Synthesis and Characterization of POM-Cubane Hybrids

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Polyoxometalates (POMs) have a wide variety of applications due to their structural diversity and tunability and therefore are of high interest in many different research areas. To improve the desired properties of the POMs, hybrid materials with covalent and non-covalent bonds can be synthesized. Herein, the formation of POM hybrids derived from a combination of POMs with different metal oxo-clusters are described. Mainly the negatively charged full-Keggin POM $\{Co(II)W_{12}O_{40}\}$, with {Na}, {K}, $\{NH_4\}$, and $\{(NCH_3)_4\}$ as counterions, was used as a starting material and combined with the positively charged $\{Co(II)_4O_4\}$ cubane $[Co(II)_4(dpy\{OH\}O)_4(OAc)_2(H_2O)_2](BF_4)_2$ (Co_4O_4-dpk). Different counterions for the cubane formation were tested in combination with the POM and influenced the crystallization process. Replacing the starting POM with an unsaturated Keggin POM $\{BiW_9O_{34}\}$ resulted in a mixture of different crystal structures, including a structure with a sandwich-type POM and a mono nuclear cobalt(III) complex as a counter cation. The structures were determined using SC-XRD and PXRD. The redox reactions and stability of the compounds were studied by cyclic voltammetry.