Verbindungen mit Pentelid-Hanteln M_2: $A^{I}_{11}M_6$ und $A^{II}_{11}M_{10}$ (A = Rb, Cs, Ba; M = Sb, Bi)

Compounds with Pentelide Dumbbells M_2: $A^{I}_{11}M_6$ and $A^{II}_{11}M_{10}$ (A = Rb, Cs, Ba; M = Sb, Bi)

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The new ternary alkali pentelides $A_{11}M_6$ (A = Rb, Cs; M = Sb/Bi) all contain non electron-precise isolated dumbbells statistically composed of Sb/Bi. Their phase ranges as determined from single crystal data were found to be on the Sb-rich side of the overall composition $A_{11}Sb_{6-x}Bi_x$ in the case of the Rb compound (*i. e.* $Rb_{11}Sb_{5.4}Bi_{0.6}$: orthorhombic *Immm*, a = 766.7(3), b = 1052.2(3), c = 1732.7(6) pm, Z = 4, $R1$ = 0.0554), and on the Bi-rich side of the overall composition $A_{11}Sb_{6-x}Bi_x$ in the case of A = Cs (*i.e.* $Cs_{11}Sb_{1.6}Bi_{4.4}$). In the series of known alkaline earth compounds $A_{11}M_{10}$, containing pentelide dumbbells among isolated Zintl anions, a redetermination of the structure of $Ba_{11}Sb_{10}$ (orthorhombic, *Immm*, a = 1265.3(2), b = 1316.1(3), c =1947.2(5) pm, Z = 4, $R1$ = 0.0724) shows, that it represents a distorted variant of the tetragonal $Ho_{11}Ge_{10}$ structure type. This distortion is not only of crystallographic importance, as it results in a major change in the nature of the anions and their bonding, which is supported by DFT band-structure calculations. Likewise, the Zintl phase $BaSb_2$ (monoclinic, $P2_1/m$, a = 1167.9(9), b = 438.1(5), c = 1257.1(9) pm, β = 100.53(2)°, Z = 6, $R1$ = 0.0648) crystallizes with a superstructure of the $CaSb_2$-type previously reported.

Key words: Bismuthides, Antimonides, Zintl Phases