



## A self-assembled non-interpenetrating cubic diamondoid coordination polymer of hexamine with linear dicopper spacer: Structural and magnetic studies

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### ARTICLE INFO

#### Article history:

Received 13 July 2011

Accepted 24 August 2011

Available online 2 September 2011

#### Keywords:

Copper(II)

Benzoate

Hexamine

Crystal structure

Magnetic properties

### ABSTRACT

Structural characterization of a new self assembled coordination polymer of Cu<sup>II</sup>, hexamine (hmt) and benzoate (OBz), [Cu<sub>4</sub>(OBz)<sub>8</sub>(hmt)]<sub>n</sub> (**1**), reveals that it is a cubic non-interpenetrating diamondoid network formed by the coordination of the μ<sub>4</sub>-hmt ligand to a linear [Cu<sub>2</sub>(OBz)<sub>4</sub>] spacer. The magnetic study reveals that the Cu(II) ions are antiferromagnetically coupled ( $J = -323.5 \text{ cm}^{-1}$ ) through the *syn-syn* carboxylate bridges.

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The design and synthesis of extended self-assembled coordination polymeric architectures have aroused extensive interest due to their interesting structures and/or unusual properties [1–12]. The synthetic strategies leading to the desired species are a continuing challenge to the synthetic chemist. Hexamethylenetetramine (hmt) as a potential tetradentate ligand is quite suitable for the self-assembly of supertetrahedral network with linear metallic synthons to generate diamondoid structures. In the realm of supramolecular chemistry and crystal engineering, diamondoid networks are of great interest due to their typical 3D orientation in space (whether cubic or hexagonal) [13]. Along with its two types considerable emphasis is concentrated on determining whether it is interpenetrating or not [14]. Among the different metal ions, Ag<sup>+</sup> that can act as efficient spacer has widely been used for the construction of various type coordination polymers with hmt [4–11]. However, in most cases, its coordination number is more than two and therefore is not a linear spacer [5–11]. On the other hand, the well known [Cu<sub>2</sub>(carboxylato)<sub>4</sub>] units with four bridging carboxylate ligands in the familiar η<sub>1</sub>:η<sub>1</sub>:μ coordination mode have accessible apical coordination sites and are ideally suited to serve as a metal-based linear spacer [3,15–18]. These compounds might therefore represent suitable prototypes for structure/function studies, especially in the area of molecular magnetism since Cu<sub>2</sub>(μ-O<sub>2</sub>CR)<sub>4</sub>-

based structures have been shown to be magnetically active [15]. However, the majority of reported polymers containing such dicopper spacers are found to be 1D chains with μ<sub>2</sub>-hmt [18–20] and a few to have 2D structures with μ<sub>3</sub>-hmt [2,3,21]. To our knowledge, no diamondoid structure with dicopper spacer and μ<sub>4</sub>-hmt has been previously reported although such structures with [Mo<sub>2</sub>(O<sub>2</sub>C–CH<sub>3</sub>)<sub>4</sub>] are known [22].

In this communication, we present the synthesis and characterization (structurally and magnetically) of a self-assembled diamondoid coordination polymer [Cu<sub>4</sub>(OBz)<sub>8</sub>(hmt)]<sub>n</sub> (**1**) (OBz = benzoate) constructed by linking the tetrahedrally disposed μ<sub>4</sub>-hmt linker to the axial sites of linear dicopper tetrabenzoate spacer, [Cu<sub>2</sub>(OBz)<sub>4</sub>].

Complex **1** was synthesized by layering method. A methanolic solution (10 ml) of Cu(OBz)<sub>2</sub>·2H<sub>2</sub>O (0.682 g, 2 mmol) was carefully layered over an aqueous solution (5 ml) of hmt (0.140 g, 1 mmol). A greenish crystalline product of **1** started to appear within few hours. The compound was collected after two weeks; some of the crystals were suitable for X-ray diffraction analysis [23]. The successful synthesis was confirmed by FTIR spectroscopy, and elemental analysis. Characteristic antisymmetric stretching (ν<sub>as</sub>) bands of the carboxylate groups for **1**, appear in the usual region at 1610 cm<sup>-1</sup> [27]. The symmetric stretching (ν<sub>s</sub>) for **1**, appears at 1409 cm<sup>-1</sup>. These values resemble the ν<sub>as</sub> and ν<sub>s</sub> of copper(II) benzoate [28,29]. Complex **1** exhibits a prominent band at 1004 cm<sup>-1</sup> and 1236 cm<sup>-1</sup> due to CN stretching of hmt moiety [30].

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The polymeric structure of **1**,  $[\text{Cu}_4(\text{OBz})_8(\text{hmt})]_n$  is shown in Fig. 1. The central hmt unit is bonded to the axial positions of four centrosymmetric  $\text{Cu}_2(\text{OBz})_4$  moieties which are in turn bridged to further hmt molecules to create a three-dimensional polymer. The coordination geometry around the copper atom can be considered to consist of a five-coordinate (4 + 1) distorted square-base pyramid.

In the  $[\text{Cu}_2(\text{OBz})_4]$  units, four bridging benzoate (OBz) ligands are in the familiar  $\eta^1:\eta^1:\mu$  coordination mode [3,15–18]. The structure of the centrosymmetric  $\text{Cu}_2(\text{OBz})_4$  moiety is shown in Fig. 1b. Four oxygen atoms (namely O11, O13', O21 and O23') from four different OBz ligands form the equatorial plane which is planar within experimental error. The Cu(1) atom is 0.133(1) Å from this plane in the direction of the axial N(1) atom from hmt. The four basal Cu–O distances fall in the range from 1.961(1) Å to 1.973(1) Å. The axial Cu(1)–N(1) distance is 2.186(1) Å. The Addison parameter ( $\tau$ ) [31] which is an index of distortion from the square-pyramidal to the trigonal-bipyramidal geometry is calculated to be 0.02.

The central hmt has symmetry, as shown in Fig. 1, and therefore there is only one independent Cu(II) atom in the asymmetric unit. The Cu–Cu distance within the  $[\text{Cu}_2(\text{OBz})_4]$  unit is 2.565(1) Å indicating a strong interaction. This distance is comparable to those found (2.561–2.678 Å) in other dicopper tetrabenzoate complexes [29,32,33].

In complex **1**, the tetradentate ligand hmt serves as a tetrahedral node along with dicopper as bridging spacers. The  $\mu_4$ -coordination mode of hmt gives rise to a diamondoid coordination polymer of hexamine and linear dicopper spacer (Fig. 2). Inspection of the structure shows that all the six membered rings, formed by the six hmt ligands and six dicopper spacers are in the chair conformation confirming that the diamondoid structure of **1** is cubic [13]. In this diamondoid coordination polymer the nitrogen atoms of the molecular hmt show Cu–Cu–N bond angles are almost linear at 176.7°, as shown in Fig. 3. Diamondoid frameworks have a high propensity for interpenetration [14], but due to the presence of bulky  $\text{Cu}_2(\text{OBz})_4$  moieties, the interpenetrating structure is not formed in the present case [14,34]. Complex **1** is short of any significant pi–pi or C–H/pi interactions.

The thermogravimetric (TG) analysis was performed in a  $\text{N}_2$  atmosphere on polycrystalline samples of complex **1**. The TG curve of **1** (Fig. S2, Supplementary material) shows a weight loss of 75.94% in the temperature range of 295–320 °C, which indicates that the

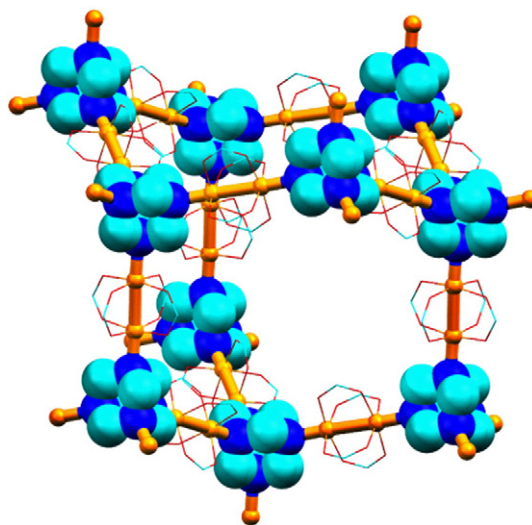


Fig. 2. Cubic diamondoid unit with dicopper spacer. [H atoms and phenyl rings are excluded for clarity] (deep blue is N atom and sky blue is C atom of hmt).

complete loss of hmt and OBz residues (calc. 76.66%) i.e. the stable cubic diamondoid skeleton ruptures into cupric oxide (CuO) in a single step. The  $T_i$  (initial temperature of decomposition) of **1** is higher than that of pure hmt (175 °C) and copper benzoate (270 °C) due to formation of the coordination network.

The magnetic properties of complex **1** as a  $\chi_M T$  vs.  $T$  plot ( $\chi_M$  is the molar magnetic susceptibility for two  $\text{Cu}^{\text{II}}$  ions) are shown in Fig. 4. The value of  $\chi_M T$  at 300 K is  $0.46 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , which is very small for two magnetically spin doublets ( $g > 2.00$ ). Starting from room temperature  $\chi_M T$  values decrease consistently to 75 K and below 75 K the value is practically  $0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . This feature is characteristic of very strong antiferromagnetic interactions. The molar magnetization at 2 K (as  $M/N\mu_B$ ) is practically  $0 N\mu_B$  clearly corroborating that the antiferromagnetic coupling is very strong.

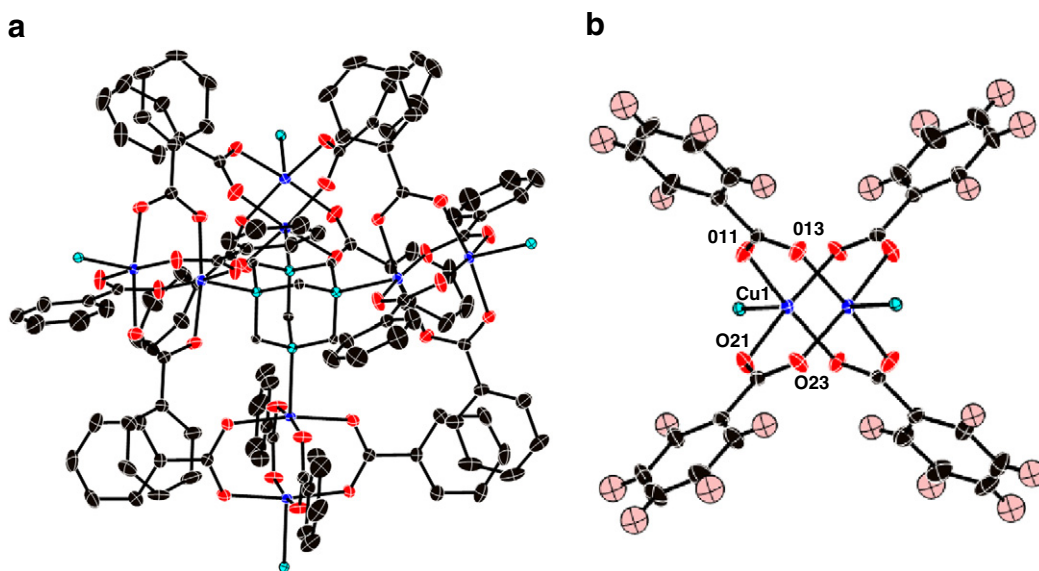


Fig. 1. a. The structure of **1**,  $[\text{Cu}_4(\text{OBz})_8(\text{hmt})]_n$  with ellipsoids at 30% probability. b. A fragment of the structure of **1**, with ellipsoids at 30% probability showing the centrosymmetric  $\text{Cu}_2(\text{OBz})_4$  moiety. Selected bond lengths [Å]: Cu1–O21 1.968(1); Cu1–O13' 1.972(1); Cu1–O11 1.964(1); Cu1–O23' 1.961(1); Cu1–N1 2.186(1); Cu1–Cu1' 2.565(1). Bond angles [°]: O23'–Cu1–O11 90.29(6); O23'–Cu1–O21 170.18(5); O11–Cu1–O21 88.65(6); O23'–Cu1–O13' 88.80(5); O11–Cu1–O13' 170.33(5); O21–Cu1–O13' 90.61(6); O23'–Cu1–N1 94.86(5); O11–Cu1–N1 97.68(5); O21–Cu1–N1 94.96(5); O13'–Cu1–N1 91.98(5). Symmetry element, ' = 1-x, 1-y, -z.

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