[MS24-P07] The New Sulfido Antimonates $(Rb/Cs)_3Sb^{III}S_3$ and $Cs_3Sb^{V}S_4 \cdot H_2O$.

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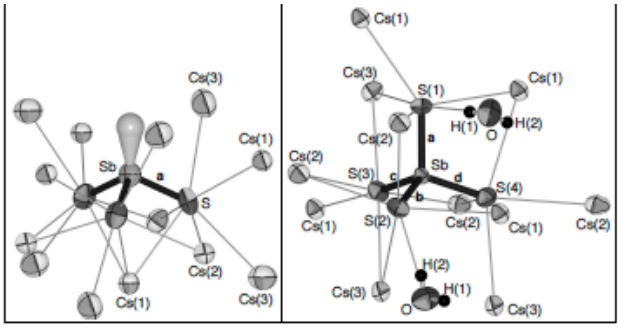
The new sulfido antimonates(III) $(Rb/Cs)_3SbS_3$ were prepared from the alkali sulfides $(Rb/Cs)_2S$ and elemental antimony/Sb_2S_3 at reaction temperatures of 700 o C. The structures of the light yellow crystals were determined using single-crystal X-ray data. Both compounds are isotypic with the respective Na and K salts [1,2] forming the Na_3AsS_3 structure type (cubic, space group $P2_13$, Rb/Cs: a = 982.28(5) / 1025.92(5) pm, Z = 4, R1 = 0.0560/0.0582). The -tetrahedral SbS^{3-}_3 anions (fig. left) with Sb−S bond lengths of 242 pm are arranged in a cubic face centered packing, in which the three crystallographically different A^+ cations occupy the tetrahedral and octahedral voids, overall exhibiting a distorted octahedral sulfur coordination. The chemical bonding and the characteristics of the stereochemically active lone electron pair are investigated by means of FP-LAPW bandstructure calculations.



Needle-shaped crystals of the monohydrate of the antimony(V) salt, $Cs_3SbS_4 \cdot H_2O$, were obtained from a suspension of Sb_2O_3, CsOH and elemental sulfur. $Cs_3SbS_4 \cdot H_2O$ crystallizes in a new structure type (monoclinic, $P2_1/c$, a =987.17(10), b = 994.83(7), c = 1600.46(14) pm, = 126.895(8) o, Z = 4, R1 = 0.0234). As expected, the Sb−S distances (233.1 - 234.7 pm) in the nearly ideally tetrahedral anion SbS3− 4 (fig. right) are considerably shorter than in the antimonates(III) but match the bond lengths in theanhydrous sulfido antimonate(V) Cs_3SbS_4 [3]. Due to their similar f.c.c.-like anion packing and the stereochemically active lone electron pair of Sb in the antimonates(III), the whole series of compounds $A_3SbS_{3/4}$ (A = Na, K, Rb, Cs [1-6]) show a coherent structural relation, which is elucidated using crystallographic group-subgroup relations. For the hydrate series $A_3SbS_{4-n}H_2O$ [7,8], hydrogen bonding, partial molar volumes of the H_2O molecules and the general trends in the number n of water molecules are discussed.

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