The Influence of the Amine Concentration onto Product Formation: Crystal Structures, Thermal Stability and Spectroscopic Properties of Two New Manganese Thiostannates Obtained under Solvothermal Conditions

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Two new thiostannates with Mn$^{2+}$ ions were obtained under solvothermal conditions applying different amine concentrations. $[\text{Mn(C}_6\text{H}_{14}\text{N}_2)_2(\text{H}_2\text{O})]_2\text{Sn}_2\text{S}_6$ (1) ($\text{C}_6\text{H}_{14}\text{N}_2 = 1,2$-diaminocyclohexane, 1,2-dach) crystallizes in the monoclinic space group $C2/c$ (with $a = 23.7500(18)$ Å, $b = 15.5655(16)$ Å, $c = 12.1072(9)$ Å, $\beta = 113.532(8)^\circ$, $Z = 8$). The second compound, $[\text{Mn(C}_6\text{H}_{14}\text{N}_2)_2]\cdot\text{Sn}_2\text{S}_6\cdot2\text{C}_6\text{H}_{15}\text{N}_2$ (2), crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.3019(6)$ Å, $b = 11.1798(9)$ Å, $c = 13.2837(11)$ Å, $\alpha = 76.877(10)^\circ$, $\beta = 74.719(9)^\circ$, $\gamma = 82.972(10)^\circ$, $Z = 1$. Both structures feature $[\text{Sn}_2\text{S}_6]^{4-}$ anions acting as bidentate ligands and joining the octahedrally coordinated Mn$^{2+}$ cations, but in 1 a molecular complex is formed, whereas in 2 a one-dimensional coordination polymer is observed. In 1 the Mn$^{2+}$ cation has bonds to four N atoms of two 1,2-dach ligands, to one H$_2$O molecule, and to one S atom of the $[\text{Sn}_2\text{S}_6]^{4-}$ anion. The $[\text{Sn}_2\text{S}_6]^{4-}$ anion is located on a center of inversion joining two symmetry related complexes. In 2 Mn$^{2+}$ is surrounded by four N atoms of two 1,2-dach ligands and by two S atoms of two neighboring $[\text{Sn}_2\text{S}_6]^{4-}$ anions. In contrast to 1 a negatively charged coordination polymer is formed with $[\text{Sn}_2\text{S}_6]^{4-}$ anions acting as linkers and the Mn$^{2+}$ centered complexes being the nodes. The co-crystallized 1,2-dach molecules are protonated, and they are located between the chains. The first compound was obtained from diluted aqueous solutions of 1,2-dach, and 2 crystallized from solutions containing < 25 % H$_2$O. In both compounds several short S···H distances indicate weak hydrogen bonding interactions. Compound 1 is stable up to 121 °C and 2 up to 220 °C. In the Raman spectra of 1 and 2 resonances which are typical for $[\text{Sn}_2\text{S}_6]^{4-}$ units could be observed. The band gaps are found to be 2.6 eV (477 nm) and 3.1 eV (400 nm) for 1 and 2, respectively.

Key words: Thiostannates, Solvothermal Syntheses, Crystal Structure, Thermal and Spectroscopic Properties