

A 3D MOF with Cu₂₀ /Cu₆ Clusters: Self-Assembly, CO₂ Encapsulation, Structural Features, and Magnetic Properties

Autorzy

Ewelina I. Śliwa

Dmytro S. Nesterov

Julia Kłak

Alexander M. Kirillov

Piotr Smoleński

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Streszczenie

Molecular design of multicopper clusters has been of increasing importance in inorganic chemistry, biomedical science, and functional materials. Herein, two new copper compounds were self-assembled from copper(II) monofluoroacetate or trifluoroacetate, elemental copper, and 1,3,5-triaza-7-phosphaadamantane (PTA). The reaction starting from copper(II) monofluoroacetate yielded a tetranuclear cluster, [Cu₄^{II}(μ₃-OH)₂(μ-L)₆(PTA=O)₂] (**1**), where L is monofluoroacetate(1-) and PTA=O is the oxide of PTA. Formation of **1** involves the oxidation of PTA and the incorporation of μ₃-OH⁻ ligands. In contrast, a similar reaction with copper(II) trifluoroacetate produced a unique three-dimensional metal-organic framework (3D MOF), formulated as [Cu₂₀^{II}(CO₃)(μ₃-O)₂(μ₃-OH)₂₂(μ-L')₁₂]{Cu₆^I(μ₃-PTA)₆(CH₃CN)₁₂}]_n·6n(L')·3n(H₂O)·2n(CH₃CN) (**2**), where L' is trifluoroacetate. It comprises Cu₂₀ clusters, with an encapsulated carbonate anion fixed from atmospheric CO₂, which are bridged by {Cu₆^I(PTA)₆} units into a 3D MOF. Control experiments confirmed that carbonate originates from ambient CO₂ rather than from added carbonate salts. Both **1** and **2** were fully characterized, and their magnetic properties were investigated, revealing dominant antiferromagnetic interactions within the Cu₄ and Cu₂₀ clusters, respectively. Density functional theory (DFT) calculations confirmed the antiferromagnetic ground spin state of **1** and disclosed the stability of the Cu₂₀ core in **2**. This work highlights the influence of fluorinated carboxylates and atmospheric conditions on the assembly and architecture of multicopper clusters, and extends their family to new examples.

Słowa kluczowe

Cluster chemistry, Copper, Inorganic carbon compounds, Ligands, Oxides

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