

MS30-O4 Giant pentaphosphaferrocene-based supramolecules

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An intriguing inorganic analogue of ferrocene, pentaphosphaferrocene, $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^{\text{R}} = \eta^5\text{-C}_5\text{R}_5$, $\text{R} = \text{Me}$ (Cp^*), CH_2Ph (Cp^{Bn})), has the ability to coordinate Cu^+ cations resulting in either coordination polymers or in giant supramolecules [1-4]. The quasi-spherical voids inside the latter can include various organic, inorganic and organometallic guest molecules and cations. This inclusion allowed us to stabilize such instable molecules as the paramagnetic 16 VE complex $[\text{CpCr}(\eta^5\text{-As}_5)]$ or light-sensitive yellow arsenic, As_4 , embedded as guests into $[\text{Cu}_{20}\text{Cl}_{20}\{\text{Cp}^*\text{FeP}_5\}_{12}]$ and $[\text{Cu}_{30}\text{I}_{30}\{\text{Cp}^*\text{FeP}_5\}_{10}(\text{MeCN})_6]$, respectively. Our recent solid state and solution study demonstrated the potential of $[\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)]$ in combination with CuX ($\text{X} = \text{Cl}, \text{Br}$) to switch between supramolecules of different porosity and shape [4]. With increasing amount of CuX the structures of the supramolecules change from spherical $[\text{Cu}_m\text{X}_m\{\text{Cp}^{\text{Bn}}\text{FeP}_5\}_{12}]$ ($m = 14\text{-}20$) to the tetrahedral aggregate $[\{\text{Cp}^{\text{Bn}}\text{FeP}_5\}_{12}\{\text{CuBr}\}_{51}\{\text{MeCN}\}_8]$ with an outer diameter of 3.56 nm. The use of Cp_2Co and $(\text{C}_6\text{H}_6)_2\text{Cr}$ as guests results in their partial oxidation and inclusion as cations into an anionic cage, e.g., $[\text{CoCp}_2^+@[(\text{Cp}^*\text{FeP}_5)_8\text{Cu}_{24}\text{Br}_{28}(\text{CuBr})_{0.25}(\text{MeCN})_4(\text{MeCN})_2]]^{3-}$ (Fig.).

Despite the objective obstacles like instability of crystals toward the loss of solvents, huge unit cells (up to 300 000 Å³), disorder of the inorganic host scaffold and guest, our structural investigations revealed some unusual phenomena. Thus, we first discovered the π -stacking interaction involving the inorganic 6-e⁻ π -systems of the *cyclo*-P₅ forming the inner cavity of the supramolecule and Cp, *cyclo*-P₅ and *cyclo*-As₅ of the guest molecules that determine their orientation inside the void. Furthermore, the spherical supramolecules sometimes form, *contra*-intuitively, low-dense packings with huge intramolecular cavities [2].

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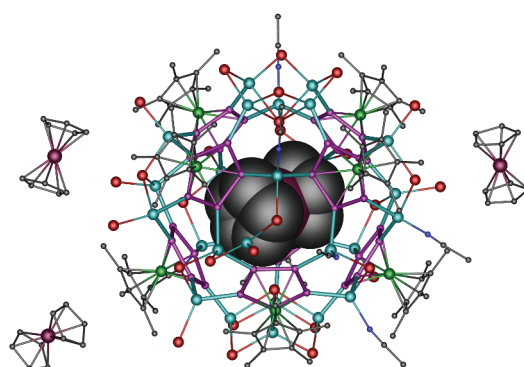


Figure 1. Inclusion of CoCp_2^+ into supramolecule (Fe green, Co purple, Cu cyan, Br brown)

Keywords: crystal structure and properties, pentaphosphaferrocene, host-guest compounds, supramolecular chemistry, disorder, intermolecular interactions