Soluble tin(IV) chalcogenide complexes play a major role in solution processing synthesis of macroelectronic tin(IV) chalcogenide based devices, e.g. thin film transistors (TFTs) and the technological interesting photovoltaic material, Cu2ZnSnS4 (CZTS). The synthesis and study of new soluble thiostannate(IV) complexes without electronic impurity atoms and with low decomposition temperature are of key importance for the further development of tin(IV) chalcogenide based devices. We have from the same aqueous ammonium tin(IV) sulfide solution, synthesized and characterized four new crystal structures with different sized thiostannate(IV) complexes (i.e. monomeric [SnS4]4-, dimeric [Sn2S6]4-, pyramids of [Sn3S9]6- and the linear chain [SnS3]2-). Hirshfeld surface analysis for the anionic dimeric [Sn2S6]4- complex in (NH4)4Sn2S6∙3H2O shows that water bound hydrogens interact equally well as the ammonium bound hydrogens with the anionic complex. The elongation of the terminal Sn-S bond depends only on the number of hydrogen atoms which interact with the sulfur atom (regardless of the hydrogen atom is bound in water molecules or in ammonium cations). We present the results for the application of the as-synthesized thiostannate(IV) crystals in solution processing of SnS2 thin films. Crystallographic and electron microscopic methods have established that all films are highly textured with the high mobility ab-plane parallel to the substrate surface. This is ideal for e.g. TFT devices where high mobility is required parallel to the substrate surface.

**Keywords:** thiostannate, hydrogen bonding, solution processing