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# An unusual half-open cubane-like tetranuclear copper(II) complex supported by both $\mu$ -alkoxo and $\mu_3$ -hydroxo bridges: Structure, magnetic properties, EPR and DFT studies

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#### 1. Introduction

# Supramolecular chemistry is an actively pursued area of research which involves the relation between organic ligands and metal ions to achieve the result of multinuclear aesthetical frameworks in the nanometer range [1–5]. Hence, the use of suitable bridging units and well-designed polydentate ligands can afford an exciting array of polynuclear coordination complexes with new aesthetical building blocks [3,4]. High nuclearity transition metal complexes are studied enthusiastically because of their relevance for the multi-metal active sites of metalloproteins as well as for their importance in the field of molecular magnetism [6,7]. Copper(II) complexes are of particular interest for both structural and functional modes of performance [8,9].

Over the years particular emphasis has been placed on copper because of its central role in biology and its diverse role and plasticity effect in coordination chemistry [10,11]. Moreover, from a magneto-structural point of view, multi-copper complexes have been extensively studied by both experimental and theoretical approaches [8,9]. In addition, they find use in the development of new functional molecule based materials [12–15]. Interest has also

#### ABSTRACT

The compound 4-methyl-2,6-bis[(2-(pyridin-2-yl)hydrazinylidene)methyl]phenol (H-PHMP) was prepared by the direct condensation of 2,6-diformyl-4-methylphenol (PCDA) and 2-hydrazinopyridine. It reacts with copper(II) nitrate to yield a self-assembled, both alkoxo- and hydroxo-bridged, tetranuclear homoleptic copper(II) complex, [Cu<sub>4</sub>(PHMP)<sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O (**1**), with a [Cu<sub>4</sub>( $\mu$ -O)<sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>]<sup>4+</sup> half-open cubane core. Compound **1** is composed of two dinuclear [Cu<sub>2</sub>(PHMP)] units linked by the two  $\mu$ -bridging alkoxide oxygen atoms of the PCDA backbone. Variable temperature magnetic susceptibility measurements indicate the existence of antiferromagnetic exchange interactions ( $J_1$  = -304.0 cm<sup>-1</sup>,  $J_2$  = -127.3 cm<sup>-1</sup> and g = 2.05) in complex **1**. The exchange pathway parameters were also evaluated from density functional theoretical calculations and fully agree with the experimental findings.

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grown in the design and in the magnetic properties of polynuclear molecules and molecule based coordination architectures with mono and multi-dimensional frameworks. The main inspiration of such studies stems from the understanding of the fundamental science of magnetic interactions and magneto-structural correlations in molecular systems [12–15].

In this context, tetranuclear cubane-like copper(II) complexes have acquired unique attention because of their scarce findings in nature [16–18]. These complexes are particularly interesting for their intermediate size between the simplest binuclear complexes and bulk materials, which may develop completely new magnetic properties, thus providing good models of nanometer sized magnetic particles [2,5]. Nevertheless, although many chiral or achiral polydentate ligands containing hydroxyl groups as terminal coordinating atoms have been employed for the synthesis of cubane-like copper(II) complexes [16–18], examples of PCDA derived ligands to form half-open cubane-like copper(II) complexes have not yet been reported. Hence, detailed new examples of different systems with well-designed structural features and correlated physical properties are needed to further understand the magnetic exchange between bridged metals.

The present work explores the synthesis and characterization of an unusual half-open cubane-like tetranuclear copper(II) complex of a PCDA derived polydentate ligand. Since these particular types of open half-cubane are rare [18], we also report an experimental



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study of its magnetic properties and carry out DFT calculations to determine the relevant exchange pathway parameters.

# 2. Experimental

# 2.1. Materials

2-Hydrazino pyridine was purchased from Aldrich and was used as received. Other commercially available chemicals and solvents were used and purified by standard procedures [19].

## 2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) of H-PHMP and metal complex 1 were carried out at the Laboratório de Análises do Instituto Superior Técnico (Lisbon, Portugal) with a Perkin Elmer CHNS/O analyzer 2400. The electronic spectrum of 1 in purified CH<sub>3</sub>OH solution was recorded on a Hitachi model U-3501 spectrophotometer. The <sup>1</sup>H NMR (in d<sub>6</sub>-DMSO) spectrum of the ligand was recorded with a Bruker AM 300L (300 MHz) superconducting FT-NMR. IR spectra (KBr pellet, 4000–500 cm<sup>-1</sup>) were recorded on a Perkin Elmer model 883 infrared spectrophotometer. The mass spectrum of the ligand was recorded on a JEOLJMS-AX 500 mass spectrometer. Simple single point room temperature magnetic susceptibility was measured with a PAR 155 vibrating sample magnetometer. Variable temperature magnetic susceptibility measurements for the compound were carried out on polycrystalline samples at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer apparatus in the range 2-300 K under magnetic fields of approximately 500 G (2-30 K) and 1000 G (35-300 K). Diamagnetic corrections were estimated by using the appropriate Pascal constant values [20]. The X-band EPR spectra were measured either at room temperature (RT) or at liquid nitrogen (LN) temperature (77 K) on a Bruker ESP 300E spectrometer. The ESP 300E spectrometer was operated at ~9.51 GHz with a frequency modulation of 100 kHz. While keeping the resolution at 2048 points, the microwave power was adjusted to 20 dB attenuations and the receiver gain was set to either  $3.2 \times 10^5$  or  $4.0 \times 10^5$ . To improve the signal to noise ratio, 10 scans of each sample were accumulated. The spectral acquisition parameters were constant for each batch of experiments. All measurements were done using 3 mm quartz tubes (Wilmad 707-SQ-250M). The EPR spectra were simulated using an EPR simulation program [21].

# 2.3. Synthesis and characterization of the compounds

# 2.3.1. Preparation of PCDA

PCDA was prepared following an establish method [22].

# 2.3.2. Synthesis of H-PHMP

A methanolic solution (20 mL) of 2-hydrazino pyridine (0.218 g, 2 mmol) was added dropwise to a methanolic solution (15 mL) of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol) with constant stirring (Scheme 1). The stirring was continued for 30 min, then the mixture was refluxed for 5 h and finally cooled to room temperature and filtered. The volume of the filtrate was reduced to 15 mL with a rotary evaporator. A yellow microcrystalline solid was obtained, which was filtered, washed thoroughly with cold methanol and dried in vacuo over fused CaCl<sub>2</sub>. Yield: 0.305 g, 80 %. M.P. 245 °C (decomp.). MS (m/z): 346 (M<sup>+</sup>, 100%). IR/cm<sup>-1</sup>: 3369 ( $v_{N-H}$ ); 1661(s), 1493 ( $v_{C=C}$ ), 1597(s) ( $v_{CO/CN}$ ), 1051(s) ( $v_{N-N}$ ), 1023(s)  $v_{(PY)}$ . Elemental *Anal.* Calc. for C<sub>19</sub>H<sub>18</sub>N<sub>6</sub>O (MM = 346.39): C, 65.89; H, 5.20; N, 24.27. Found: C, 65.7; H, 5.3; N, 24.2%.

The ESI-mass spectrum of H-PHMP is shown in Fig. SI-1. The molecular ion peak was found at m/z 369 (M+Na<sup>+</sup>) with 100% probability for the formation of H-PHMP.

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Scheme 1. Schematic representation and preparation of H-PHMP and one perspective of its binding mode in the complex isolated.

Table 1	l
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Experimental crystallographic data for complex 1.

Empirical formula	$C_{38}H_{54}Cu_4N_{16}O_{25}$
Formula weight	1389.13
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	16.5486(8)
b (Å)	17.0167(5)
c (Å)	20.2529(9)
α (°)	90
β (°)	107.944(5)
γ (°)	90
Volume (Å <sup>3</sup> )	5425.9(4)
Z	4
Densitycalc (Mg m <sup>-3</sup> )	1.698
Absorption coefficient (mm <sup>-1</sup> )	1.645
F(000)	2840
Crystal size (mm <sup>3</sup> )	$0.52 \times 0.47 \times 0.38$
$\theta$ range (°) for data collection	4.68-32.64
Index ranges	$-25 \leqslant h \leqslant 24$
	$-24 \leqslant k \leqslant 17$
	$-28\leqslant l\leqslant 28$
Goodness-of-fit on F <sup>2</sup>	0.915
Completeness to theta = 25.00°	98.6%
Independent reflections	17688 [R(int) = 0.0575]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84022
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	17688/10/758
Reflections collected	39493
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0625, wR = 0.1676$
R indices (all data)	$R_1 = 0.1394, wR_2 = 0.1866$
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.865 and -0.983

#### Table 2

Selected bond distances (A) and angles ( $^{\circ}$ ) for 1.	elected bond distances (A	<ol> <li>and angles (</li> </ol>	°) for 1.
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Bond distances (Å)			
Cu(1)-O(2A)	1.924(3)	Cu(3)-O(2A)	2.487(3)
Cu(1)-N(2A)	1.940(4)	Cu(3)-O(21N)	2.534(3)
Cu(1)-O(1A)	1.944(3)	Cu(3)-Cu(4)	2.898(7)
Cu(1)-N(1A)	1.973(3)	Cu(4)-N(3B)	1.931(4)
Cu(1)-O(11N)	2.404(3)	Cu(4)-O(2B)	1.932(3)
Cu(1)-O(1B)	2.882(3)	Cu(4)-O(1B)	1.955(3)
Cu(1)-Cu(2)	2.930(7)	Cu(4)-N(4B)	1.956(4)
Cu(2)-O(2A)	1.914(3)	Cu(4)-O(22N)	2.339(3)
Cu(2)-N(3A)	1.944(3)	Cu(4)-O(1A)	3.126(3)
Cu(2)-O(1A)	1.947(3)	N(2A)-C(6A)	1.312(6)
Cu(2)-N(4A)	1.964(3)	N(2A)-N(5A)	1.342(5)
Cu(2)-O(2B)	2.397(3)	N(3A)-C(14A)	1.284(5)
Cu(2)-O(12N)	3.265(5)	N(3A)-N(6A)	1.351(5)
Cu(3)-N(2B)	1.938(3)	N(2B)-C(6B)	1.294(5)
Cu(3)-O(2B)	1.944(3)	N(2B)-N(5B)	1.365(5)
Cu(3)-O(1B)	1.968(3)	N(3B)-C(14B)	1.275(6)
Cu(3)-N(1B)	1.970(4)	N(3B)-N(6B)	1.376(5)
Rond angles (°)			
O(2A) - Cu(1) - O(1A)	80.87(11)	O(2A) = Cu(2) = O(1A)	81 04(11)
O(2A) - Cu(1) - O(11N)	97 15(12)	O(2A) - Cu(2) - O(2B)	84 82(10)
O(1A) - Cu(1) - O(11N)	103 59(12)	O(1A) - Cu(2) - O(2B)	91.29(11)
O(2A)-Cu(1)-O(1B)	75.71(10)	O(2A)-Cu(2)-O(12N)	73.89(10)
O(1A)-Cu(1)-O(1B)	82.49(10)	O(1A)-Cu(2)-O(12N)	78.46(11)
O(11N) - Cu(1) - O(1B)	169.95(11)	O(2B)-Cu(2)-O(12N)	157.50(9)
O(2B)-Cu(3)-O(1B)	81.23(12)	O(2B)-Cu(4)-O(1B)	81.86(12)
O(2B)-Cu(3)-O(2A)	81.77(10)	O(2B)-Cu(4)-O(22N)	100.06(13)
O(1B)-Cu(3)-O(2A)	85.39(10)	O(1B)-Cu(4)-O(22N)	91.03(12)
O(2B)-Cu(3)-O(21N)	89.62(12)	O(2B)-Cu(4)-O(1A)	71.86(10)
O(1B)-Cu(3)-O(21N)	85.90(12)	O(1B)-Cu(4)-O(1A)	75.93(10)
O(2A)-Cu(3)-O(21N)	168.59(10)	O(22N)-Cu(4)-O(1A)	165.34(10)
Cu(1) - O(1A) - Cu(2)	97.73(13)	Cu(1)-O(2A)-Cu(3)	106.14(11)
Cu(1) - O(1A) - Cu(4)	96.70(10)	Cu(3) - O(1B) - Cu(1)	91.83(10)
Cu(2) - O(2A) - Cu(3)	94.89(10)	Cu(4) - O(2B) - Cu(3)	96.81(12)
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#### 2.3.3. Synthesis of $[Cu_4(PHMP)_2(\mu_3-OH)_2(NO_3)_2](NO_3)_2 \cdot 9H_2O(1)$

H-PHMP (0.346 g, 1 mmol) was added to a hot solution of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.591 g, 2.0 mmol) in purified CH<sub>3</sub>OH (30 mL). The suspension was stirred for an additional 1 h until complete dissolution of the compound. The resulting deep green solution was filtered to remove any solid and left at room temperature. Rectangular dark green crystals were isolated after standing for several days. Yield: 0.749 g, 80%. IR/cm<sup>-1</sup>: 3401, 3385 ( $\nu_{NH/H2O}$ ); 1625(s), 1539(s) ( $\nu_{CO/CN}$ ); 1084(s) ( $\nu_{N-N}$ ); 1019(s) ( $\nu_{py}$ ). UV–Vis ( $\lambda_{max}/nm$ ): 453, 417, 375, 345, 248.  $\mu_{RT}$  2.95 B.M. Elemental *Anal.* Calc. for [Cu<sub>4</sub>(PHMP)<sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (**1**) (MM = 1387.12): C, 32.87; H, 3.75; N, 16.15. Found: C, 32.8; H, 3.8; N, 16.1%.

#### 2.3.4. Single crystal X-ray diffraction study of 1

Selected crystal data of 1 are given in Table 1 and selected metrical parameters are also listed in Table 2. Data collection of 1 was made using an Oxford Diffraction Gemini diffractometer equipped with a Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) source in the  $\omega$  scan mode at 200(2) K. Data collection, cell parameters and data reductions were carried out using the CRYSALIS RED (Oxford Diffraction Ltd., version 1.171.32.15) [23]. The structure was solved by conventional direct methods and refined by full-matrix least squares methods using  $F^2$  data. shelxs-97 and shelxl-97 programs [24] were used for the structure solution and refinement, respectively. Positions of the hydrogen atoms were calculated from the geometry of the molecular skeleton. For the water molecules some H's could be located in reasonable positions in the difference Fourier maps. Subsequently they were idealized and allowed to refine as a group. For some water molecules no reasonable positions could be located in the difference Fourier maps so these H's were not included in the refinement. The hydrogen atoms on O2(A/B) were located in difference Fourier maps and then idealized. Refinement of  $F^2$  was done against all reflections.

# 2.3.5. DFT computational details

The computational strategy to calculate the exchange coupling constants in transition metal complexes has been described previously. [25,26] For the calculation of the exchange coupling constants for any polynuclear complex with *n* different exchange constants, at least the energy of n + 1 spin configurations must be calculated. For **1** the energy corresponding to eight different spin distributions was calculated to obtain (by least-squares fitting) the six exchange coupling constants, with their standard deviations indicated in parentheses. The eight spin distributions calculated correspond to the high spin solution, S = 2 [+,+,+,+], four S = 1, [-,+,+,+], [+,-,+,+], [+,+,-,+], [+,+,+,-] and three S = 0, [-,-,+,+], [-,+,+,-], [-,+,+,-]. The calculations were carried out with GAUSSIAN03 [27] using guess functions generated with Jaguar 6.0 [28]. The hybrid B3LYP functional [29] was used in all calculations. A triple- $\xi$  all electron basis set with a two 'p' polarization function was employed for copper atoms [30] and a double- $\xi$  all electron basis set for the other elements, as proposed by Schaefer et al. [31]. All energy calculations were done including 10<sup>-8</sup> density-based convergence criterion.

# 3. Results and discussion

Using the PCDA precursor, the polytopic ligand H-PHMP was prepared by a one step synthesis, as depicted in Scheme 1. The prepared H-PHMP was characterized by IR, NMR and ESI-MS studies, as well as elemental analysis. Upon dissolving and mixing H-PHMP and Cu(NO<sub>3</sub>)<sub>2</sub> in methanol, after several days crystals of **1**, suitable for X-ray diffraction studies, were obtained.



Fig. 1. Representation of the molecular structure of compound 1.



Fig. 2. Representation and atom numbering scheme of the tetranuclear core in 1.

The <sup>1</sup>H NMR spectrum of H-PHMP in d<sub>6</sub>-DMSO is shown in Fig. SI-2. The <sup>1</sup>H NMR ( $\delta_{\rm H}$ , ppm) spectrum displays a singlet at  $\delta$  2.25 (3H) assignable to C<sub>4</sub>-CH<sub>3</sub> (benzene ring). Singlets at  $\delta$  7.36 (2H) and  $\delta$  8.26 (2H) are due to C<sub>3/5</sub>-H (benzene ring) and two imine -C-H, respectively, whilst multiplets at  $\delta$  6.75 (2H) and at  $\delta$  7.62 (2H) are ascribed to C<sub>4</sub>-H (pyridine rings) and C<sub>5</sub>-H (pyridine rings), respectively. A doublet at  $\delta$  7.02 (2H) and a triplet at  $\delta$  8.10 (2H) are ascribed to C<sub>3</sub>-H (pyridine rings) and C<sub>6</sub>-H (pyridine rings), respectively. A singlet at  $\delta$  10.97 (2H) is assignable to the two -NH protons of PHMP. A singlet at  $\delta$  11.64 (1H) confirms the presence of the phenolic -OH.

# 3.1. Molecular structure of 1

From the X-ray diffraction data, it was found that 1 consists of a half-open 'cubic' unit,  $[Cu_4(\mu-O)_2(\mu_3-OH)_2]^{4+}$ , in which the four

copper atoms are bridged with two by two by two alkoxo oxygen atoms (O1A/B) from two anionic ligands PHMP and three by three by two hydroxo groups (O2A/B). The molecular structure of  $[Cu_4(PHMP)_2(\mu_3-OH)_2(NO_3)_2](NO_3)_2\cdot9H_2O$  (1) is shown in Fig. 1 and the corresponding tetranuclear core is shown in Fig. 2. Complex 1 crystallizes in the monoclinic space group  $P12_1/n1$ ; it contains nine  $H_2O$  molecules of crystallization, this being consistent with the analytical results. Out of the four copper(II) centers, three of them, namely Cu1, Cu2 and Cu4, are penta-coordinated with a  $N_2O_3$  binding set, while the remaining copper(II) Cu3 center is hexa-coordinated with a  $N_2O_4$  binding set.

The coordination environment of Cu1, Cu2 and Cu4 are best described as square-pyramidal ( $\tau = 0.83$  for Cu1, 0.38 for Cu2 and 0.50 for Cu4, where  $\tau$  = 0 and 1 are for the perfect square pyramidal and trigonal bipyramidal geometries, respectively) [32] with the basal plane established by the O2A, N2A, N1A, O1A atoms for Cu1: O2A. N3A. N4A. O1A atoms for Cu2 and O2B. N3B. N4B. O1B atoms for Cu4 of the PCDA units of the two Schiff base ligands. The apical positions of Cu1 and Cu4 are occupied by the two nitrogen atoms (O11N and O22N) of the two  $NO_3^{-1}$  ligands at rather long donor distances, while the apical position of Cu2 is satisfied by O2B from the hydroxo group. The donor atoms of the basal coordination planes of Cu1 and Cu4 centers lie in almost same plane and the related copper(II) centers are slightly displaced (0.118 Å for the Cu1 center and 0.132 Å for the Cu4 center) towards the apical positions (O11N and O22N). The donor atoms of all basal coordination planes of Cu2 and Cu3 centers deviate by 0.013 and 0.006 Å, respectively (for Cu1 and Cu4, it is 0 Å), from the corresponding mean planes, and the related copper(II) centers are only slightly displaced (0.118 Å for Cu1, 0.051 Å for Cu2, 0.026 Å for Cu3 and 0.132 Å for Cu4) towards the apical position (O11N for Cu1, O2B for Cu2, O2A for Cu3 and O22N for Cu4).

By a self-assembly process, two [Cu<sub>2</sub>(PHMP)] building blocks form the tetranuclear complex **1** with a half-open cubane-like [Cu<sub>4</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ <sub>3</sub>-OH)<sub>2</sub>]<sup>4+</sup> core. The vertices of the cube are alternatively occupied by four copper(II) and four oxygen atoms (O1A/B and O2A/B), leading to a interlocked half-open cubane structure. Consequently, the two copper(II) centers are linked in a  $\mu$ <sub>3</sub>-bridging fashion by two O2A/B atoms of the hydroxo groups. The C13(A/B) alkoxide oxygen atoms O1A/B are deprotonated, affording a monoanionic ligand fragment.

Out of the four  $\rm NO_3^-$  anions, two are bonded to copper(II) centers and other two serve as counter ions. Each PHMP acts as a hexadentate ligand, binding two copper(II) ions, leading to two five-membered and two six-membered chelate rings with bite angles of  ${\sim}82^\circ$  and  ${\sim}90^\circ$ , respectively.

According to the Cu–O bond lengths in the  $[Cu_4(\mu-O)_2(\mu_3-OH)_2]^{4+}$  cores, the structure of **1** should be described as consisting of two dimeric  $[Cu_2(\mu-O)(\mu_3-OH)]^{2+}$  units with short (~1.91 Å) and long (~1.95 Å) Cu–O bonds within the dinuclear units. The two resulting Cu1Cu2 and Cu3Cu4 units are constituted by the respective copper-ligand moieties. These short and long Cu–O contacts lead to the non-planarity of the  $[Cu_2(\mu-O)(\mu_3-OH)]^{2+}$  core fragments of the dinuclear units. The dihedral angles between the CuO<sub>2</sub> planes of the resulting butterfly-type structures of the Cu1Cu2 and Cu3Cu4 units are 171° and 158°, respectively. Hence, this leads to Cu–O–Cu bond angles at the bridging oxygen atoms within the dimeric units Cu1Cu2 and Cu3Cu4 in the range between 98° and 96° (Table 2), which are relatively small angles for alkoxobridged compounds with a Cu<sub>2</sub>O<sub>2</sub> core fragment.

It is interesting to note that the Cu1Cu2 pair can be virtually transformed into the analogous dimer found in complex **1** by simply rotating through an angle of 90° in the plane of the paper around the  $C_2$  axis. Complex **1** also has an inversion center. The Cu1…O1B and Cu4…O1A axial contacts (2.882 and 3.126 Å) are very weak when compared with the Cu…O axial distances usually



**Fig. 3.** Plot of  $\chi_M T vs T$  for **1** (molar value referred to four Cu atoms). The solid line corresponds to the best fit (see text).

reported for octahedral arrangements around copper [16–18]. Also the Cu2···O12N contact (3.265 Å) is much longer than the common coordination distances [16–18]. Therefore, the coordination arrangements around the Cu1, Cu2 and Cu4 centers should be regarded as predominantly square pyramidal, and consequently the  $[Cu_4(\mu-O)_2(\mu_3-OH)_2]^{4+}$  unit should be considered as an 'open cubane-like core'. In the crystal structure of **1**, an additional nine water molecules of crystallization are present, located at fully occupied positions in the asymmetric unit.

A space filling packing diagram of 1 is shown in Fig. SI-3, and it is interesting to note that complex **1** forms a grid-like cage throughout the whole lattice, thus acquiring stability. To the best of our knowledge, the title compound represents the first structurally characterized example of a tetranuclear copper(II) complex in which two hydroxo groups and two N<sub>4</sub>O-pentadentate ligands (involving an alkoxo oxygen, two imine nitrogens as central donors and two terminal pyridine nitrogen atoms) are coordinated to give a copper(II) complex with a half-open single cubane core,  $[Cu_4(\mu O_{2}(\mu_{3}-OH)_{2}^{4+}$ . In **1**, the two dinuclear  $[Cu_{2}(\mu-O)(\mu_{3}-OH)]^{2+}$  units are puckered to each other, the angle between the two planes being  $\sim$ 4°. The only known example of a copper(II) complex containing a half-open Cu<sub>4</sub>O<sub>4</sub> cubane-like arrangement is [NEt<sub>4</sub>]<sub>3</sub>  $[WOS_3(CuI)_3(\mu_2-I)]$ ·H<sub>2</sub>O, reported by Shu Shi et al. [18]. The skeleton of the anionic cluster is composed of one W, three  $\mu_3$ -S, three Cu and one  $\mu_2$ -I atom. So, the title compound is totally different from the point of view of the skeleton atom arrangements in the cubane core.

#### 3.2. Further characterization of 1

Polycrystalline samples of **1** gave satisfactory C, H and N analyses. Spectral properties of the complexes are briefly described below.

# 3.2.1. IR spectra

The IR spectrum of **1** was recorded in the region 4000– 500 cm<sup>-1</sup>. The stretching frequency of the imine (–CH=N) group in the ligand was observed near 1597 cm<sup>-1</sup>; upon complexation it is shifted by 58 cm<sup>-1</sup> to ~1539 cm<sup>-1</sup>, suggesting coordination via the imine group [33–35]. In metal complexes this vibration is often coupled to vibrations in the nearby aromatic rings [33,34]. The increase in  $v_{(N-N)}$  from 1051 to 1084 cm<sup>-1</sup> in **1** is due to the increase in the double bond character of N–N, offsetting the loss of electron density via donation to the metal ion. In addition **1** shows a broad band around 3400 cm<sup>-1</sup> for  $v_{(N-H)}$  of the hydrazino moieties and  $v_{(O-H)}$  of hydrogen bonded H<sub>2</sub>O; the  $v_{(C-O)}$  stretching also decreases from 1625 cm<sup>-1</sup> (in H-PHMP) to 1661 cm<sup>-1</sup> (in **1**).

#### 3.2.2. Electronic spectra

The UV–Vis spectrum of **1** was recorded at room temperature in methanol. It depicts six bands at 248, 345, 375, 417, 453 and 650 nm. The low intensity broad band at ca. 650 nm may be attributed to the d–d transitions of the copper(II) ion [36]. The intense bands in the 300–453 nm range can be assigned to both the  $n \rightarrow \pi^*$  transitions of the imine groups and to LMCT bands [37,34]. The higher energy bands below 300 nm may be attributed to the  $\pi \rightarrow \pi^*$  ring transitions. As emphasized below, in solution complex **1** does not maintain its integrity as  $[Cu_4(PHMP)_2(\mu_3-OH)_2(NO_3)_2]^{2*}$ .

# 3.3. Variable temperature magnetic susceptibility studies and DFT calculations

The variable temperature magnetic data for crystals of **1** were recorded between 300 and 2 K, and the plot of  $\chi_M T$  vs *T* is shown in Fig. 3. At 300 K, a  $\chi_M T$  value of 1.103 cm<sup>3</sup> mol<sup>-1</sup> K is observed (for the tetranuclear unit), smaller than that expected for four uncoupled *S* = 1/2 ions with *g* = 2.0 (1.5 cm<sup>3</sup> K mol<sup>-1</sup>). On cooling,



**Fig. 4.** (a) Exchange coupling constants in 1:  $J_4$  (interaction between Cu1–Cu3) and  $J_5$  (interaction between Cu2–Cu4) are not represented for clarity. (b) Schematic view of the two dinuclear models for Cu<sub>2</sub>O<sub>2</sub> used in the B3LYP calculation. (c) Structure of the [Cu3–Cu4] core showing  $\tau$  (out of plane hydrogen displacement) and  $\gamma$  (hinge distortion) angles.



**Fig. 5.** Antiferromagnetic interaction, *J*, vs the out-of-plane hydrogen atom displacement,  $\tau$ .  $J_1$  and  $J_2$  are represented with circles and squares, respectively. The open symbols are the  $J_{B3LYP}$  values for the dinuclear models. The solid ones correspond to *J* values of the tetranuclear compound calculated for  $\tau = 20^{\circ}$ .

 $\chi_M T$  decreases quickly, indicating a very strong antiferromagnetic coupling, reaching a value close to zero at 30 K, indicating diamagnetic behaviour.

Based on the topology and the structural parameters of the compound, which is a tetramer built of two consociated dimers, we count six exchange pathways in the compound, grouped into six averaged different exchange parameters,  $J_1$ – $J_6$ , corresponding to the different alkoxo bridges between the copper atoms.

The analysis of the experimental susceptibility data was carried out using the CLUMAG program [38], resolving the following Hamiltonian:

$$H = -J_1(S_1 \cdot S_2) - J_2(S_3 \cdot S_4) - J_3(S_2 \cdot S_3) - J_4(S_1 \cdot S_3) - J_5(S_2 \cdot S_4) - J_6(S_1 \cdot S_4)$$
(1)

Here the numbering of the spins follows the numbering of the copper atoms in Fig. 4a.

In the fitting attempts of the experimental data we obtained different low *J* values for  $J_3$ – $J_6$ , with large errors depending of the starting parameters, while the  $J_1$ ,  $J_2$  and 'g' parameters always converged to values of ca. –300 cm<sup>-1</sup>, –125 cm<sup>-1</sup> and 2.05, respectively. Taking into account the expected relatively low  $J_3$ – $J_6$ values in contrast with  $J_1$  and  $J_2$ , we can consider that in the compound the magnetic coupling is mainly dominated by those strongest interactions, which 'reduces' the system to two dinuclear units magnetically isolated in the compound. To test this approximation, the experimental magnetic data were fitted again to the following simplified Hamiltonian:

$$H = -J_1(S_1 \cdot S_2) - J_2(S_3 \cdot S_4)$$
(2)

The best fit parameters found in this case were:  $J_1 = -304.0 \text{ cm}^{-1}$ ,  $J_2 = -127.3 \text{ cm}^{-1}$  and g = 2.05. These values are consistent with the values found in the first fit. To check the validity of



**Fig. 6.** Spin density distribution for **1** corresponding to the calculated S = 0 ground state B3LYP solution. Positive and negative values are represented as white and dark surfaces, respectively. The isodensity surface represented corresponds to a value of 0.02 e-bohr<sup>-3</sup>.

this approach, DFT calculations were carried out to evaluate the sign and the magnitude order of the six possible exchange pathways by using the experimental atomic coordinates of the compound. Based on the well known correlation established by Ruiz et al. [39] between the magnetic interaction and the out of plane hydrogen displacement ( $\tau$  angle) in dinuclear hydroxo bridged compounds (Fig. 4 b and c), as the hydrogen atoms of O2A and O2B were not detected by X-ray diffraction, we anticipate this may make the determination of the correct 'J' values more difficult as their position can influence the exchange pathways between the copper atoms.

To overcome these difficulties, two steps of calculation were done:

Step 1: The two interactions  $J_1$  and  $J_2$  between Cu<sub>1</sub>–Cu<sub>2</sub> and Cu<sub>3</sub>–Cu<sub>4</sub> atoms, respectively, were calculated separately using two dinuclear models (1 and 2) as is shown in Fig. 4b, by varying the  $\tau$  angle in the range [10–40°]. These calculations showed a linear tendency in the two models with the same slope: the antiferromagnetic interaction and absolute values increase when the  $\tau$  angle decreases, by approximately 3.2 cm<sup>-1</sup> for each degree (Fig. 5). It seems therefore that the calculated  $J_1 = -309.4$  cm<sup>-1</sup> and  $J_2 = -137.9$  cm<sup>-1</sup> values agree with the above experimental fit when the  $\tau$  angle is equal to 20°.

Step 2: The results of step 1 were used to evaluate the magnitude and the sign of the six  $J_1$ – $J_6$  values between the Cu(II) atoms in the tetranuclear compound (see computational details). The calculation yielded the following parameters:  $J_1 = -255.7(1) \text{ cm}^{-1}$ ,  $J_2 = -113.3(1) \text{ cm}^{-1}$ ,  $J_3 = +0.1(1)$ ,  $J_4 = +3.4(1)$ ,  $J_5 = +5.0(1) \text{ cm}^{-1}$  and  $J_6 = -0.3(1) \text{ cm}^{-1}$ .

It is clearly observed that the interactions corresponding to  $J_1$  and  $J_2$  are found to be strongly antiferromagnetic through  $\mu_2$ -OH and  $\mu_2$ -OR bridging ligands, with  $J_1 > J_2$  due to the larger Cu–O–Cu angle (a few degrees but enough to vary the magnitude of the

#### Table 3

Main geometrical (average) parameters and exchange coupling constants for 1.

Cu <sub>ij</sub> <sup>a</sup>	α(Cu−O−Cu)/°	$d_1(Cu-O)/Å$	$d_2(Cu \cdots Cu)/Å$	$J_{\rm B3LYP}/{\rm cm}^{-1}$ dinuclear models	$J_{\rm B3LYP}^{\rm b}/{\rm cm}^{-1}$ full structure	$J_{\rm exp}/{\rm cm}^{-1}$
Cu <sub>12</sub>	97.7/99.6	1.919/1.946	2.930	-309.4	-255.7(1)	-304.0
Cu <sub>34</sub>	95.2/96.8	1.938/1.962	2.898	-137.9	-113.3(1)	-127.3
Cu <sub>23</sub>	94.9/97.0	1.929/2.442	3.265	-	+0.1(1)	-
Cu <sub>13</sub>	91.8/106.1	1.923/[2.487-2.882]	3.542	-	+3.4(1)	-
Cu <sub>24</sub>	85.9/110.3	1.932/[2.397-3.126]	3.562	-	+5.0(1)	-
Cu <sub>14</sub>	96.7/104.6	1.950/3.004	3.869	-	-0.3(1)	-

<sup>a</sup> Cu<sub>ij</sub>, i and j indicates the copper number considered in the exchange coupling in each cube face.

<sup>b</sup> The J values are calculated for  $\tau$  = 20° and the number in parentheses indicates the standard deviation of the least-squares fitting (see computational details).



Fig. 7. First derivative EPR spectra of a polycrystalline sample of 1 at room temperature (a) and at 77 K (b).



**Fig. 8.** Experimental and stimulated first derivative EPR spectrum of **1** in solution (methanol) at 77 K.

coupling, see Table 3), and to the greater hinge distortion (Fig. 4c) in the dinuclear fragment of model 2, which is  $11^{\circ}$  versus 5° for the dinuclear fragment of model 1. These two situations confirm the well-known established assumption that the increase of the Cu–O–Cu angle and the increment of the hinge distortion in the [Cu<sub>2</sub>O<sub>2</sub>] core reduce the antiferromagnetic behaviour [40].

On the other hand, the difference observed in the  $J_1$  and  $J_2$  values between the dinuclear and the tetranuclear models (-309.4/ 137.9 cm<sup>-1</sup> and -255/-113.3 cm<sup>-1</sup>) can be understood considering the conclusion recently reported by Tercero et al. [41] for 2+4 cubane compounds. The structure of this type of compound corresponds to two dinuclear entities with long Cu–O bond distances,  $d_1$ , (see Table 3) which causes an increase in the antiferromagnetic coupling between the dinuclear units. Therefore the antiferromagnetic interaction is higher in dinuclear entities than in tetranuclears ones.

The  $J_3$ – $J_6$  interactions were found to be very low ( $J_3$  and  $J_6$  are anti- or ferromagnetic close to zero, while  $J_4$  and  $J_5$  are ferromagnetic). Again these values are in agreement with the previously reported results [41], the J values usually being weak ferromagnetic or sometimes antiferromagnetic.

The spin distribution is localized mainly in  $d_{x^2-y^2}$  orbitals at the paramagnetic centers, as is observed in the spin density map represented in Fig. 6, which corresponds to the *S* = 0 ground state of the tetranuclear compound. In the bridging oxygen atoms there are two lobes with spin densities of different sign that appear

due to the presence of neighbouring Cu(II) cations with opposite spin density. This spin density is probably an artefact due to the single-determinant wave function considered. The spin population on the copper atoms is around  $0.66 e^-$  and the remaining spin density, relative to one unpaired electron, appears mainly delocalized over the oxygen and nitrogen atoms of the ligands.

# 3.4. EPR spectroscopy

The X-band EPR spectra of a polycrystalline sample of **1** at room temperature (Fig. 7a) shows an isotropic band centered at g = 2.192(3109 G for v = 9.52(96) GHz) which corresponds to the transition  $\Delta M_{\rm S}$  = ±1. No clearly detectable zero field splitting or half-filled signals were observed. The spectrum at 77 K (Fig. 7b) shows a band centered at g = 2.15 (3164 G for v = 9.52(23) GHz) which also corresponds to the transition  $\Delta M_{\rm S}$  = ±1. By simulation of the spectrum [21,42], the following gyromagnetic factors were obtained:  $g_1 = 2.049$ ,  $g_2 = 2.174$  and  $g_3 = 2.222$ . The geometric parameter G, which is a measure of the exchange interaction between the copper centers in the polycrystalline compound, is calculated using the equation: for rhombic spectra  $G = (g_3 - 2.003)/(g_1 - 2.003)$ , where  $g_{\perp} = (g_1 + g_2)/2$ . If G < 4.0, a considerable exchange interaction is indicated in the solid complexes [42]. The G value for compound **1** in the polycrystalline state at 77 K is 2.018. For complexes of this type, the parameter *R* can be indicative of the predominance of the  $d_{z^2}$  or  $d_{x^2-y^2}$  orbital in the ground state, where  $R = (g_z - g_y)/2$  $(g_y - g_x)$ . If R > 1, the greater contribution to the ground state arises from the  $d_{z^2}$  orbital and the structure is closer to a trigonal bipyramid than to a square pyramid. Instead, if R < 1, a greater contribution to the ground state arises from the  $d_{x^2-y^2}$  orbital and the structure is closer to a square pyramid than to a trigonal bipyramid [43–45]. In the present case, R = 0.384; this is in agreement with the X-ray crystal structure, magnetochemistry and the DFT results of the studied complex.

The EPR spectrum measured for a frozen solution in methanol at 77 K is depicted in Fig. 8. It is clear that the predominant EPR-active species in solution is not the same as that obtained in the solid state. The complex depicts a major signal from a 'mononuclear species' of S = 1/2. The following gyromagnetic factors are obtained:  $g_{\perp} \sim 2.084$ ,  $g_{\parallel} \sim 2.429$  [ $g_{av} \sim 2.199$ ],  $A_{\parallel} \sim 121 \times 10^{-4}$  cm<sup>-1</sup> and  $A_{\perp} \sim 12 \times 10^{-4}$  cm<sup>-1</sup> by simulation of the spectrum [42].

A weaker signal is also discernible. It is probably due to a species with strong copper(II)–copper(II) interactions. As the powder spectra are very broad and not resolved, it is not clear whether the paramagnetic species present in the solid state is the same as in solution or not. For this weaker signal, the separation between the two *Z*-components directly gives the value of 2D, which works out to be 303 G (0.0287 cm<sup>-1</sup>). The distance between the metal centres can be approximately evaluated by the use of the following equation:  $R = (0.650 g_z^2/D)^{1/3}$  [44]. Following this relationship, the copper–copper distance in the species in solution under discussion is estimated as 6.08 Å [45].

The main EPR-active complex detected in methanolic solution has  $g_{||} > g_{\perp} > 2.0023$ , revealing that the Cu(II) centers lie in a distorted octahedral coordination geometry with a predominant  $d_{x^2-y^2}$  ground state [46–48]. The representation of  $(g_{||}, A_{||})$  in the Peisach–Blumberg plot [49] lies between the N<sub>4</sub> and the O<sub>4</sub> lines, this being consistent with a N<sub>4</sub>O or N<sub>3</sub>O binding set, suggesting for the Cu complex present in methanolic solution a N<sub>3</sub>O set for the 'equatorial' donor atoms. The  $g_{||}/A_{||}$  value is ~200, is consistent with significant distortion from a planar geometry [50].

## 4. Conclusions

Over the past two decades, PCDA-derived polynuclear, heteronuclear and macrocycle containing metal complexes have been extensively studied. In this work the self-assembly of two building blocks of [Cu<sub>2</sub>(PHMP)], with PHMP<sup>-</sup> being a polydentate ligand derived from PCDA, led to the half-open cubane-like copper(II) tetranuclear complex [Cu<sub>4</sub>(PHMP)<sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (1). Compound 1 consists of a half-open cubic-like unit which is substantially distorted; this distortion is due to the geometric prerequisites given by the PCDA-based ligand (H-PHMP). The two constituting dinuclear [Cu<sub>2</sub>(PHMP)] units, with a [Cu<sub>2</sub>( $\mu$ -O)( $\mu_3$ -OH)]<sup>2+</sup> core, are stabilized by forming a half-open cubane-like building block with another dinuclear unit bridging through the  $\mu_3$ -hydroxo group supplied from the mother liquor. From the space filling packing diagram of 1 it is observed that 1 forms a grid-like cage throughout the whole lattice, thus acquiring stability.

The variable temperature magnetic study revealed that **1** shows a net antiferromagnetic interaction. Super exchange via the  $\mu$ -oxygen atoms affords an unusual antiferromagnetic interaction which is attributed to the large Cu–O–Cu bridging angles. The large Cu–O–Cu angles and the long axial Cu–O distances are responsible for the strong antiferromagnetic interaction in **1**. Besides being the first example of both an alkoxo and hydroxo bridged tetranuclear copper(II) complex with a  $[Cu_4(\mu-O)_2(\mu_3-OH)_2]^{4+}$  core, having an anti-ferromagnetic signature, complex **1** is also a rare example for the class of molecules having an half-open cubane structure.

The EPR spectroscopic data indicates that in methanolic solution complex **1** does not maintain its integrity as  $[Cu_4(PHMP)_2 (\mu_3-OH)_2(NO_3)_2]^{2+}$ ; in fact the main EPR signal recorded is characteristic of a mononuclear Cu-species.

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#### Appendix A. Supplementary data

CCDC 895171 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.poly.2013.01.044.

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