

Synthesis of Inorganic-Organic Hybrid Thiometallate Materials with a Special Focus on Thioantimonates and Thiostannates and *in situ* X-Ray Scattering Studies of their Formation

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A rich variety of inorganic-organic hybrid thioantimonates and thiostannates were prepared during the last few years under solvothermal conditions applying organic amine molecules or transition metal complexes as structure directors. In this review synthetic approaches to and structural features of these thiometallates are discussed. For thioantimonates(III) the structures range from well isolated thioanions to three-dimensional networks, whereas the structural chemistry of thiostannates(IV) is strongly dominated by the $[\text{Sn}_2\text{S}_6]^{4-}$ anion, and no three-dimensional thiostannate has been reported so far. In the structures of thioantimonates(III) several primary building units like the $[\text{SbS}_3]$ trigonal pyramid, the $[\text{SbS}_4]$ unit or even the $[\text{SbS}_5]$ moiety are joined by vertex- and/or edge-linkages to form building blocks of higher structural hierarchy like $[\text{Sb}_3\text{S}_4]$ semi-cubes or Sb_xS_x heterocycles. A pronounced difference between thioantimonate and thiostannate chemistry is the tendency of Sb(III) to enhance the coordination geometry *via* so-called secondary bonds. In most cases the environment of Sb(III) is better described as a $3 + n$ polyhedron with $n = 1 - 3$. The thioantimonate(V) structural chemistry is less rich than that of thioantimonates(III), and the $[\text{SbS}_4]^{3-}$ anion shows no tendency for further condensation. By applying suitable multidentate amine molecules, transition metal cations which normally prefer bonding to the N atoms of the amines can be incorporated into the thiometallate frameworks.

Key words: Thiometallates, Inorganic-Organic Hybrid Compounds, Solvothermal Synthesis, *in situ* X-Ray Scattering