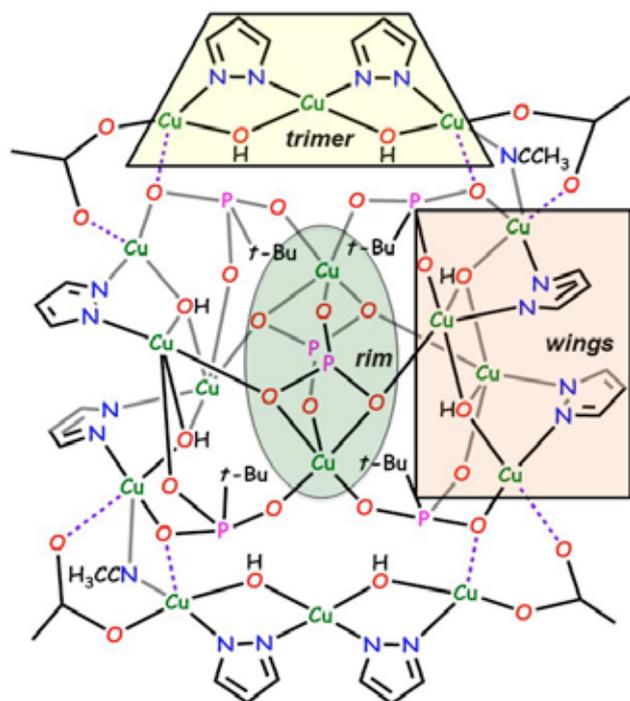


# Poster Presentations

## [MS24-P06] Butterfly Cored Deca- and Hexadecacopper(II) Phosphonates

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Metal phosphonates ( $M_n(PO_3)_m$ ) are relatively of recent origin. A majority of  $M_n(PO_3)_m$  possess extended layered structures (1D, 2D and 3D). Discrete molecular phosphonates (0D) are relatively rare with only a few general methods available for the synthesis of molecular metal phosphonates.<sup>1b-c,2</sup> We developed a novel multi-component approach involving transition metal salt ( $CuX_2$ ), ancillary pyrazole (3-RPzH, R = H, Me, 2-Py, Ph, naphthyl and  $CF_3$ ) ligands, phosphonic acid ( $t-BuPO_3H_2$ ) and triethylamine base which yields a series of isostructural discrete decacopper(II) phosphonates  $[Cu_5(\mu-OH)_2(R-Pz)_2(t-BuPO_3)_3 \cdot X_2]_2 \cdot Y$  {X = (RPzH)<sub>4</sub> or  $(t-BuPO_3H)_4$  and Y = H<sub>2</sub>O or MeOH} ( $Cu_{10}$ )<sub>3</sub>. It was found that the use of ancillary ligands controls the oligomerisation by occupying

some of the metal coordination sites available for the phosphonate coordination.<sup>2b</sup> In other words, a soluble metal-ligand complex was generated in situ to which the addition of phosphonic acid in presence of suitable base enhances the solubility and helps in isolating the molecular products rather than forming the usual polymeric structures. In the case of 2-PyPzH as co-ligand, an indirect route involving various copper(II)-pyrazolide precursors afforded a polymorphic form of the original  $Cu_{10}$  cage, while in the case of PzH and 3-MePzH as the co-ligands, depending on the reaction conditions, either pyrazole rich (8:6) neutral  $Cu_{10}$  or phosphonate rich (10:4) tetra-anionic  $Cu_{10}$  were obtained. The use of an acetonitrile and ethyl acetate (1:1) solvent mixture afforded a  $Cu_{16}$  cage  $[Cu_8(\mu-OH)_4(Pz)_4(t-BuPO_3)_3(CH_3COO)_2(CH_3CN)_2]_2$  as the only product formed as a result of the in situ ethyl acetate hydrolysis.<sup>4</sup> To the best of our knowledge,  $Cu_{16}$  was the second highest nuclearity known for the copper(II) phosphonates. Single crystal X-ray analysis shows that all of them ( $Cu_{10}$  and  $Cu_{16}$ ) have a butterfly cored structure contained in it.  $Cu_{10}$  is made up of a dimeric  $[Cu_2(t-BuPO_3)_2]_2$  central rim unit attached to two other tetrameric  $[Cu_4(RPz)_4 \cdot X \cdot Y]$  wings on both of its sides, mediated through four  $t-BuPO_3^{2-}$  ligands. In  $Cu_{16}$ , each of the four  $t-BuPO_3^{2-}$  ligands of the wings extends its arm to hold one more copper atom of the trimeric  $[Cu_3(\mu-OH)_2(Pz)_2(CH_3COO)_2(\mu-CH_3CN)]$  unit on both sides of the  $Cu_{10}$  cage. Also, four  $CH_3COO$  ligands and two  $CH_3CN$  solvent molecule of the trimeric motif tightly knit the  $Cu_{10}$  and  $Cu_3$  parts together to form the  $Cu_{16}$  cage. All the cages and various structural motifs (vide infra) are stable under ESI mass conditions. The magnetic analysis reveals the presence of the dominant anti-ferromagnetic interactions at lower temperatures. In one selected case, we also tested the nuclease activity of the  $Cu_{10}$  cage to modify the plasmid pBR322 DNA. It shows 100% conversion from supercoiled form I to nick form II in 90 minutes in the absence of any oxidizing agent.

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