distinguished
22 visually by their thin platy shape from the neighbouring phases.
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29 The crystal structure consists of discrete Se_{10}^{2+} cations and of polymeric chloridobismutate
30 anions $^{2-}_\infty[\text{Bi}_4\text{Cl}_{14}]$. The cation (Fig. 1) is built of a six-membered ring in boat conformation
31 bearing a Se_4 chain bridging over the 1,4 positions of the Se_6 ring. The Se–Se bonds show the
32 typical separation in short bonds around 2.29 Å at the two-coordinated Se atoms and long
33 bonds around 2.43 Å at the three-coordinated Se atoms. The Se–Se–Se angles are almost
34 equalised in the narrow range between 99.73(4) and 102.68(4) °. The structure of the cation is
35 thus analogous to the ions found in the structures of $\text{Se}_{10}[\text{SbF}_6]_2$ [10], $\text{Se}_{10}[\text{AlCl}_4]_2$ [10],
36 $\text{Se}_{10}[\text{SO}_3\text{F}]_2$ [11], and $\text{Se}_{10}[\text{Bi}_5\text{Cl}_{17}]$ [3]. The crystal structure is acentric. Since the structure of
37 the Se_{10}^{2+} ion allows only for a twofold axis as the only symmetry operation, which is
38 approximately fulfilled in the presented structure, the ion is enantiomeric.
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49 The Bi–Cl bonds in the chloridobismutate anion are spread over a wide range beginning from
50 2.490(2) Å (Bi(1)–Cl(1)). A first large gap in the bond lengths is present after Bi(3)–Cl(2)^{IV} =
51 3.379(2) Å (Fig. 2). If all Bi–Cl distances up to this limit are taken into account, all four
52 independent Bi atoms obtain coordination polyhedra with coordination number seven. These
53 polyhedra are connected via common edges to layers spread out in the crystallographic *a-b*
54 plane. The Se_{10}^{2+} cations are embedded between the layers of the polymeric anions (Fig. 3).
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3 Four compounds are now known, which all contain the $[\text{Bi}_4\text{Cl}_{14}]^{2-}$ anion, $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$
4 $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$, $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$, and $\text{Te}_8[\text{Bi}_4\text{Cl}_{14}]$ [12]. It is remarkable that the anions in all four
5 structures are not isostructural, despite the identical formula and the shared structural feature
6 of forming two-dimensional arrangements. The differences between the anions, but also their
7 relationship, can be understood if, for simplification, only the arrangement of the Bi atoms is
8 considered. The respective nets of the Bi atoms are depicted in Fig. 4. The nets present in the
9 structures of the selenium containing compounds $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ (a), $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ (b), and
10 $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ (c) are closely related. They show an arrangement of the Bi atoms analogous to
11 the motif of the oxide ions in the rutile structure. This is in line with the tetragonal symmetry
12 of $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ as the representative with the highest symmetry. Orthorhombic $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$
13 and triclinic $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ are distorted variants. The three nets share the same connection type,
14 expressed by the Schläfli symbol 3^34^2 [13]. The arrangement of triangles and quadrangles is
15 different in the net belonging to the structure of $\text{Te}_8[\text{Bi}_4\text{Cl}_{14}]$ (d), but the connection type 3^34^2
16 is also valid for this arrangement.
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39 data set.
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[6] Formula $\text{Bi}_4\text{Cl}_{14}\text{Se}_{10}$; orthorhombic; space group $P2_12_12_1$; 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 ($\lambda = 0.71073$ Å); crystal dimensions $0.12 \times 0.065 \times 0.006$ mm³; range of data collection $5.8 \leq 2\theta \leq 59.2$ °; range of indices $h \pm 16$, $k \pm 16$, $l \pm 30$; 68190 measured reflections; 8322 independent reflections; R_{int} for averaging data 0.065, absorption coefficient $\mu = 35.32$ 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 $(F_o) > 4\sigma(F_o) = 0.029$, $wR(F^2) = 0.054$; Flack x parameter $-0.042(4)$; max. / min. residual density $+1.61 / -1.80$ e Å⁻³.

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Legends for Figures

Fig. 1 The Se_{10}^{2+} cationic cluster in the structure of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$. 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).

Fig. 2 The four independent Bi atoms in the structure of $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ and their coordination by surrounding Cl 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.

Fig. 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 $[\text{Bi}_4\text{Cl}_{14}]^{2-}$ anion and the directly neighboured Se_{10}^{2+} cations. The thermal ellipsoids represent a probability level of 50 %.

Fig. 4 The nets of Bi atoms in a layer of the $[\text{Bi}_4\text{Cl}_{14}]^{2-}$ anions in the structures of $\text{Se}_8[\text{Bi}_4\text{Cl}_{14}]$ (a), $\text{Se}_{10}[\text{Bi}_4\text{Cl}_{14}]$ (b), $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ (c), $\text{Te}_8[\text{Bi}_4\text{Cl}_{14}]$ (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 Bi atoms perpendicular to the viewing direction amount between 3 and 3.5 Å.

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