



# Single crystal EPR spectroscopy, magnetic studies and catalytic activity of a self-assembled $[2 \times 2]$ $\text{Cu}_4^{\text{II}}$ cluster obtained from a carbohydrazone based ligand



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## ARTICLE INFO

### Article history:

Received 27 September 2014

Accepted 28 November 2014

Available online 27 December 2014

### Keywords:

Single crystal EPR  
Magnetic studies  
Catalytic epoxidation  
 $[2 \times 2]$   $\text{Cu}_4^{\text{II}}$  cluster  
Exchange coupling

## ABSTRACT

A new tetranuclear  $[2 \times 2]$  cluster of Cu(II) with a symmetric carbohydrazone based ligand,  $[\text{Cu}_4\text{L}_4](\text{NO}_3)_4 \cdot 1.6(\text{H}_2\text{O})$  (**1**), {where HL donates bis-[(*E*)-*N'*-(1-(pyridin-2-yl)ethylidene)]carbohydrazone} was synthesized and characterized by spectroscopic methods and X-ray analysis. The EPR spectra were performed on single crystals of complex **1** at various temperatures and allowed the identification and separation of two types of magnetic objects contributing to magnetism: single atoms of Cu(II) and a tetranuclear  $\text{Cu}_4$  cluster. The main values of the *g*-factor and hyperfine structure were determined for single ions of Cu(II). The copper atoms in the tetramer are coupled antiferromagnetically with an isotropic antiferromagnetic exchange  $J = 215 \text{ K}$  ( $149.4 \text{ cm}^{-1}$ ). A small anisotropic exchange of the order of  $0.06 \text{ K}$  ( $0.04 \text{ cm}^{-1}$ ) is responsible for the initial zero-field splitting of the energy levels in the tetramer spectrum. Magnetic measurements of complex **1** confirmed the existence of a strong antiferromagnetic exchange coupling between four Cu(II) ions. Complex **1** showed high potential for the catalytic and selective oxidation of *cis*-cyclooctene with aqueous  $\text{H}_2\text{O}_2$ .

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## 1. Introduction

The construction of multinuclear transition metal complexes (MTMCs) remains a popular research area in the field of coordination and material chemistry [1]. This is mainly due to the peculiar structure diversity of MTMCs and their potential application as functional materials in fields such as catalysis [2], photochemistry [3], ion exchange [4], sensor technology [5] and magnetic materials [6]. In recent years polynuclear  $[2 \times 2]$ ,  $[3 \times 3]$  and  $[n \times n]$  molecular grid systems containing conformationally rigid tetranuclear macrocyclic ring systems with approximately  $90^\circ$  bond angles about each metallic corner have attracted the eyes of various research groups [7]. Some of these clusters show strong magnetic interactions and single molecule magnet (SMM) behavior [8]. In this context, copper(II) complexes are of particular interest because of the flexible coordination sphere of the Cu(II) ion and the versatile applications of its complexes in various fields such

as magnetism [9], biology [10] and medicine [11]. As catalysts, for example, Cu(II) complexes show catalytic activities for the epoxidation of olefins [12], oxidation of alkanes [13], sulfoxidation [14], cycloaddition [15] and polymerization reactions [16].

The controlled preparation of MTMCs with pre-established structures, properties and functions is one of the challenges in synthetic coordination chemistry. Among the various strategies for the design of MTMCs, the self-assembly reaction between metal sources and specifically designed precursors may lead to various interesting polynuclear structures [17]. However, the self-assembly of materials for this kind of complex does not occur by chance and requires structural specificity together with particular multi-dentate ligands [18]. The structure of the ligand plays the most important role in the construction of MTMCs [19]. Some hydrazone based ligands bearing multi-dentate donor atoms in specific regions are good candidates for the design of grid-like metal ion arrays, and  $[4 \times 4]$  and  $[3 \times 3]$  grid networks of Cu(II) have been reported by a symmetric multidentate hydrazone ligand [20]. Carbohydrazone based ligands are a special type of symmetric ligand in the hydrazone family which are ideal precursors for the design of  $[2 \times 2]$  clusters. Surprisingly, however, there are a few reports

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including Fe [21], Cd [22], Zn [23] and Co [24] examples concerning structural characterization of this type of system. Recently, it has been reported that lanthanide complexes of carbohydrazone based ligands show SMM behavior [25]. To the best of our knowledge and according to the reported structures in the Cambridge Structural Database (CSD) [26], there are no reports regarding the structures of  $[2 \times 2]$  Cu complexes using symmetric hydrazone ligands. Furthermore, understanding the magnetic interactions in novel  $[2 \times 2]$  clusters with symmetric ligands will be interesting. The exchange clusters of magnetic ions in the MTMCs are the simplest ferromagnets or antiferromagnets where exchange interactions between a small numbers of magnetic ions has to be taken into account. On the other hand, their magnetic properties depend strongly on the symmetry and electronic nature of the magnetic ions and the structures of the nearest neighboring ligands. These factors strongly affect the EPR spectrum. The EPR technique is known to be a useful tool in the study of exchange clusters, ensuring its effectiveness because of the high sensitivity, selectivity and large analytical background accumulated over many decades of using EPR. In this article we report the synthesis, crystal structure, EPR spectrum, magnetic behavior and catalytic activity of a tetranuclear  $[2 \times 2]$  cluster of Cu(II) with a symmetric carbohydrazone based ligand. To achieve the full advantage of using EPR spectroscopy, the presented EPR study was performed on single crystals.

## 2. Experimental

### 2.1. Materials and instrumentations

All starting materials were purchased from Acros and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded as KBr disks with a Bruker FT-IR spectrophotometer (model: TENSOR 27). UV–Vis spectra of solutions were recorded on a thermo spectronic, Helios Alpha spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ligand in DMSO- $d_6$  solution were measured on a Bruker 250 MHz spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. The atomic absorption analysis was carried out using Varian Spectra AA-220 equipment. The magnetic susceptibility and magnetization vs. magnetic field were measured with a Quantum Design SQUID MPMS XL magnetometer in a magnetic field up to 5 T and in the temperature range 2–300 K. The magnetic susceptibility measurements were carried out both in the zero-field-cooled (ZFC) and field-cooled (FC) modes. No differences between the ZFC and FC results and no magnetic phase transitions were observed. The EPR measurements were carried out using a Bruker EMX spectrometer working at a fixed frequency of 9.25 GHz (X-band) with an Oxford helium-flow cryostat instrument operating in the temperature range from 3.8 to 300 K. A 100 kHz magnetic field modulation and phase sensitive detection were used to record the derivative of the absorbed microwave power. The samples were maintained in a rotatable sample holder to record the angular variation of the EPR spectra.

### 2.2. Synthesis of bis-[(E)-N'-(1-(pyridin-2-yl)ethylidene)]carbohydrazone (HL)

A methanol (10 mL) solution of carbohydrazone (0.50 g, 5.55 mmol) was added dropwise to a methanol solution (10 mL) of 2-acetylpyridine (1.34 g, 11.10 mmol) and the mixture was refluxed for 6 h. The solution was evaporated on a steam bath to 5 mL and cooled to room temperature. The resulting white precipitate was separated and filtered off, washed with 5 mL of cooled methanol and recrystallized. Yield: 95% (1.56 g). *Anal. Calc.* for  $\text{C}_{15}\text{H}_{16}\text{N}_6\text{O}$  (MW = 296.33): C, 60.80; H, 5.44; N, 28.36. Found: C,

60.73; H, 5.46; N, 28.42%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3445 (m, br), 3355 (m), 3206 (m, N–H), 3061 (m), 2923 (m), 1700 (vs C=O), 1680 (vs), 1578 (m), 1518 (s), 1462 (s), 1433 (s), 1310 (w), 1261 (s), 1132 (s), 991 (w), 808 (m), 788 (s), 739 (m), 598 (w), 528 (w), 441 (w), 404 (w).  $^1\text{H}$  NMR (250.13 MHz, DMSO- $d_6$ , TMS)  $\delta$  (ppm): 10.87 (s, 2H, N–H), 8.61 (d, 2H,  $J = 7.25$  Hz), 8.12 (d, 2H,  $J = 7.5$  Hz), 7.91 (m, 2H), 7.43 (t, 2H,  $J = 7.5$  Hz), 2.45 (s, 6H).  $^{13}\text{C}$  NMR (250.13 MHz, DMSO- $d_6 + \text{D}_2\text{O}$ )  $\delta$  (ppm): 7.39–8.70 (10 H, aromatic), 2.59 (s, 6H).  $^{13}\text{C}$  NMR (62.90 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 12.4, 120.8, 124.7, 136.4, 144.9, 149.1, 152.1, 157.3. UV–Vis (in  $\text{CH}_3\text{OH}$ ,  $c = 5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ,  $\lambda_{\text{max}}$  [nm] with  $\epsilon$  [ $\text{M}^{-1} \text{cm}^{-1}$ ]): 214 (33 000), 298 (36 000), 380<sup>sh</sup> (5600).

### 2.3. Synthesis of the complex $[\text{Cu}_4\text{L}_4](\text{NO}_3)_4 \cdot 1.6(\text{H}_2\text{O})$ (1)

The appropriate amount of the ligand HL (0.296 g, 1 mmol) was dissolved in methanol (30 mL) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.242 g, 1.00 mmol) was added. The solution was gently refluxed for 6 h. After cooling, the resulting solid was filtered off, washed with cooled absolute ethanol and dried at 100 °C. Purple crystals of **1** were prepared by slow solvent evaporation over one week. Yield 77% (0.33 g). *Anal. Calc.* for  $\text{C}_{60}\text{H}_{63.2}\text{Cu}_4\text{N}_{28}\text{O}_{17.6}$  (MW = 1712.34): C, 42.09; H, 3.72; N, 22.90; Cu, 14.84. Found: C, 41.95; H, 3.75; N, 22.86; Cu, 14.78%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3413 (m, br), 3058 (w), 1622 (m), 1601 (m), 1573 (s), 1548 (s), 1469 (m), 1384 (vs), 1353 (m), 1267 (m), 1155 (s), 1088 (m), 1011 (m), 789 (m), 775 (m), 699 (w), 570 (w), 403 (w). UV–Vis (in  $\text{CH}_3\text{OH}$ ,  $c = 2.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ,  $\lambda_{\text{max}}$  [nm] with  $\epsilon$  [ $\text{M}^{-1} \text{cm}^{-1}$ ]): 221 (100 800), 369 (60 600), 470 (32 200), 695 (500).

### 2.4. X-ray crystallography

A summary of the crystal data and refinement details for complex **1** are given in Table 1. Only special features of the analyses are

**Table 1**  
Crystallographic data of **1**.

	Complex <b>1</b>
Net formula	$\text{C}_{60}\text{H}_{60}\text{Cu}_4\text{N}_{24}\text{O}_4(\text{NO}_3)_4 \cdot 1.6(\text{H}_2\text{O})$
$M_r$ ( $\text{g mol}^{-1}$ )	1712.34
Crystal size (mm)	$0.25 \times 0.20 \times 0.15$
Crystal shape	block
Color	purple
$T$ (K)	100(2)
Radiation ( $\text{\AA}$ )	Mo $K\alpha$ (0.71073)
Diffractometer	Xcalibur PX with Onyx CCD
Crystal system	tetragonal
Space group	$I4_1/a$
$a, b$ ( $\text{\AA}$ )	13.929(3)
$c$ ( $\text{\AA}$ )	35.16(2)
$V$ ( $\text{\AA}^3$ )	6822(5)
$Z$	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.667
$\mu$ ( $\text{mm}^{-1}$ )	1.32
Absorption correction	analytical
Reflections measured	33 214
$R_{\text{int}}$	0.027
$h, k, l$	$-19 \rightarrow 19, -14 \rightarrow 19, -50 \rightarrow 50$
$\theta$ range	$2.9\text{--}30.6$
Observed reflections	5242
Hydrogen refinement	mixed
Reflections in refinement	4003
Parameters/restraints	297/18
$F(000)$	3504
$R(F_{\text{obs}})$	0.028
$R_w(F^2)$	0.081
$S$	1.03
Shift/error <sub>max</sub>	0.001
Maximum/minimum electron density	0.39/−0.29
( $\text{e \AA}^{-3}$ )	

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