New tricopper(II) cores self-assembled from aminoalcohol biobuffers and homophthalic acid:synthesis, structural and topological features, magnetic properties and mild catalytic oxidation of cyclic and linear C_5-C_8 alkanes.

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Streszczenie

Two new crystalline materials $[Cu_3(\mu_2\text{-}H_3bis\text{-}tris)_2(\mu_2\text{-}Hhpa)_2]\cdot H_2O$ (**1**) and $[Cu_3(\mu_2\text{-}H_2tea)_2(\mu_2\text{-}hpa)(\mu_3\text{-}hpa)]_n$ (**2**) bearing distinct tricopper(II) cores were easily generated by the aqueous medium self-assembly method from copper(II) nitrate, bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane (H_5bis-tris) or triethanolamine (H_3tea) aminoalcohol biobuffers and homophthalic acid (H_2hpa). The obtained products were characterised by IR, UV-vis and EPR spectroscopy, ESI-MS(±), thermogravimetric, elemental and single crystal X-ray diffraction analysis. Apart from possessing different dimensionality, the crystal structures of the discrete 0D trimer **1** and the zigzag 1D coordination polymer **2** show distinct symmetric $[Cu_3(\mu\text{-}O)_4(\mu\text{-}COO)_2]$ and asymmetric $[Cu_3(\mu\text{-}O)_3(\mu\text{-}COO)_2]$ tricopper(II) cores, respectively. An intense pattern of intermolecular O–H···O hydrogen bonds provides a 0D → 3D (**1**) or 1D → 2D (**2**) extension of the structures into intricate topologically unique H-bonded nets. After additional simplification, these were classified as a uninodal 6-connected 3D framework with the **snk** topology in **1** and a binodal 3,5-connected 2D layer with the **3,5L50** topology in **2**. Variable-temperature magnetic susceptibility studies indicate a predominant ferromagnetic coupling [J = 39.1(1) and 29.5(1) cm^{-1} for **1** and **2**, respectively] within the mixed-bridged tricopper(II) cores. Both compounds **1** and **2** were also applied as rather efficient bio-inspired pre-catalysts for the mild homogeneous oxidation, by aqueous H_2O_2 at 50 °C in acidic MeCN–H_2O medium, of cyclic (cyclopentane, cyclohexane, cycloheptane and cyclooctane) and linear (*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) alkanes to the corresponding alcohols and ketones with overall yields up to 26% based on the alkane. The effects of different reaction parameters (type of pre-catalyst and acid promoter, reaction time and substrate scope) and various selectivity features were investigated and discussed, supporting a free-radical mechanism in the present alkane oxidations.

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https://www.rsc.org/