Abstract

The focus of this thesis is on the synthesis and characterization of coordination polymers containing fluorinated carboxylates. A total of eleven new compounds, based on the anions of 2,4,6-trifluorobenzoic acid (HtfB), 2-fluorotrimesic acid (H_3mfBTC) and 2,4,6-trifluorotrimesic acid (H_3pfBTC) are presented.
Five of these compounds contain the tfB^- anion as a structural building block. These are ${}^1_\infty[Li(tfB)_{3/3}(H_2O)_{1/1}]$ ($P2_1$, Z=2, **1**), ${}^2_\infty[Cs(tfB)_{2/2}(HtfB)_{3/3}]$ ($P2_1/c$, Z=4, **2**), ${}^1_\infty[Ag(tfB)_{2/2}(H_2O)_{2/2}]$ (C2/c, Z=8, **3**), ${}^1_\infty[Cu(tfB)_{2/1}(H_2O)_{4/2}]$ ($P\bar{1}$, Z=1, **4**) and ${}^0_\infty[Cu(tfB)_{4/2}(MeOH)_{1/1}]$ ($P2_1/c$, Z=4, **5**).
Compounds **1** to **4** are coordination polymers that form strands (**1**, **3**, **4**) or corrugated layers (**2**). In **1** and **2** the metal cations are bridged via the 2,4,6-trifluorobenzoate ligand, whereas in **3** and **4** the bridging results from coordinating water molecules. In addition, in **4** and **5** dimeric Ag_2- or Cu_2-units with short metal-metal distances are found. In **4** the dimers are additionally bridged via coordinating water molecules, while **5** forms the ”paddlewheel” structural motif.

Furthermore, the synthesis of the mono-potassium salts of 2-fluorotrimesic acid (${}^3_\infty[K(H_2mfBTC)_{6/6}]$, **6**) and 2,4,6-trifluorobenzene-1,3,5-tricarboxylic acid (${}^3_\infty[K(H_2pfBTC)_{6/6}]$, **8**) succeeded for the first time. The products were synthesized as phase-pure compounds and structurally characterized by single-crystal structure determination. Crystal structures of compounds containing the $mfBTC^{3-}$ and $pfBTC^{3-}$ anion have not been reported in the literature up to now. The crystal structures of these two compounds are related and crystallize in the acentric space groups Pc (**6**, Z=2) and Cc (**8**, Z=4). The comparison of the thermal behavior shows, contrary to expectations, that **6** exhibits a higher thermal stability than **8**.
Moreover, with ${}^3_\infty[Cu_{14}(mfBTC)_8(Py)_{12}(H_2O)_4(OH)_4]$ ($P2_1/c$, Z=1, **7**) a second compound containing the $mfBTC^{3-}$ anion as a linker is described. In **7** dimeric and pentameric Cu units are bridged via the $mfBTC^{3-}$ anion to form layers, which are in turn linked by a further $mfBTC^{3-}$ anion resulting in a three dimensional network.

Compound **8** served as starting material for three other compounds that contain the $pfBTC^{3-}$ anion, namely ${}^3_\infty[K_5H(pfBTC)_2(H_2O)_4]$ ($P\bar{1}$, Z=2, **9**), ${}^1_\infty[Sc(pfBTC)_{3/3}(H_2O)_{3/1}] \cdot 4\,H_2O$ ($P\bar{1}$, Z=2, **10**) and ${}^2_\infty[Cu_3(pfBTC)_2(Py)_4(H_2O)_4]$ ($P\bar{1}$, Z=2, **11**). These compounds crystallize as pure phases and were also characterized by x-ray single crystal structure analysis.