Poster

Surprising Formation of a $[Bi_6O_4(OH)_4]^{6+}$ Cation in the Dodecahydro-*closo*-Dodecaborate Hydrate $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3 \cdot 10\ H_2O$

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Previous studies showed that cations with polarizing properties can lead to B−H bond activation of hydroborates, as evidenced by a shift of the B−H stretching vibration band in the Raman spectra[1]. In extreme cases, this bond activation results in a substitution reaction, as the reaction between Bi^{3+} cations and $[B_{12}H_{12}]^{2-}$ anions to the neutral molecule $BiB_{12}H_{11}$ has proven[2]. In addition to this substitution, other reactions can also take place, as it occurs with the formation of the salt $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3 \cdot 10\ H_2O$ under basic conditions. The formation of $[M_6O_4(OH)_4]^{6n-12}$ cations is known for $M = U^{4+}$[3], Ce^{4+}[4] and Bi^{3+}[5]. In bismuth salts, they can be formed as products of the thermal decomposition of simple hydrated salts[6]. In particular, the nitrate of the $[Bi_6O_4(OH)_4]^{6+}$ has been investigated with regard to its suitability for the use as anode materials in lithium-ion batteries [6]. Also the *closo*- dodeca(carba)borate salts of the light alkali metals show promising electrochemical properties[7]. So the salts resulting from the combination of both complex ions are of great interest for electrochemical investigations.

The new compound was obtained by the reaction of $(H_3O)_2[B_{12}H_{12}]$ with an excess of $Bi_2O_2[CO_3]$ in aqueous solution at 40 °C. The free acid of the dodecahydro-*closo*-dodecaborate was produced before by an acidic cation exchanger from $Cs_2[B_{12}H_{12}]$. From the obtained sample, a prism-shaped single crystal was separated and measured at low temperature.

$[Bi_6O_4(OH)_4][B_{12}H_{12}]_3 \cdot 10\ H_2O$ crystallizes monoclinically in the space group $P2_1/c$ with the unit-cell parameters $a = 1823.04(9)$ pm, $b = 1794.86(9)$ pm, $c = 1358.31(7)$ pm and $\beta = 91.023(3)°$ at 100 K for four formula unit per unit cell. In its structure, the complex cation $[Bi_6O_4(OH)_4]^{6+}$ is present, which consists of a distorted heterocubane made from four oxide with shorter (d(Bi−O) = 207 – 230 pm) and four hydroxide anions with longer distances (d(Bi−OH) = 226 – 260 pm) surrounding a $(Bi^{3+})_6$ octahedron (Figure 1). The coordination spheres of the Bi^{3+} lone-pair cations are completed by water molecules and $Bi^{3+}–H^{\delta-}$ contacts to the negatively polarized hydrogen atoms of the icosahedral $[B_{12}H_{12}]^{2-}$ anions (Figure 2).

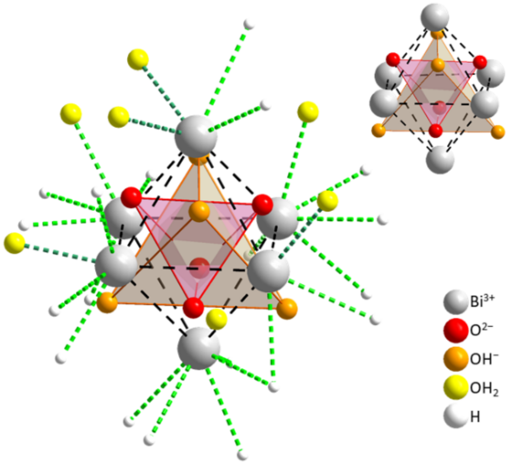

Figure 1. The complex cation $[Bi_6O_4(OH)_4]^{6+}$ with (*left*) and without (*right*) the complete Bi^{3+} coodination sphere in the crystal structure of $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3 \cdot 10\ H_2O$.

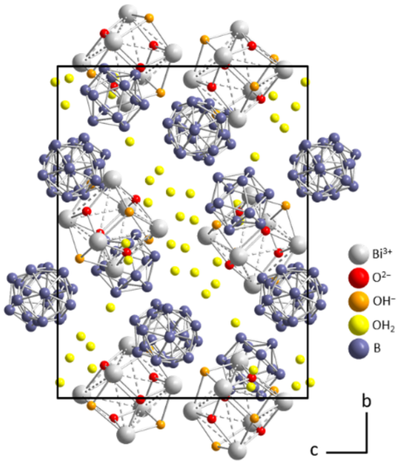

Figure 2. Extended unit-cell content of $[Bi_6O_4(OH)_4][B_{12}H_{12}]_3 \cdot 10\ H_2O$.

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