# In-situ EXAFS investigations of the formation of $Ni(C_6N_4H_{18})SnS_3$ under solvothermal conditions

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The thiostannates are an interesting group of compounds among the class of main group thiometalates which in part behave like zeolithes [1]. Some materials with attractive structural features and properties were prepared under solvothermal conditions [1]. With the integration of transition metals into the thiostannate network it can be expected that the physical and chemical properties of such compounds are altered and that such compounds are interesting for different applications. At the moment investigations are in progress to elucidate the materials as catalysts. Recently we published new thiostannates containing Ni and Co as transition metals [2]. $Ni(tren)SnS_3$ (tren = tris-(2-aminoethyl)amine; $C_6N_4H_{18}$) is one of these compounds with $Ni^{2+}$ being incorporated in the thiostannate network.

Solvothermal reactions are complex and the formation of thiostannates is not well understood. Hence, it is impossible to design new and promising porous materials based on thiostannate building blocks. Recently, we investigated the synthesis of $[Co(tren)][Sb_2S_4]$ with combined in-situ energy dispersive X-ray scattering (EDXRD) and extended X-ray absorption fine structure (EXAFS) experiments at different temperatures [3]. The combination of both methods yielded a much better understanding of the mechanism occurring during the chemical reactions under solvothermal conditions.

In the new campaign we started with investigations of the formation of $Ni(tren)SnS_3$ under different reaction conditions. The influence of the starting reactants onto product formation was probed with EDXRD at beamline F3 at different temperatures [4]. The first in-situ EXAFS experiments (under the same reaction conditions) were performed at the Sn K-edge at beamline X1. Elemental Ni, Sn and S or compounds like $[Ni(tren)ClH_2O]Cl$ and $SnCl_2·2H_2O$ were applied in several combinations to understand the formation and crystal growth of $Ni(tren)SnS_3$. The results of such experiments are a prerequisite for the prediction of possible compounds. Furthermore, the influence of the different parameters are collected in a systematic way.

In the ongoing evaluation and analyses of the experimental data the following differences are observed :

Starting with Sn, Ni and S no $SnS_x$ species could be detected in the EXAFS spectra. This result suggests that Sn is dissolved very fast and all Sn species react immediately to form $Ni(tren)SnS_3$ which precipitated during the measurements of the solution. The temperature influences the reaction rate but not the velocity of the dissolution of Sn.

Reactions with Sn, $[Ni(tren)ClH_2O]Cl$ and S showed the same results.

Good and precise Sn-K edge spectra were obtained applying $SnCl_2·2H_2O$, Ni and S or $SnCl_2·2H_2O$, $[Ni(tren)ClH_2O]Cl$ and S. One possible explanation is the high solubility of $SnCl_2·2H_2O$ producing very fast a high concentration of $SnS_x$ species. Compared to the formation of these species the precipitation of the product is slow. Further evaluations are under way to identify the dissolved Sn species.

## References

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[1] N. Pienack, C. Näther, W. Bensch, Solid State Sci., in press (2006).
[2] M. Behrens, S. Scherb, C. Näther, W. Bensch, Z. Anorg. Allg. Chem. 629, 1367 (2003).
[3] R. Kiebach, N. Pienack, M.-E. Ordolff, F. Studt, W. Bensch, Chem. Mater. 18, 1196 (2006).
[4] M.-E. Ordolff, N. Pienack, W. Bensch, in preparation.