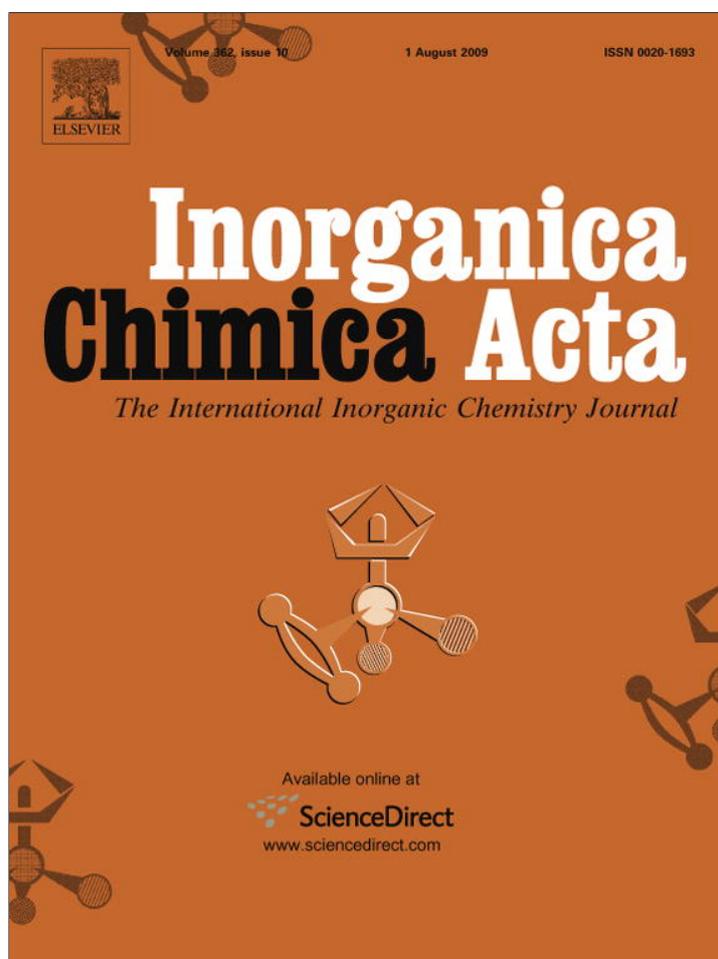


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Structure and magnetic properties of a tetranuclear Cu_4O_4 open-cubane in $[\text{Cu}(\text{L})]_4 \cdot 4\text{H}_2\text{O}$ with $\text{L}^{2-} = (E)\text{-}N'\text{-(2-oxy-3-methoxybenzylidene)benzohydrazide}$

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ABSTRACT

The *in-situ* formed hydrazone Schiff base ligand $(E)\text{-}N'\text{-(2-oxy-3-methoxybenzylidene)benzohydrazide}$ (L^{2-}) reacts with copper(II) acetate to a tetranuclear open cubane $[\text{Cu}(\text{L})]_4$ complex which crystallizes as two symmetry-independent ($Z' = 2$) S_4 -symmetrical molecules in different twofold special positions with a homodromic water tetramer. The two independent (A and B) open- or pseudo-cubanes with Cu_4O_4 cores of 4 + 2 class (Ruiz classification) each have three different magnetic exchange pathways leading to an overall antiferromagnetic coupling with $J_{1B} = J_{2B} = -17.2 \text{ cm}^{-1}$, $J_{1A} = -36.7 \text{ cm}^{-1}$, $J_{2A} = -159 \text{ cm}^{-1}$, $J_{3A} = J_{3B} = 33.5 \text{ cm}^{-1}$, $g = 2.40$ and $\rho = 0.0687$. The magnetic properties have been analysed using the $H = -\sum_{i,j} J_{ij}(S_i S_j)$ spin Hamiltonian.

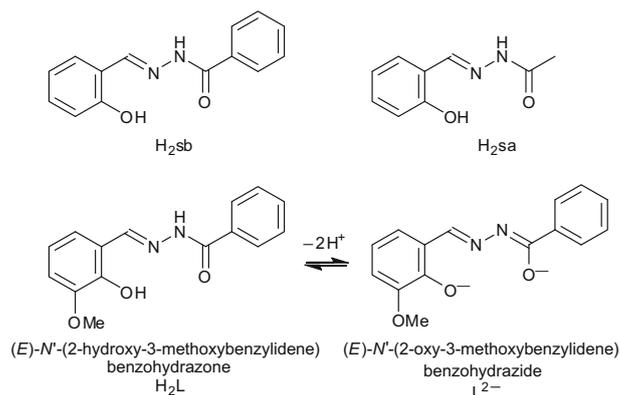
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1. Introduction

The design of polynuclear transition-metal clusters with novel magnetic properties is a major goal of current research in the field of condensed matter physics and material chemistry [1–3]. Copper(II) complexes are of particular interest from both structural and functional points of view. Tetranuclear copper(II) clusters which exhibit a large diversity of structural types, e.g. cyclic [4], pin-wheel [5], square planar [6], dimeric [7], face-to-face [8], roof-shaped [9] and cubane type [10], are of permanent interest in magnetostructural research, bioinorganic modeling, catalysis and multielectron transfer.

Salicylaldehyde benzoylhydrazone (H_2sb) possesses mild bacteriostatic activity [11] and inhibits DNA synthesis and cell growth [12]. The copper(II) complex was shown to be significantly more potent than the metal-free chelate, leading to the suggestion that the metal complex was the biologically active species. Salicylaldehyde acetylhydrazone (H_2sa) displays radioprotective properties [13], and a range of acylhydrazones have been shown to be cytotoxic, the copper complexes again showing enhanced activity. Because of the biological interest in this type of chelate system, several structural studies have been carried out on copper

[14–16] with H_2sb and analogues. Structurally there is a preference for planar, phenolato bridged Cu(II) dimers with these ligands which often exhibit antiferromagnetism [15,16].



This class of diprotic ligands typically acts as tridentate, planar chelate ligands coordinating through the phenolic and amide oxygen and the imine nitrogen atom. The actual ionization state is dependent upon the conditions and metal employed. With Cu(II) in basic media, both the phenolic and amide protons are ionized. In neutral and mild acidic solution the ligands are monoanionic. Strongly

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acidic conditions are necessary to form compounds formulated with a neutral ligand.

A few structurally characterized multinuclear complexes containing Schiff base ligands have been reported [17,18]. Herein, we describe the structural and magnetic properties of a tetranuclear hydrazide Schiff base open-cubane copper(II) complex $[\text{Cu(L)}]_4 \cdot 4\text{H}_2\text{O}$.

2. Experimental

Benzhydrazide, 2-hydroxy-3-methoxybenzaldehyde, copper(II) acetate monohydrate and solvents with high purity were purchased from Merck and Fluka and used as received. IR spectra were recorded as KBr disks with a Matson 1000 FT-IR spectrophotometer in the range of 4000–450 cm^{-1} . Microanalytical (CHN) data were obtained with a Carlo ERBA Model EA-1108 analyzer.

2.1. Synthesis of tetrakis{(E)-N'-(2-oxo-3-methoxybenzylidene)benzohydrazidocopper} tetrahydrate, $[\text{Cu(L)}]_4 \cdot 4\text{H}_2\text{O}$

Benzhydrazide (0.040, 0.33 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.044 g, 0.28 mmol) and copper(II) acetate monohydrate (0.058 g, 0.28 mmol) were placed in the main arm of the branched tube ('branched tube' method [19]). A mixture of methanol and ethanol (50:50 v/v) was carefully added to fill the arms, the tube was sealed and the reagents containing arm immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. Other solvents like $\text{H}_2\text{O}:\text{EtOH}$ and EtOH were also examined but in the methanol:ethanol mixture the crystals grew fastest. After 1 week, deep green crystals were deposited in the cooler arm, which were filtered off, washed with methanol and air dried (yield 0.20 g, 49%). $\text{C}_{60}\text{H}_{48}\text{Cu}_4\text{N}_8\text{O}_{12} \cdot 4\text{H}_2\text{O}$ (1399.29), calcd. C 51.50, H 4.03, Cu 18.16, N 8.01; found C 51.9, H 4.1, Cu 18.1, N 8.1%. IR (KBr, cm^{-1} , see Fig. S1 in Supporting information): 3415 (s, br,

2923 (s), 2854 (m), 1746 (w), 1616 (m), 1500 (vs), 1454 (s), 1369 (m), 1254 (s), 1223 (s), 1177 (w), 1108 (m), 1046 (w), 977 (w), 923 (w), 854 (w), 800 (w), 746 (m), 715 (s), 662 (w), 462 (w).

2.2. X-ray structure determination

A suitable single crystal was carefully selected under a polarizing microscope. Data Collection: Rigaku R-axis Spider with image plate detector, temperature 223(2) K, Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromator, double-pass method ω -scan. Data collection with d*trek [20], cell refinement and data reduction with Fspoc [20], empirical absorption correction. Structure Analysis and Refinement: The structure was solved by direct methods (SHELXS-97) [21]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [21]. All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms on the carbon atoms were placed at calculated positions with an appropriate riding model (AFIX 43 for aromatic CH, AFIX 33 for CH_3) and an isotropic temperature factor of $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{CH})$ and $1.5(\text{CH}_3)$, respectively. The hydrogen atoms of the water of crystallization were found and refined with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ (see Table S1 in Supporting information). Graphics were obtained with DIAMOND [22]. Computations on the supramolecular π -interactions were carried out with PLATON for Windows [23]. Crystal data and details on the structure refinement are given in Table 1.

2.3. Magnetic susceptibility measurements

Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9–300 K by means of a Quantum Design SQUID magnetometer operating at 10 000 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per Cu(II)] and the magnetization of the sample holder.

3. Results and discussion

3.1. Synthesis

The hydrazone pro-ligand H_2L was obtained by the *in-situ* condensation of benzhydrazide and 2-hydroxy-3-methoxybenzaldehyde. By potentiometric titration the acidity constant $\text{pK}_{\text{a}1}$ of the phenolic hydroxy group is about 9.00, whereas the $\text{pK}_{\text{a}2}$ value obtained for the second amide acidity constant is 10.92 in $\text{MeOH}/\text{H}_2\text{O}$ (0.9/0.1 v/v) at 25.0 °C [24]. In reaction with basic copper(II) acetate, H_2L forms a dinegative ligand and occupies three Cu(II) coordination sites [25].

The ligand H_2L shows IR bands assigned to $\nu(\text{OH})$ (3563 cm^{-1}), $\nu(\text{NH})$ (3377 and 3215 cm^{-1}), $\nu(\text{C}=\text{O})$ (1654 cm^{-1}), and $\nu(\text{C}=\text{N}) + \text{amide}$ (1608 – 1576 cm^{-1}). On complexation the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N}) + \text{amide}$ bands for the ligand are shifted, showing that coordination involves the carbonyl-O and imine-N atoms.

3.2. Crystal structure of $[\text{Cu(L)}]_4 \cdot 4\text{H}_2\text{O}$

The title compound forms a tetrameric and tetranuclear complex where each two-fold deprotonated Schiff base ligand coordinates to a Cu atom with its imine nitrogen atom, its phenolate and its amide carboxyl oxygen atoms thereby forming a six- and a five-membered chelate ring. At the same time each ligand bridges to a neighboring Cu atom through its phenolate group (Fig. 1). In the tetramer, four Cu(II) atoms and four oxygen atoms

Table 1
Crystal data and structure refinement for $[\text{Cu(L)}]_4 \cdot 4\text{H}_2\text{O}$.

Empirical formula	$\text{C}_{60}\text{H}_{48}\text{Cu}_4\text{N}_8\text{O}_{12} \cdot 4\text{H}_2\text{O}$
M/g mol ⁻¹	1399.29
Crystal size/mm	$0.33 \times 0.32 \times 0.07$
Crystal appearance	plate, green
2 θ range/°	6.06 – 54.96
h; k; l range	$\pm 27; \pm 17; -31, 33$
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.1817(9)
b/Å	13.4560(6)
c/Å	26.1343(11)
β [°]	126.795(3)
$V/\text{\AA}^3$	5964.9(4)
Z	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.558
$F(000)$	2864
μ/mm^{-1}	1.483
Max./Min. transmission	0.9033/0.6403
Reflections collected	83 126
Indep. reflections	13 630 ($R_{\text{int}} = 0.0616$)
Observed reflect [$I > 2\sigma(I)$]	10 164
Parameters refined	827
Max./Min. $\Delta\rho^a/\text{e \AA}^{-3}$	0.575/–0.438
R_1/wR_2 [$I > 2\sigma(I)$] ^b	0.0355/0.0730
R_1/wR_2 (all reflect.) ^b	0.0587/0.0803
Goodness-of-fit (GOF) on F^2 ^c	1.036
Weight. scheme w: a/b ^d	0.0310/3.4427

^a Largest difference peak and hole.

^b $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]$ ^{1/2}.

^c Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

^d $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$.

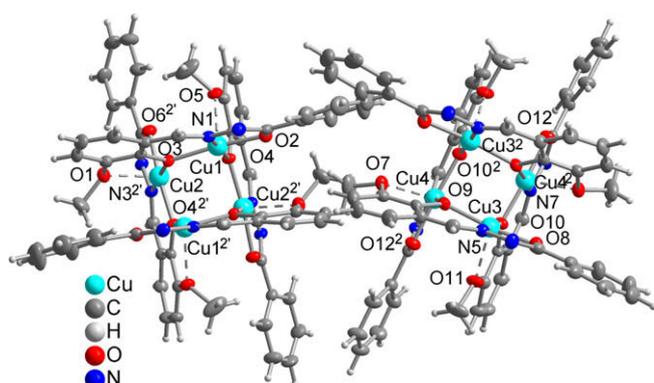
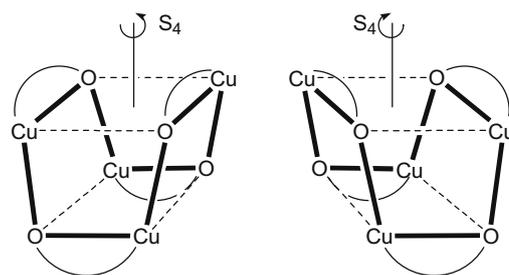


Fig. 1. Thermal ellipsoid plot (at 50% probability level) of the two crystallographically independent tetranuclear complexes $[\text{Cu}(\text{L})_4]$ and their relative orientation; bond lengths and angles in Table 2. Cu–O(methoxy) bonds as thin dashed lines. For increased ligand-labelled pictures, see Figs. S2 and S3 in Supporting information.

alternatingly occupy the vertices of a cube where four of the twelve edges are longer. Hence, the tetranuclear unit forms an open- or pseudo-cubane structure with a Cu_4O_4 core with idealized S_4 -symmetry (Fig. 2, Scheme 1). The geometry of the Cu atoms is best described as square planar with additional (Jahn–Teller distorted) longer contacts to the methoxy oxygen atom and very long contacts to the already bridging phenolate along the open edge.

The crystal structure contains two independent tetranuclear molecules ($Z' = 2$) in different twofold special positions [26], that is, only half (2 ligands + 2 Cu) of each pseudo-cubane is symmetry independent (unique).

The two independent tetramers have largely similar structural data (Fig. 1 and Table 2). There is a crystallographic pseudo mirror symmetry between the two independent molecules. Yet, the two molecules are no “enantiomeric” mirror images but superimposable through a simple rotation (e.g. $\text{Cu}3^2$ matches with $\text{Cu}2^2$, $\text{O}9^2$ with $\text{O}4$ and so on in Fig. 2). One distinct difference between the two independent molecules lies in the orientation of the methoxy group – bent out of the aryl ring plane in molecule 1 and positioned in line with the aromatic plane in molecule 2 (Fig. 1). The presence of two independent molecular halves may be explained with packing frustration. Here, the aryl-group decorated molecules of $[\text{Cu}(\text{L})_4]$ apparently cannot pack efficiently through π – π or C–H... π stacking [27–29]. Crystal water tetramers with homodromic hydrogen bonds [30] are found in cavities created by the $[\text{Cu}(\text{L})_4]$ molecules (Fig. 3 and Fig. S4–S6 in Supporting information). The crystal water is not lost upon air-drying. There is an ongoing discussion on the origin of so-called $Z' > 1$ structures. Different ideas have been put forward to rationalize this phenomenon [31]: A



Scheme 1. Schematic representation of the S_4 -symmetrical Cu_4O_4 core of the two crystallographically inequivalent tetranuclear open-cubane complexes $[\text{Cu}(\text{L})_4]$.

“fossil relic” of a more stable form [32], a crystal “on the way” [33–35] or strong and special supramolecular interactions between the two (or more) symmetry-independent units [36–38]. The frustration between chirality and the formation of centrosymmetric synthons almost invariably has to lead to the presence of two independent hydrogen bonding functionalities [39]. A high Z' is also obtained when the molecule has different equi-energetic conformations, with these conformations co-existing in the crystal [40].

Related open or pseudo-cubanes have been structurally described and magnetically analyzed (see Table S2 in Supporting information) [41–45].

3.3. Magnetic properties

The thermal dependence of $\chi_{\text{M}}T$ of $[\text{Cu}(\text{L})_4]_4 \cdot 4\text{H}_2\text{O}$ in the temperature range 1.9–300 K is depicted in Fig. 4 (χ_{M} being the magnetic susceptibility per mol of Cu_4). The $\chi_{\text{M}}T$ value at room temperature is $1.56 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and the curve shows a continuous decay tending to a plateau at temperatures below 10 K. The value at 1.9 K is $0.11 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This behaviour is indicative of a dominant antiferromagnetic coupling that leads to a $S = 0$ spin ground state together with some paramagnetic impurities that make the $\chi_{\text{M}}T$ vs. T curve to deviate from 0 at low temperatures. As has been described in the structural part, the copper(II) ions build two different cubane-like tetramers, A and B. Both cubanes have the same pattern (4 + 2 class, Scheme 2) [46–48]. However, the $\text{Cu}(\text{II}) \cdots \text{Cu}(\text{II})$ distances and the $\text{Cu}–\text{O}–\text{Cu}$ angles have significant differences that argue for their separate analysis. Cubane A (Table 2) has $\text{Cu}(\text{II}) \cdots \text{Cu}(\text{II})$ distances that range from 3.28 to 3.40 Å and three different magnetic exchange-pathways can be defined, J_{1A} , J_{2A} and J_{3A} . In cubane B the distances range from 3.21 to 3.51 Å and the $\text{Cu}–\text{O}–\text{Cu}$ angles are different from those of cubane A. Then three additional coupling constants can be defined (Scheme 3).

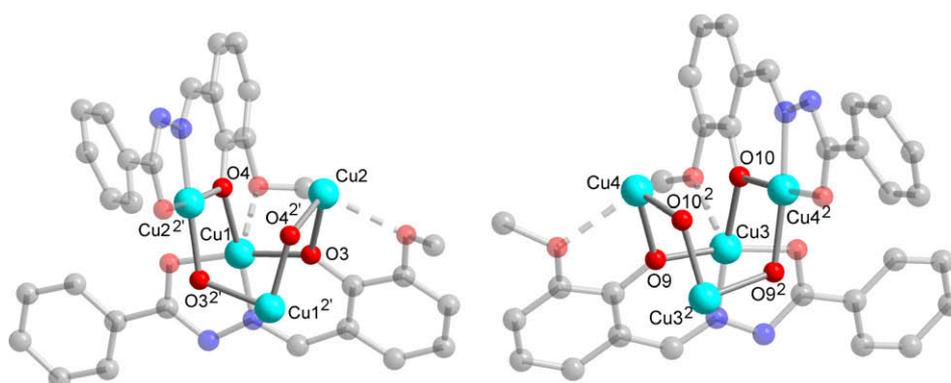
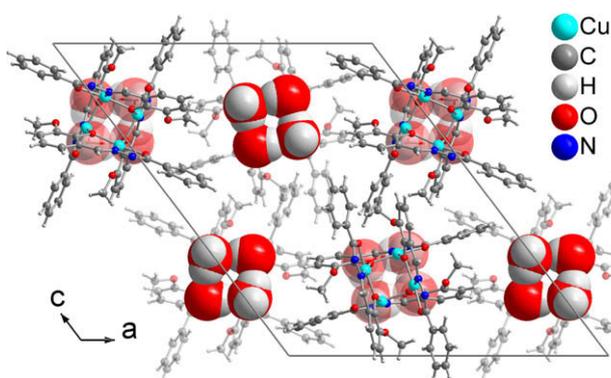


Fig. 2. Open-cubane structures of the two crystallographically independent tetranuclear complexes $[\text{Cu}(\text{L})_4]$ with two ligands and H atoms omitted for clarity.

Table 2
 Selected bond lengths [Å] and angles [°] in [Cu(L)]₄·4H₂O.

Cubane A		Cubane B	
Cu1–N1	1.920(2)	Cu3–N5	1.925(2)
Cu1–O2	1.934(2)	Cu3–O8	1.923(2)
Cu1–O3	1.970(2)	Cu3–O9	1.971(2)
Cu1–O4	1.981(2)	Cu3–O10	1.987(2)
Cu1–O5	2.300(2)	Cu3–O11	2.328(2)
Cu2–N3 ^{2'}	1.921(2)	Cu4–N3 ²	1.923(2)
Cu2–O1	2.291(2)	Cu4–O7	2.339(2)
Cu2–O3	1.986(2)	Cu4–O9	2.003(2)
Cu2–O4 ^{2'}	1.967(2)	Cu4–O10 ²	1.932(2)
Cu2–O6 ^{2'}	1.945(2)	Cu4–O12 ²	1.915(2)
Cu1–O3 ^{2'}	2.679(2)	Cu3–O9 ²	2.597(2)
Cu2–O4	2.745(2)	Cu4–O10	2.697(3)
Cu1...Cu2	3.3242(4)	Cu3...Cu4	3.2577(6)
Cu1...Cu2 ^{2'}	3.2860(5)	Cu3...Cu4 ²	3.2197(4)
Cu1...Cu1 ^{2'}	3.3598(4)	Cu3...Cu3 ²	3.4052(5)
Cu2...Cu2 ^{2'}	3.4058(6)	Cu4...Cu4 ²	3.5131(6)
O3–Cu1–O4	88.55(6)	O9–Cu3–O10	90.49(7)
O3–Cu2–O4 ^{2'}	88.28(6)	O10–Cu4–O9 ²	88.59(7)
Cu1–O3–Cu2	114.36(8)	Cu3–O9–Cu4	110.13(8)
Cu1–O4–Cu2 ^{2'}	112.67(7)	Cu3–O10–Cu4 ²	110.46(8)

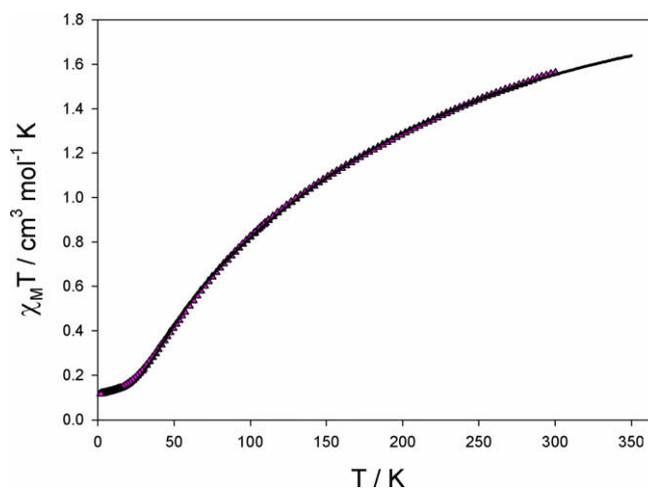
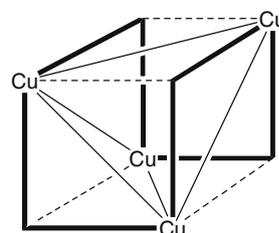
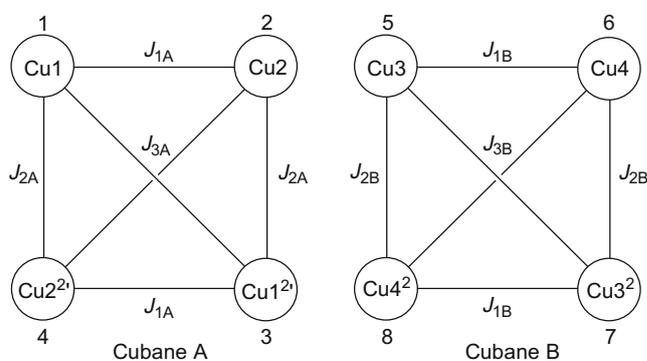
Symmetry labels: 2' = 1 – x, y, 1.5 – z; 2 = –x, y, 1.5 – z.


Fig. 3. Crystal packing in [Cu(L)]₄·4H₂O with the water tetramers in space-filling mode. The water clusters are situated above and below, hence, in-between the tetranuclear complexes, with hydrogen bonds to the deprotonated amide nitrogen atoms (Figs. S4–S6 and Table S1 in Supporting information). Building blocks in the rear are depicted semi-transparent.

Under this approach the magnetic properties of [Cu(L)]₄·4H₂O should be analyzed by means of the following zero-field spin Hamiltonian (Eq. (1)).

$$\hat{H} = -J_{1A}(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - J_{2A}(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) - J_{3A}(\hat{S}_2\hat{S}_4 + \hat{S}_1\hat{S}_3) - J_{1B}(\hat{S}_5\hat{S}_6 + \hat{S}_7\hat{S}_8) - J_{2B}(\hat{S}_5\hat{S}_8 + \hat{S}_6\hat{S}_7) - J_{3B}(\hat{S}_5\hat{S}_7 + \hat{S}_6\hat{S}_8) \quad (1)$$

The magnetic susceptibility expression for such a system can be obtained as given in the [Supplementary material](#) [46,49]. However, it is not possible to achieve a satisfactory fitting by least squares regression with 9 parameters to be determined. It becomes necessary to put some constraints to the exchange coupling constants and the *g* parameters in order to get a plausible result. A recent DFT study of the magnetostructural correlations in copper(II) cubane complexes performed by Tercero and co-workers has been taken into consideration [50]. The intensity and the ferro-/antiferromagnetic nature of the coupling constants is determined by the Cu–O–Cu angles, the Cu...O distances and the relative orientation of the metallic orbitals bearing the unpaired electrons. As deduced from that study, in 4 + 2 class cubanes, *J*_{3A} and *J*_{3B} coupling constants (cf. [Scheme 3](#)) are expected to be ferromagnetic


Fig. 4. Thermal dependence of the $\chi_M T$ for [Cu(L)]₄·4H₂O.

Scheme 2. 4 + 2 Cubane according to the classification of Ruiz et al. [47].

Scheme 3. Magnetic coupling scheme of the copper(II) ions in [Cu(L)]₄·4H₂O.

and little dependent on geometrical parameters. Thus, under this approach, these two *J* values were constrained to be equal for the fitting of the magnetic susceptibility data. On the other hand, *J*₁ and *J*₂ are expected to be antiferromagnetic, in both cubanes A and B, as they exhibit Cu–O–Cu angles larger than 104°. These angles are very similar in cubane B, thus *J*_{1B} = *J*_{2B} has been constraint during the fitting. Finally *g*_A = *g*_B has also been fixed as both cubanes have the same pattern and the copper(II) ions are complexed by the same ligands and in the same geometry. Under these conditions the best fit parameters are *J*_{1B} = *J*_{2B} = –17.2 cm^{–1}, *J*_{1A} = –36.7 cm^{–1}, *J*_{2A} = –159 cm^{–1}, *J*_{3A} = *J*_{3B} = 33.5 cm^{–1}, *g* = 2.40 and $\rho = 0.0687$ with *R* = 0.9999. The calculated curve matches very well the experimental data in the whole temperature range studied. The *J*₃ coupling constants are ferromagnetic and they are in agreement with the recent study performed by Tercero and co-workers [50]. These exchange pathways involve the interaction

between the $d_{x^2-y^2}$ and d_{z^2} orbitals, that provide a very poor overlap between the orbitals bearing the unpaired electrons that usually lead to ferromagnetism [51]. J_{1B} and J_{2B} indicate a weak antiferromagnetic coupling among the copper(II) ions in cubane B. The values obtained also fall in the expected range [50] and in particular they are very close to those found by Walz and co-workers for a compound with very similar structural parameters [52]. J_{1A} and J_{2A} are antiferromagnetic as expected from their large Cu–O–Cu angles, also they are stronger in intensity than J_{1B} and J_{2B} , following the general trend that predicts stronger antiferromagnetic couplings for larger Cu–O–Cu bridging angles [50]. The g values are higher than expected; they may be contaminated by some correlation in the evaluation of J_{2A} which has also a slightly higher value than expected. However, in general, the result of the magnetic analysis is in agreement with recent previous studies for this class of compounds [50].

4. Conclusions

The tetranuclear open-cubane complex $[\text{Cu}(\text{L})_4]$ with an *in-situ* formed dinegative 2-hydroxy-3-methoxybenzylidene)benzohydrazide ligand crystallizes as the stable tetrahydrate $[\text{Cu}(\text{L})_4] \cdot 4\text{H}_2\text{O}$ with two symmetry-independent S_4 -symmetrical tetranuclear molecules in a $Z' = 2$ structure. Both open Cu_4O_4 cubanes have significant differences that lead to a system with 6 different magnetic exchange pathways, three each between the Cu(II) atoms in cubane A and cubane B, respectively. One of these exchange pathways in each cubane is ferromagnetic, the other two are antiferromagnetic. All of them have been determined and their nature and intensity show a full agreement with the conclusions of recent previous magnetostructural studies [50].

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.04.042.

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