

# 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  $\text{Mn}^{2+}$  ions were obtained under solvothermal conditions applying different amine concentrations.  $[\text{Mn}(\text{C}_6\text{H}_{14}\text{N}_2)_2(\text{H}_2\text{O})]_2\text{Sn}_2\text{S}_6$  (**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  $a = 23.7500(18)$ ,  $b = 15.5655(16)$ ,  $c = 12.1072(9)$  Å,  $\beta = 113.532(8)^\circ$ ,  $Z = 8$ ). The second compound,  $[\text{Mn}(\text{C}_6\text{H}_{14}\text{N}_2)_2]\text{Sn}_2\text{S}_6 \cdot 2 \text{C}_6\text{H}_{15}\text{N}_2$  (**2**), crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 7.3019(6)$ ,  $b = 11.1798(9)$ ,  $c = 13.2837(11)$  Å,  $\alpha = 76.877(10)$ ,  $\beta = 74.719(9)$ ,  $\gamma = 82.972(10)^\circ$ ,  $Z = 1$ . Both structures feature  $[\text{Sn}_2\text{S}_6]^{4-}$  anions acting as bidentate ligands and joining the octahedrally coordinated  $\text{Mn}^{2+}$  cations, but in **1** a molecular complex is formed, whereas in **2** a one-dimensional coordination polymer is observed. In **1** the  $\text{Mn}^{2+}$  cation has bonds to four N atoms of two 1,2-dach ligands, to one  $\text{H}_2\text{O}$  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**  $\text{Mn}^{2+}$  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  $\text{Mn}^{2+}$  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 %  $\text{H}_2\text{O}$ . In both compounds several short  $\text{S} \cdots \text{H}$  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