Topological diversity of supramolecular networks constructed from copper(II) aminoalcohol blocks, and 2,6-naphthalenedicarboxylate linkers: self-assembly synthesis, structural features, and magnetic properties.

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Streszczenie

A series of copper(II) aminoalcohol derivatives [Cu_2(μ-dmea)$_2$(μ-nda)(H_2O)$_2$]$_n$·2$n$$H_2O$ (**1**), [Cu_2(μ-Hmdea)$_2$(μ-nda)]$_n$·2$n$$H_2O$ (**2**), [Cu_2(μ-Hbdea)$_2$(μ-nda)]$_n$·2nH_2O (**3**), and [Cu_2(H_4etda)$_2$(μ-nda)]·nda·4H_2O (**4**) were generated by aqueous medium self-assembly at ∼25 °C from copper(II) nitrate, various aminoalcohols [*N*,*N*′-dimethylethanolamine (Hdmea), *N*-methyldiethanolamine (H_2mdea), *N*-butyldiethanolamine (H_2bdea), or *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)ethylenediamine (H_4etda) for **1**–**4**, respectively], sodium hydroxide, and 2,6-naphthalenedicarboxylic acid (H_2nda). They were isolated as crystalline solids and fully characterized by IR and electron paramagnetic resonance spectroscopy, electrospray ionization mass spectrometry (ESI–MS(±)), thermogravimetric, elemental, and single-crystal X-ray diffraction analyses. The latter revealed that **1**–**3** are one-dimensional (1D) coordination polymers assembled from dicopper(II) aminoalcohol blocks and μ-nda linkers, whereas **4** is a discrete zero-dimensional (0D) dimer composed of two [Cu(H_4etda)]$^{2+}$ fragments interlinked by the μ-nda moiety. In spite of some structural similarities, the main distinctive features of **1**–**4** arise from the different H-bonding patterns driven by the crystallization H_2O molecules, thus giving rise to a further extension of the structures [1D → 3D (**1**, **2**), 1D → 2D (**3**), or 0D → 3D (**4**)] into distinct supramolecular networks. Their topological analysis disclosed very complex multinodal nets with unique (**1**, **2**, **4**) or rare (**3**) topologies, which, upon further simplification, furnished a binodal 4,6-connected net with the sqc513 topology in **1**, a trinodal 3,4,6-connected net with the 3,4,6L6 topology in **3**, and trinodal 3,4,6- or 3,4,8-connected nets with undocumented topologies in **2** and **4**, respectively. The magnetic susceptibility studies of **1**–**3** indicate a strong antiferromagnetic coupling between the Cu^{II} atoms through the μ-alkoxo bridges [J = −470(2), −100(2), and −590(1) cm^{-1}, respectively], which was described by the Bleaney–Bowers dinuclear model. In contrast, **4** is devoid of any significant magnetic interaction within the dicopper(II) units.

Adres publiczny

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