Unique copper–organic networks self-assembled from 1,3,5-triaza-7-phosphaadamantane and its oxide : synthesis, structural features, and magnetic and catalytic properties.

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Streszczenie

Three new coordination compounds, namely, a zero-dimensonal dicopper(II) complex $[Cu_2(\mu\text{-}MeCOO)_4(MeOH)_2]$ (PTA = O)$_2$ (**1**), a three-dimensional (3D) copper(II)-organic framework $[Cu_3(\mu\text{-}MeCOO)_6(\mu_3\text{-}PTA{=}O)]_n{\cdot}3.5n$MeCN (**2**), and a mixed-valence copper(I/II) one-dimensional (1D) coordination polymer $[Cu_3(\mu\text{-}MeCOO)_4(MeCOO)(\mu\text{-}PTA)_2(PTA)]_n$ (**3**), were self-assembled from copper(II) acetate and cage-like aminophosphine 1,3,5-triaza-7-phosphaadamantane (PTA) or its P-oxide (PTA═O). The obtained products were isolated as air-stable crystalline solids and characterized by IR and electron paramagnetic resonance spectroscopy, thermogravimetric and elemental analysis, as well as single crystal X-ray diffraction. Although all compounds bear dicopper(II) paddle-wheel tetraacetate $[Cu_2(\mu\text{-}MeCOO)_4]$ blocks, they are arranged into very distinct metal–organic architectures. The structure of **2** reveals an intricate 3D metal–organic framework (MOF) driven by the μ_3-PTA═O spacers acting in an unusual N,N,O-tridentate mode, whereas the compound **3** discloses an infinite 1D wave-like metal–organic chain with the dicopper(II) $[Cu_2(\mu\text{-}MeCOO)_4]$ and monocopper(I) [Cu(PTA)(MeCOO)] blocks being interlinked by the μ-PTA linkers acting in an N,P-bidentate mode. Topological analysis of underlying nets was performed, revealing a decorated uninodal 3-connected framework with the **ths** topology in **2** and a uninodal 2-connected chain with the **2C1** topology in **3**. Compounds **2** and **3** broaden a still very limited family of MOFs or coordination polymers assembled from PTA or its P-oxide building blocks, also showing that PTA can be applied for the generation of unusual mixed-valence copper(I/II) derivatives. Besides, **2** represents the first example of a copper-containing 3D MOF that is driven by PTA═O or any other PTA-derived block. Magnetic properties of **1**–**3** were investigated, modeled, and discussed in detail, resulting in the exchange coupling parameters (J = −310, −320 cm^{-1}) that indicate a strong antiferromagnetic interaction within the dicopper(II) paddle-wheel blocks. Moreover, compounds **1** and **2** show a notable catecholase activity in the aerobic oxidation of 3,5-di-*tert*-butyl-catechol to 3,5-di-*tert*-butyl-*o*-benzoquinone; turnover frequency values of up to 81 min^{-1} were attained.

Adres publiczny

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