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A new three-dimensional Cu(II) coordination polymer with triaminoguanidin building blocks

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Abstract

The reaction between the tris(2-hydroxybenzylidene)triaminoguanidin hydrochloride $(H_6L)Cl$ and copper(II) chloride in the presence of triethylamine leads to a three-dimensional coordination polymer with two interpenetrating (10,3)-a networks of opposite chirality. Magnetic studies revealed strong antiferromagnetic coupling between copper ions of the spin frustrated trinuclear building unit.

Keywords: Coordination polymer; Copper(II) complex; Crystal structure; Magnetic properties; Self-assembly

The design and synthesis of metal-organic frameworks is of great interest owing to their potential applications as functional solid materials, as well as due to their fascinating variety of architectures and topologies [1–6]. Wells has analyzed and classified a great number of nets using the simple node-and-connection approach. The (10,3)-a topology is the most symmetrical 3-connected network which may be regarded as the analogue of the diamond net with respect to the 4-connected series [7]. The large chiral cavities of a single (10,3)-a net may be filled either with disordered solvent molecules as well as other guest molecules [8–10] or with additional nets of the same topology, but of opposite handedness [11–14]. Self-assembly processes of transition metal ions with multifunctional ligands are a basic strategy toward coordination polymers with a brought variety of different architectures [2]. In particular the assembly of (10,3)-a nets is based on trigonal molecular building blocks with additional connecting units, both can be either appropriate ligands or metal fragments [15]. Ligand systems based on triaminoguanidin have recently been employed in the synthesis of a variety of interesting discrete cage molecules with different topologies [16].

In this work, we report a new three-dimensional coordination polymer containing two interpenetrated networks of (10,3)-a topology, which is obtained by self-assembly process of the Schiff base type ligand tris(2-hydroxybenzylidene)-triaminoguanidin H_5L with copper(II) chloride as shown in Fig. 1. Small dark brown crystals of $[Cu_6L_2Cl_2(DMF_3)(H_2O)] \cdot H_2O \cdot \frac{1}{3}Et_3N$ (**1**) were obtained by slow diffusion of methanol into the dark green DMF solution containing $(H_6L)Cl$, $CuCl_2 \cdot 2H_2O$ and triethylamine in a 1:3:6 molar ratio at room temperature [17].

A single-crystal X-ray diffraction study revealed a polymeric structure with two interpenetrated three-dimensional coordination frameworks of (10,3)-a topology with opposite chirality [18]. The network structures can be described as composed of trigonal $\{Cu_3L\}^+$ building blocks that are interlocked into a three-dimensional coordination polymer through the formation of bis(phenoxide)-bridged binuclear copper(II) units as depicted in Fig. 2. The distance between the copper ions within the trinuclear building blocks is about 479 pm. For **1** a dihedral angle of 138° is observed for the bis(phenoxide)-bridged binuclear copper(II) unit with a copper–copper distance of 297 pm. The typically observed symmetric planar bridging mode is prevented due to the steric requirements of the given ligand. This leads to an asymmetric bridging unit, with the bridging

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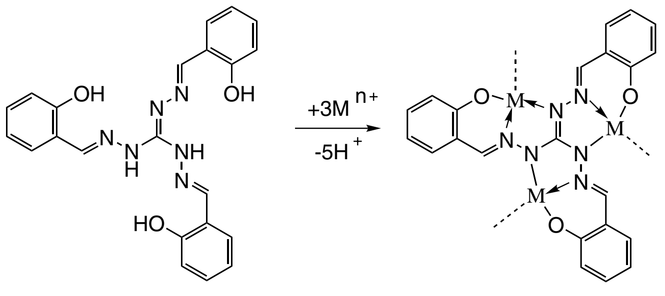

Fig. 1. Schematic drawing of the synthetic procedure.

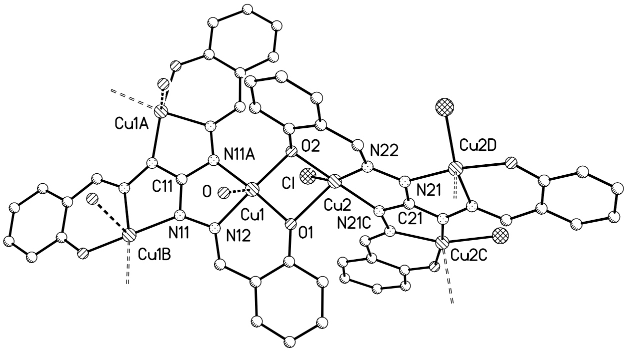

Fig. 2. Molecule structure of the interlocked $\{Cu_6L_2\}$ building unit of the three-dimensional coordination polymer **1**. Hydrogen atoms and solvent molecules are omitted for clarity; the DMF molecule is represented by the coordinating oxygen atom; open broken lines represent connections to neighboring $\{Cu_3L\}^+$ units; symmetry equivalent atoms are denoted by A–D. Selected bond lengths (pm) and angles (°): Cu1–O1 190.8(5), Cu1–O2 201.7(5), Cu1–N12 195.4(6), Cu1–N11A 196.8(6), N11–N12 139.0(8), Cu2–O1 227.0(6), Cu2–O2 197.9(5), Cu2–N22 196.0(6), Cu2–N21C 197.0(6), Cu2–Cl 229.1(7), N21–N22 139.2(9); O1–Cu1–O2 82.1(2), N12–Cu1–N11A 80.6(2), O1–Cu2–O2 74.4(2), O2–Cu2–Cl 87.1(2), N22–Cu2–N21C 79.9(2), Cu1–O1–Cu2 90.0(2), Cu1–O2–Cu2 95.8(2).

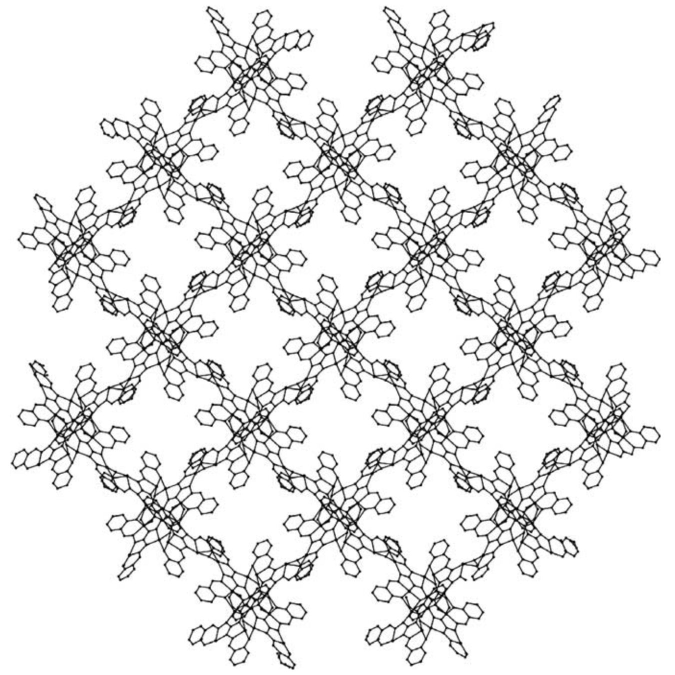

Fig. 3. View of the network structure for one of the interpenetrating (10,3)-a frameworks of **1**.

oxygen atoms O1 and O2 in an equatorial position at Cu1, whereas for Cu2 they occupy axial and equatorial positions, respectively. Nevertheless both copper ions of the two crystallographically distinct $\{Cu_3L\}^+$ units exhibit a penta-coordinate square-pyramidal coordination environment with a DMF molecule coordinated at the Cu1 atom. In the case of Cu2 the bridging oxygen atom O1 is in the apical position at a distance of 227 pm and the fourth equatorial position, not occupied by the ligand, is filled by a chloride counter ion or a water molecule. Therefore distinct conformational variations are observed for the two crystallographically independent $\{Cu_3L\}^+$ units (see Fig. 2). The Cu1 center shows only minor distortions from the idealized square-pyramidal coordination geometry with a τ value of 0.05, whereas for the Cu2 center a significant distortion from this idealized coordination geometry is observed with a τ value of 0.24. The observed distortions lead to a dihedral angle between the interlinked $\{Cu_3L\}^+$ units of about 70°.

One of the two interpenetrating (10,3)-a networks of **1** is depicted in Fig. 3 showing the resulting cavities and the fourfold. These large chiral channel-shaped cavities the fourfold helices of the same handedness running along the three coordinate axes are characteristic features of (10,3)-a nets. In **1** the resulting cavities are filled by a second interpenetrated (10,3)-a network as shown by the simplified view given in Fig. 4. Although two different $\{Cu_3L\}^+$ trigonal building blocks assemble the frame-

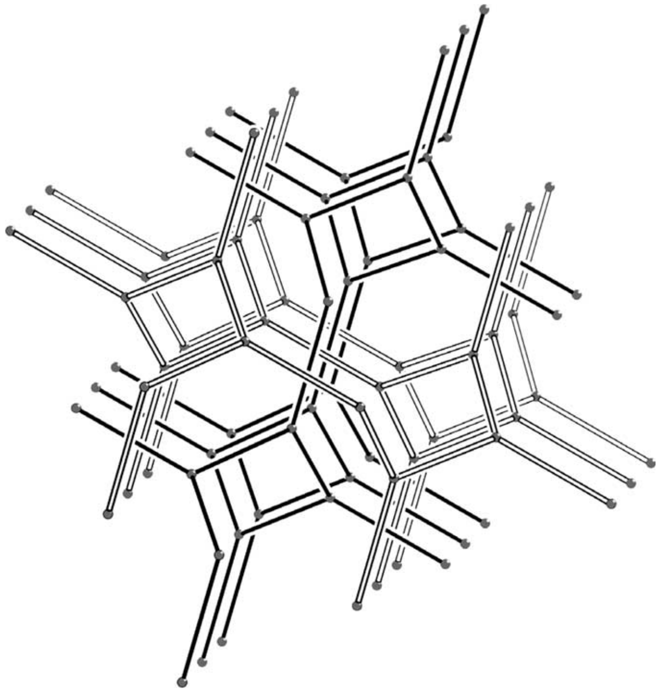

Fig. 4. Schematic drawing of the topology of the two interpenetrated (10,3)-a nets of **1** (view approximately along [001]); the nodes represent the central carbon atoms C11 and C21 of the $\{Cu_3L\}^+$ building blocks.