

Solventothermal Synthesis of the Lamellar Selenidostannates(IV) $A_2Sn_4Se_9 \cdot H_2O$ (A = Rb, Cs) and $Cs_2Sn_2Se_6$

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Reaction of A_2CO_3 with Sn and Se in an H_2O/CH_3OH mixture at 115 - 130°C affords the isotypic lamellar selenidostannates $A_2Sn_4Se_9 \cdot H_2O$ **1** (A = Rb) and **2** (A = Cs). The polyanions ${}^2_{\infty} [Sn_4Se_9]^{2-}$ exhibit Sn_4Se_5 molecular building units, in which two adjacent Sn(IV) atoms of an Sn_4Se_4 8-membered ring are bridged by an additional Se atom. These units connect through $(SnSe)_2$ 4-membered rings to afford a 4^4 anionic net with 16-membered cavities. $Cs_2Sn_2Se_6$ (**3**) may be prepared by methanolothermal reaction of Cs_2CO_3 with SnSe and Se at 130°C and contains porous ${}^2_{\infty} [Sn_2Se_6]^{2-}$ sheets in which ${}^1_{\infty} [SnSe_3]^{2-}$ ribbons are linked through Se-Se bonds. The resulting 4^4 net displays 14-membered pores in which the Cs cations reside.

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