Structure and magnetic behavior of Cu^{II} MOF_S supported by 1,2,4-triazolyl-bifunctionalized adamantane scaffold.

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Streszczenie

New triazole-based Cu^{II} metal–organic frameworks, $[Cu(tr_2ad)(SO_4)]\cdot 3H_2O$ (**1**), $[Cu_3(tr_2ad)_4(H_2O)_2(SO_4)_2]SO_4\cdot 28H_2O$ (**2**), $[Cu_3(tr_2ad)_4(H_2O)_4](SiF_6)_3\cdot 16H_2O$ (**3**), constructed utilizing a rigid adamantane scaffold, tr_2ad = 1,3-bis(1,2,4-triazol-4-yl)adamantane, were prepared hydrothermally, and their crystal structures were determined. The structure of **1** is built up from straight chains of corner-sharing CuN_4O_2 octahedra supported by short μ_2-tr (tr = 1,2,4-triazole) and μ_2-SO_4^{2-} bridges. The tetradentate character of tr_2ad results in the formation of layers. The 2D structures of **2** and **3** consist of discrete secondary building blocks $[Cu_3(\mu_2\text{-}N^1,N^2\text{-tr})_6]$ with triple [–N–N–] triazole links between the adjacent Cu centers [the Cu-(tr)-Cu separations are 3.806 and 3.756 Å for **2** and **3**, respectively]. The distorted octahedral N_4O_2 environment of the peripheral Cu atoms is completed by water molecules and/or terminal sulfate anions. The linear magnetic clusters, which act as nodes, are joined together at average distances of 11.2 and 15.0–15.6 Å into square-grid-like networks that exploit the double-bridging μ_3- and μ_4-bis(triazole) modules. Uncoordinated counteranions and crystal water molecules fill the interlayer space and channels in the complexes and form extensive H-bonding patterns. The exchange integrals J_1 = 9.8 and $J_2 \approx 0$ cm^{-1} for the interaction $J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + J_2\hat{S}_1\hat{S}_3$ were determined for **3** from magnetic susceptibility data and reproduced by a broken-symmetry DFT calculation. The spin Hamiltonian parameters of **3** were found from high-field electron paramagnetic resonance (EPR) spectra.

Adres publiczny

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