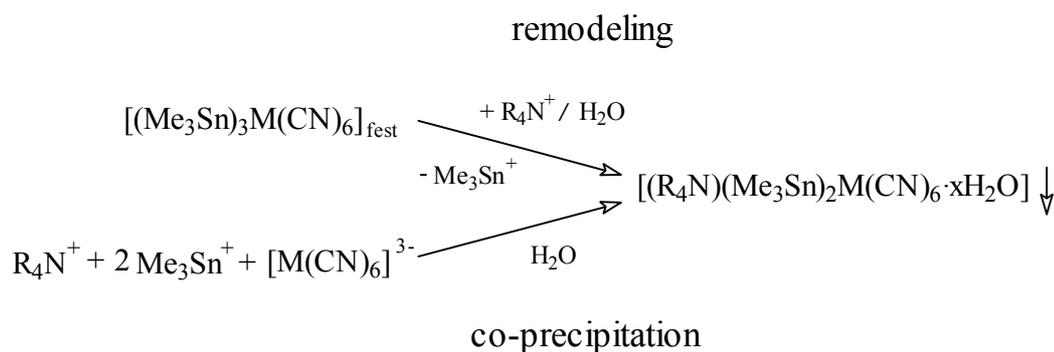


11. Summary

This thesis is focused on the effect of quaternary ammonium ions on *super*-Prussian-blue-derivates as structure directing agents. *Super*-Prussian-blue-derivates are coordination compounds of the type $[(\text{Me}_3\text{Sn})_x\text{M}(\text{CN})_6]$ ($x = 3, 4$; $\text{M} = \text{Fe}^{\text{III}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{III}}, \text{Ir}^{\text{III}}$).

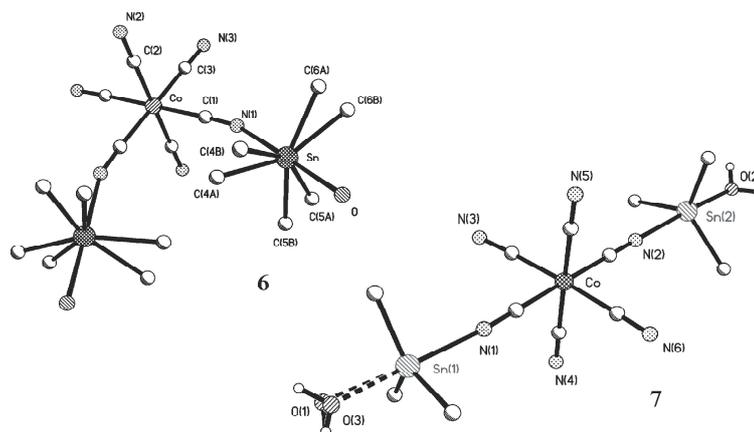
The three-dimensional coordination compounds $[(\text{Me}_3\text{Sn})_3\text{M}(\text{CN})_6]$ with $\text{M} = \text{Co}$ (**5**), Fe (**3**) react in „exchange“-based remodeling and co-precipitation, respectively with R_4N -cations ($\text{R} = \text{Et}, n\text{Pr}, n\text{Bu}, n\text{Pen}, n\text{Hex}$):



An elongation of the alkyl groups, and the concomitant decrease of the hydrophilic properties, results in host-guest compounds of different structures and H_2O -contents. As the Et_4N -cation exerts no effect on $[(\text{Me}_3\text{Sn})_3\text{M}(\text{CN})_6]$ (**5**), with $n\text{Pr}_4\text{N}$ two isomeric, new 3D-frameworks of the compound $[(n\text{Pr}_4\text{N})(\text{Me}_3\text{Sn})_2\text{M}(\text{CN})_6 \cdot 2 \text{H}_2\text{O}]$ (**6** resp. **7**) result. Both modifications contain anionic $[(\text{Me}_3\text{SnOH}_2)_2\text{M}(\text{CN})_6]$ -units, connected only by electrostatic and hydrogen short-range forces and stabilized by $\text{C-H}\cdots\text{N}$ -hydrogen bonds ($\text{E} = \text{O}$ resp. N) between the non disordered $n\text{Pr}_4\text{N}$ -cation and terminal cyanide N atoms. The shortest observed $\text{E-H}\cdots\text{N}$ -distances ($\text{E} = \text{O}$ resp. N) are for $d(\text{O}\cdots\text{N}) = 268$ pm and for $d(\text{C}\cdots\text{N}) = 313\text{-}337$ pm.

The essential difference between both modifications is the orientation of the two Me_3SnOH_2 -fragments. While the remodeling reaction leads to the *cis*-isomer **6**, co-precipitation affords the *trans*-isomer **7** (Picture 11.1).

Contrary to previous publications^[14, 16, 25, 67] the structure of the already known host-guest-compound $[(n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})_2\text{M}(\text{CN})_6 \cdot \text{H}_2\text{O}]$ (**4**^[14, 16, 25, 67] resp. **4a**) must be considered as a similar β -pleated sheet network with the guests between the sheets. The structure is also stabilized by hydrogen bonds ($d(\text{O}\cdots\text{N})$ about 270 pm and $d(\text{C}\cdots\text{N})$ about 317 pm).



Picture 11.1: ORTEP-Plots of the $[(\text{Me}_3\text{SnOH}_2)_2\text{M}(\text{CN})_6]$ -units of the cis-isomer **6** and the trans-Isomer **7**.

The largest of the structure directing agents adopted is the $n\text{Pen}_4\text{N}$ -cation which leads with $\text{M} = \text{Fe}$ vis. Co to $[(n\text{Pen}_4\text{N})(\text{Me}_3\text{Sn})_2\text{M}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$ (**8** resp. **9**) a 3D-framework with cavities of 2 nm^3 . In each cavity, two $n\text{Pen}_4\text{N}$ -cations and one H_2O -molecule are located, and fixed via E-H \cdots N-short-range forces ($\text{E} = \text{O}$ resp. N) to the framework ($d(\text{O}\cdots\text{N})$ about 298 pm and $d(\text{C}\cdots\text{N})$ about 333 pm).

The host-guest compounds **4a**, **6**, **7** and **9** were also analysed by DSC or DTA/TG. Like $[(\text{Me}_3\text{Sn})_3\text{M}(\text{CN})_6]$ (**5**), they finally decomposed to Co_2SnO_4 and SnO_2 .^[27]

In contrast, the quaternary ammonium ions show no structure directing effect towards the compound typ $[(\text{Et}_3\text{Sn})_3\text{M}(\text{CN})_6]$ with $\text{M} = \text{Co}$ (**10**), Ir (**12**).

Corresponding to **5**, the quaternary ammonium ions R_4N^+ with $\text{R} = n\text{Pr}$ and $n\text{Bu}$ show a structure directing effect also in „exchange“-based remodeling reactions to the heavier homologue $[(\text{Me}_3\text{Sn})_3\text{Ir}(\text{CN})_6]$ (**11**). Thus, reaction of **11** with $n\text{Pr}_4\text{N}$ -cations affords the cis-isomer $[(n\text{Pr}_4\text{N})(\text{Me}_3\text{Sn})_2\text{Ir}(\text{CN})_6 \cdot \text{H}_2\text{O}]$ (**13**), which is also stabilized by hydrogen bonds ($d(\text{O}\cdots\text{H}\cdots\text{N})$ about 265 pm and $d(\text{C}\cdots\text{H}\cdots\text{N})$ about 354 pm). $[(n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})_2\text{Ir}(\text{CN})_6 \cdot \text{H}_2\text{O}]$ (**14**) which is not isostructural with **4** resp. **4a** displays nevertheless stoichiometric similarity with the latter systems.

With the heavier $n\text{Pr}_4\text{P}$ -cation, both „exchange“-based remodeling (with **5**) and co-precipitation leads to the trans isomer $[(n\text{Pr}_4\text{P})(\text{Me}_3\text{Sn})_2\text{M}(\text{CN})_6 \cdot 2 \text{H}_2\text{O}]$ (**15** resp. **16**) which resemble **7**. As co-precipitation clearly affords the trans-isomer **16**, crystals for the structure determination were obtained from the mother liquor of the remodeling reaction. As for **7**, the resulting structure was stabilized by hydrogen bonds with $d(\text{O}-\text{H}\cdots\text{N})$ about 270 pm and $d(\text{C}-\text{H}\cdots\text{N})$ about 340 pm.

As single crystals had finally become available, the structure of the longer known compound $[(n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Cu}_2(\text{CN})_4]$ ^[31] (**17**) could also be determined. **17** forms a congruent 2D-layered framework with interlayer distances of $d(\text{Cu}\cdots\text{Cu})$ about 0.709 nm and $d(\text{Sn}\cdots\text{Sn})$ about 0.619 nm. Owing to an eclipsed arrangement of the sheets, hexagonal channels result, wherein the $n\text{Bu}_4\text{N}$ -cations are located. The short-range forces of **17** resulting here are shorter with $d(\text{C}-\text{H}\cdots\text{N})$ about 357 pm and $d(\text{C}-\text{H}\cdots\text{Cu})$ about 358 pm than those mentioned for $[(n\text{Bu}_4\text{N})\text{Cu}_2(\text{CN})_3]$ ^[25, 31] (**19**). Based on the structural data of **17**, it was possible to develop a model of the architecture of $[(n\text{Bu}_4\text{N})(\text{Me}_2\text{Sn}(\text{CH}_2)_3\text{SnMe}_2)_{0.5}\text{Cu}_2(\text{CN})_4]$ ^[18] (**20**). Owing to the trimethylene containing spacer, $\{\text{Me}_2\text{Sn}(\text{CH}_2)_3\text{SnMe}_2\}$, a 3D host-guest framework results for **20**.

Inspired by the result of the co-precipitation product $[(n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})_2(\mu\text{-OH})\text{Ni}(\text{CN})_4]$ ^[25, 67] (**31**), the coordination compound $[(\text{Me}_3\text{Sn})_2\text{Ni}(\text{CN})_4]$ (**27**) was also reacted with $n\text{Bu}_4\text{N}$ - and $n\text{Pen}_4\text{N}$ -cations, respectively, in remodeling and co-precipitation reactions. Depending on specific details of the synthesis, the following products resulted: $[(n\text{Bu}_4\text{N})(\text{Me}_3\text{Sn})\text{Ni}(\text{CN})_4]$ (**30**; remodeling), $[(n\text{Pen}_4\text{N})(\text{Me}_3\text{Sn})\text{Ni}(\text{CN})_4]$ (**32**; co-precipitation) and in the remodeling reaction the **31** like compound $[(n\text{Pen}_4\text{N})(\text{Me}_3\text{Sn})_2(\mu\text{-OH})\text{Ni}(\text{CN})_4]$ (**26**). All these compounds differ from each other. In contrast to **31**, the $\text{Ni}_2\text{Sn}_4\text{O}_2(\text{CN})_8$ units in **26** are connected by $\text{O}-\text{H}\cdots\text{N}$ -contacts ($d(\text{O}\cdots\text{N})$ about 286 pm) to infinite ribbons, which are stabilized by $\text{C}-\text{H}\cdots\text{N}$ -hydrogen bonds with the $n\text{Pen}_4\text{N}$ -cations ($d(\text{C}\cdots\text{N})$ about 331 pm).

It was also possible to isolate the $(\text{CH}_2)_3$ -linked spacer $\{\text{Me}_2\text{Sn}(\text{CH}_2)_3\text{SnMe}_2\}$ ^[18] (**21**) (initially introduced by Schütze) in the supramolecular assembly $[\{\mu\text{-}(\text{CH}_2)_3(\text{Me}_2\text{SnBr})_2\} \cdot 2(\text{H}_2\text{O} \cdot 2,2'\text{-bipyridine})]$ (**22**) which holds together only by short-range forces. The intramolecular distance of the Sn-atoms turns out to be $d(\text{Sn}\cdots\text{Sn})$ about 0.617 nm.

In analogy to the Me₃Sn-homologue **5**, [(Me₂Sn(CH)₃SnMe₂)_{1.5}Co(CN)₆]^[18] (**35**) was also subjected both to „exchange“-based remodeling and co-precipitation with R₄N-cations (R = Me, Et, *n*Pr, *n*Bu, *n*Pen). The „inherent“ structure directing effect of the {Me₂Sn(CH)₂SnMe₂} spacer leads to the product [(*n*Pr₄N)(L₂)Co(CN)₆·2 H₂O] (**36**) and [(*n*Bu₄N)(L₂)Co(CN)₆·2 H₂O] (**38**) co-precipitation, which display structures similar to the cis-isomer **6**. The remodeling product [(*n*Bu₄N)_{0.5}(L₂)_{1.25}Co(CN)₆·H₂O]^[18] (**37**) and the co-precipitation product [(*n*Pen₄N)_{0.625}(L₂)_{1.18}Co(CN)₆]·H₂O (**39**) differ structurally from the comparable Me₃Sn-homologues.

It was, furthermore, shown that the treatment of „[(Me₂Sn(CH)₃SnMe₂)₂Fe(CN)₆]^[18] (**40**) with CH₃CN results in a product which compares better with the Me₃Sn-homologue [(Me₃Sn)₄Fe(CN)₆]^[11] (**3**). As for the former compound **35**, the spacer L₂ affects the reaction of [(Me₂Sn(CH)₃SnMe₂)₂Fe(CN)₆] (**41**) and R₄N-cations significantly. Only the host-guest compounds [(Et₄N)(L₂)_{1.5}Fe(CN)₆] (**42**; co-precipitation) and [(Et₄N)Cl(L₂)₂Fe(CN)₆] (**44**; insertion) could be isolated. In spite of the different stoichiometry both the X-ray-powder diffraction patterns and the CP/MAS-solid-state NMR features turn out to be surprisingly similar with those of [(Et₄N)(Me₃Sn)₃Fe(CN)₆]^[13, 14, 39] (**43**).

This thesis was completed by a first attempt to solve the structure of the host-guest-compound [(Et₄N)(Me₃Sn)₃Fe(CN)₆]^[13, 14, 39] (**43**) by means of the Rietveld method. The heavy-atom positions could in fact be located with the Patterson method in the space group C2/m.