

Dimere und polymere Pnictidostannat(IV)-Anionen – Darstellung und Kristallstrukturen von $\text{Na}_2\text{K}_3[\text{SnP}_3]$, $\text{Na}_2\text{Cs}_3[\text{SnP}_3]$ und $\text{Na}_2\text{K}_3[\text{SnBi}_3]$

Dimeric and Polymeric Pnictidostannate(IV) Anions – Preparation and Crystal Structures of $\text{Na}_2\text{K}_3[\text{SnP}_3]$, $\text{Na}_2\text{Cs}_3[\text{SnP}_3]$ and $\text{Na}_2\text{K}_3[\text{SnBi}_3]$

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Disodium Tripotassium Triphosphidostannate(IV), Disodium Tricesium Triphosphidostannate(IV), Disodium Tripotassium Tribismutidostannate(IV), Dimeric Tetrahedral Anions, Zweier Single Chains

The metallic lustrous compounds $\text{Na}_2\text{K}_3[\text{SnP}_3]$, $\text{Na}_2\text{Cs}_3[\text{SnP}_3]$, and $\text{Na}_2\text{K}_3[\text{SnBi}_3]$ were prepared from melts of mixtures of the elements. The isotypic compounds $\text{Na}_2\text{K}_3[\text{SnP}_3]$ and $\text{Na}_2\text{Cs}_3[\text{SnP}_3]$ crystallize in the orthorhombic system, space group Cmca (No 64), $Z = 8$, with lattice constants $a = 1996.1(4)/2047.9(4)$ pm, $b = 669.5(1)/686.5(2)$ pm, $c = 1494.5(2)/1617.8(3)$ pm. The structure is characterized by dimeric units $[\text{Sn}_2\text{P}_6]^{10-}$ of edge-sharing $[\text{SnP}_4]$ tetrahedra, which are coordinated by the alkali cations. $\text{Na}_2\text{K}_3[\text{SnBi}_3]$ crystallizes in the orthorhombic system, space group Ibca (No 73), $Z = 8$, with lattice constants $a = 718.2(1)$ pm, $b = 1692.6(2)$ pm, $c = 2159.5(2)$ pm. In the anionic partial structure $[\text{SnBi}_4]$ tetrahedra are connected *via* common corners to infinite ${}^1_\infty[\text{SnBi}_3]^{5-}$ Zweier single chains. The sodium and potassium cations separate the chains from each other. Neglecting the distortions caused by covalent bonding and different radii both structure types can be classified as superstructure defect variants of the Li_3Bi structure. Different orderings in the occupation of the tetrahedral voids lead to the variants in the anionic assemblies.

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