Structural and Magnetic Characterization of two Tetranuclear Cu(II) complexes with closed-cubane like core Framework

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Two novel tetranuclear Cu(II) complexes $[Cu_4(L^1)_4]\cdot 3(H_2O)$ (**1**) and $[Cu_4(H_2L^2)_4(H_2O)_4]$ (**2**) (H_2L^1 = (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol; H_4L^2 = 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-hydroxymethylpropane-1,3-diol) were synthesized from the self-assembly of copper(II) perchlorate and the tridentate Schiff base ligands. Both complexes crystallize in the tetragonal system with space group $I\ 4_1/a$ and form tetranuclear species with closed-cubane like core framework. Both the complexes possess a S_4 axis but of different stereochemistry due to the different arrangement of the ligands about the copper ions. Variable temperature magnetic susceptibility measurements indicate an overall weak antiferromagnetic exchange coupling in **1**, while ferromagnetic exchange coupling in **2**. In agreement with their closed-cubane structure, the magnetic behavior of the two complexes have been studied by employing the isotropic spin Hamiltonian of type $H = J_1 (S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) - J_2 (S_1S_2 + S_3S_4)$ (J_1 describes the magnetic exchange coupling between the four Cu(II) pairs with short Cu···Cu distances, while J_2 characterizes the magnetic exchange coupling between the remaining two intermetallic pairs with long distances). The PHI program was used to study their magnetic behavior. A good agreement between the experimental and fitted curves was found with the following parameters: $g = 2.14$, $J_1 = -20.3$ cm^{-1} and $J_2 = 0$ cm^{-1} for **1** and $g = 2.10$, $J_1 = 101.1$ cm^{-1} and $J_2 = -51.5$ cm^{-1} for **2**.

Introduction

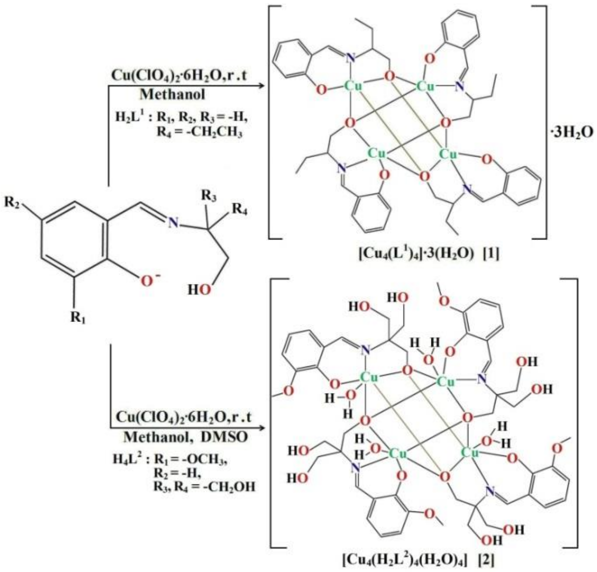
Polynuclear 3d-metal coordination compounds have attracted continuous attention in the recent decades due to their interesting structure and molecular properties.[1] Among the high nuclear complexes, M_4X_4 (where M = Cu, Ni, Co, Fe, Mn; X= O, S) have been broadly investigated for their relevance in the field of magnetism,[2] catalysis [3] and bio-inorganic chemistry [4]. In particular Cu_4O_4 alkoxo, hydroxo and phenoxo bridged cubane like complexes have been widely studied adopting experimental and theoretical approach for exploring their magneto-structural correlation.[5] Based on the arrangement and connectivity of the copper and oxygen atom in the tetranuclear Cu_4O_4 core, the cubane geometries may be of various types e.g; regular cubane,[6] single-open cubane,[7] double-open cubane[8] and face sharing dicubane.[9] Depending on the distribution of Cu-O bond distances in the cube, Mergehenn and Haase classified cubane of type I and type II.[10] Cu_4O_4 cubane complexes having four long Cu-O distances between two dinuclear subunits are designated as type I, whereas if the long Cu-O distances are within each dinuclear subunit, cubanes are classified as type II. [11, 16] On the other hand, taking into account the Cu···Cu distances within the Cu_4O_4 cubane unit, Alvarez *et al*. described [12] three types the compounds: (i) (2+4) having two short and four long Cu···Cu distances, which is equivalent to type I (defined above); (ii) (4+2) with four short and two long Cu···Cu distances, an equivalent description to type II and (iii) (6+0), where all six Cu···Cu bonds have comparable distances (Scheme 1S).

Polydentate Schiff base ligands possessing alkoxo, hydroxo and phenoxo donor centers are potential ligand for the synthesis of multinuclear copper complexes. As an extension in the synthesis of cubane copper compounds we have used two Schiff bases namely (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol (H_2L^1) and 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-hydroxymethylpropane-1,3-diol (H_4L^2), which have potentiality to coordinate metal ions with alkoxo, hydroxo and phenoxo donor centres. In the present contribution we report the synthesis, the crystal structure and magnetic properties of two copper complexes $[Cu_4(L^1)_4]\cdot 3(H_2O)$ (**1**) and $[Cu_4(H_2L^2)_4(H_2O)_4]$ (**2**), both comprising a closed cubane like core structure.

Results and discussion

Synthesis of the Complexes

The complexes have been synthesized adopting procedures which are schematically given in Scheme 1.



Scheme 1. Synthesis of complexes **1-2.**

Molecular structure of complexes $[Cu_4(L^1)_4]\cdot 3(H_2O)$ (1) and $[Cu_4(H_2L^2)_4(H_2O)_4]$ (2).

A perspective view of the molecular structure of complexes $[Cu_4(L^1)_4]$ and $[Cu_4(H_2L^2)_4(H_2O)_4]$ is depicted in Figures 1 and 2, respectively, and relevant bond distances and angles are summarized in Table 1. Both the complexes consist of neutral tetrameric moiety comprising four Cu(II) ions and four symmetry related di-anionic Schiff base ligands to form a cubane-like core of alternating copper and oxygen atoms that occupy the corners of the cube.

In fact each copper center is chelated by the tridentate Schiff base ligand through the imine nitrogen, the phenoxo and the deprotonated alkoxo oxygen atoms, and in addition is bound to two deprotonated alkoxo O atoms from symmetry related ligands. With these donor atoms copper ions in complex **1** exhibit a square pyramidal geometry, while a highly distorted hexagonal environment is detected in **2** for the presence of an additional aqua ligand located at longer distance. The Addison index (τ) [13] to define the distortion of the coordination environment from trigonal bipyramidal (TBP) to square pyramidal (SP) is calculated to be 0.358 in **1**. In both complexes the doubly deprotonated ligands are found in η^3:η^1:η^1:μ_3 coordination mode. In complex **1** the basal distances Cu-O and Cu-N range from 1.894(3) to 1.994(3) Å, while the fifth site at apical position filled by a deprotonated alkoxo O atom shows a longer contact of 2.349(3) Å. Correspondently the equatorial distances in **2** fall in a narrower range (1.915(4)-1.970(4) Å), while the axial oxygen donors, of an alkoxo oxygen and water molecule, are at 2.569(4) and 2.797(6) Å, respectively, the latter indicating a very weak interaction. In the ligand H_2L^2 the methoxy group on the ring does not participate in coordination as well as the two CH_2-OH fragments that are far apart from the Cu_4O_4 core. An interesting feature of complex **1** compared to **2** is the shorter Cu-O distance at apical position (2.349(3) vs 2.569(4) Å) and the different stereochemistry of ligand disposition about the metals as discussed below.

Alvarez et al. [14] in order to study the magneto structural correlations, used the Cu•••Cu distances within the Cu_4O_4 cubane unit to classify these complexes: (i) 2+4, comprising two short and four long Cu•••Cu distances, (ii) 4+2, with four short and two long Cu•••Cu distances, and (iii) 6+0, which contains six similar Cu•••Cu distances. The present complexes having a S_4 symmetry are of type (ii) with Cu•••Cu short and long distances of 3.097 and 3.372 Å in **1** and of 3.190, 3.479 Å in **2**, respectively.

Since the lattice water molecules are disordered in the crystal of complex **1** (occupancy of 0.25 and 0.5) we interpret the complexes as isolated species in the crystal. On the contrary the water molecule in **2** forms H-bond connections with phenolato O1 and hydroxyl oxygen O4 (Table 1S) of symmetry related complexes giving rise to a 3D network. The long Cu-O6 (water) bond distance of 2.797(6) Å observed in **2** is likely modulated with the aim for the water molecule to realize the cited H-bonds.

However, it is worth of note that the two complexes here reported have a different stereochemistry as shown in the schematic illustrations of Figures 3 and 4, where the ligands have been simplified, thus removing ethyl substituents in **1** and methoxy and CH_2OH groups in **2**. The difference is clearly evident, especially by comparison of Figures 3b and 4b, showing the arrangement of ligands about the tetranuclear Cu_4 core.

The Cambridge structural database [15] was searched for similar complexes comprising a tetra nuclear Cu_4O_4 core built by variously substituted salicilidene-ethanolato ligands of Scheme 1. The structures retrieved (beside the recently published structures of Colacio et al.) [16] are summarized in Table 2S, where the Cu-O distances and space groups are also reported. Some of the complexes, built with the same ligands,[13-15, 17-18, 19-20, 24-25, 29-30] crystallize in different space groups tuned in some cases by the presence of lattice solvent molecules, which affect the packing. Although in the majority of cases the complexes do not reside about an improper fourfold axis, the symmetry is close to a pseudo-S4, being the differences in solid state imposed by the packing or the different conformation of substituents on the ligands. Some observations are worth of note from Table 2S: the coordination bond lengths fall in the range 1.882-2.001 Å, that is within 2-3 e.s.d's. in most cases. On the other hand a large range is detected for the long Cu…O distances. In particular values up to 3.0 Å were measured associated with a boat conformation of the Cu_4O_4 central moiety, [21-22, 29] dictated by the existence of π-π interactions between the naphthyl rings. Actually it is worth of note that all the cubane like structures reported so far present the same arrangement of ligands, namely as that schematically depicted for complex **2** (Figure 4). Thus at our knowledge complex **1** represents the first example where the tridentate Schiff bases assume a different configuration about the tetranuclear Cu_4O_4 core, as described above. An inspection of Table 1 indicates that in complex **1** the four symmetry related Cu…O distances of 2.349(3) Å are the shortest among those reported, likely indicating that this configuration lead to a more compacted Cu_4O_4 moiety.

Magnetic properties of complexes

The $\chi_M T$ versus T curve for complex **1** starts from a value of 1.47 cm^3 K mol^{-1} at room temperature, in agreement with the value of 1.48 cm^3 K mol^{-1} expected for four uncoupled $S = ½$ spins assuming $g = 2$, and decreases continuously until 0.04 cm^3 K mol^{-1} is reached at 10 K. Below this temperature the $\chi_M T$ value decreases smoothly, showing the tendency to form a plateau at a value different than 0. This behavior evidences the presence of an overall antiferromagnetic interaction and an $S = 0$ ground state in the complex, suggesting the presence of small amounts of paramagnetic mononuclear impurities. On the other hand the $\chi_M T$ versus T curve for complex **2** shows a value of 2.06 cm^3 K mol^{-1} at room temperature, which is significantly higher than the value expected for four uncoupled $S = ½$ spins assuming $g = 2$. The curve increases exponentially up to reach value of 2.67 cm^3 K mol^{-1} at 34 K. Below this temperature the $\chi_M T$ versus T curve decreases sharply down to a $\chi_M T$ value of 0.85 cm^3 K mol^{-1} at 2 K. As opposed to complex **1**, relatively strong ferromagnetic exchange interactions are operating in complex **2**, despite the similar skeleton of the two compounds.

Both complexes present a cubane-like structure characterized by a $[Cu_4O_4]$ core that possesses four short and two long Cu···Cu distances as a result of the particular relative arrangement of the axial axes and equatorial planes of the Cu(II) ions, leading to a [4+2] geometric type of cubane compounds proposed by Ruiz *et al.* [12c] The corresponding equatorial or axial character of the bridging atoms with respect to the two connected Cu(II) ions in each pair is shown in Scheme **2A**. Taking this structural arrangement in consideration, the magnetic behavior of the two complexes can be studied by employing the isotropic spin Hamiltonian of equation 1, based on the model showed in Scheme **2B**.

$$H = J_1 (S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) - J_2 (S_1S_2 + S_3S_4) \qquad \text{eq. 1}$$

J_1 describes the magnetic exchange coupling between the four Cu(II) pairs with short Cu···Cu distances, while J_2 characterizes the magnetic exchange coupling between the remaining two Cu(II) pairs with long intermetallic distance. Those pairs with short Cu···Cu distances are bridged by two different O atoms, of which one belongs to the equatorial plane of both the Cu(II) ions in the pair. On the contrary, Cu(II) pairs characterized by a long Cu···Cu distance always involve an axial coordination of the O bridging atom to one Cu(II) ion in any of their bridging pathways. Therefore, in the second case there is always a non-magnetic orbital involved in the exchange, and consequently the interaction is expected to be very weak. Thus, while J_1 can be either ferro or antiferromagnetic in nature, it will be definitely stronger than J_2 in these [4+2] type of cubane systems.

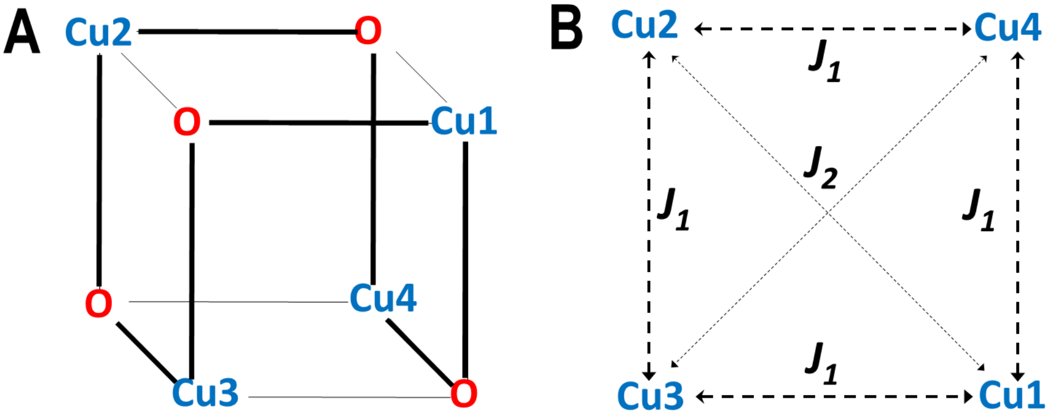
The $\chi_M T$ versus T curves of complexes **1** and **2** were fitted with the PHI program.[35] One single g value was assigned for the four Cu(II) ions in each complex due to their equivalence in the crystal, i.e. $g_1 = g_2 = g_3 = g_4$. For the spin Hamiltonian described in equation 1, a good agreement between the experimental and fitted curves was found with the following parameters: $g = 2.14$, $J_1 = -20.3$ cm^{-1} and $J_2 = 0$ cm^{-1} for complex **1** and $g = 2.10$, $J_1 = 101.1$ cm^{-1} and $J_2 = -51.5$ cm^{-1} for complex **2**. Temperature-independent paramagnetism (TIP) was considered equal to 120×10^{-6} cm^3 mol^{-1} for both complexes. Additionally the fit was improved when considering the presence of a 7% Cu(II) mononuclear impurity in complex **1**. The fitted curves are represented together with the experimental ones in Figure 5.

The nature and magnitude of J_i exchange constants in [4+2] cubane structures were theoretically studied by Tercero *et al.* [14] As deduced from Scheme 2, J_1 is the result of the combined exchange through two different pathways, of which that involving two short Cu-O bonds is the most efficient, since only magnetic orbitals participate to it. According to the previously mentioned work of Tercero *et al.*, the sign and magnitude of the J_1 magnetic exchange constant should correlate with the Cu-O-Cu angle characteristic of this short exchange pathway, since this will determine the degree of overlapping between the two magnetic orbitals of the Cu(II) ions in the pair. In fact, calculations suggest that antiferromagnetic interactions can be expected in [Cu_4O_4] compounds with angles larger than ca. 103°, in which case the overlapping of magnetic orbitals becomes effective.

In agreement with this prediction, Papadakis *et al.* recently reported an analogous compound exhibiting a weak antiferromagnetic J_1 interaction associated to a Cu-O-Cu angle of 103.5°, similar to that detected for complex **1** in this work, which shows a Cu-O-Cu angle of 102.6°.[36]

However, many previously reported [Cu_4O_4] compounds with a [4+2] cubane-like structure (see Table 2S) show ferromagnetic J_1 interactions, even though their Cu-O-Cu angle is larger than 103°.[25, 26, 37] This is also the case of complex **2** reported in this work, which shows a moderate ferromagnetic exchange constant with a Cu-O-Cu angle of 109°. Several structural parameters, often correlated with the nature and magnitude of the magnetic exchange coupling have been compared between complexes **1** and **2**, but none of them seems to justify such different behavior by itself: Complex 2 shows a larger Cu-O-Cu angle, shorter Cu-O distances, a less perpendicular arrangement of the {Cu_2O_2} planes containing the magnetic metal orbitals and a smaller out-of-plane shift of the carbon atom connected to the bridging oxygen, and consequently all these factors would suggest a larger overlap of the magnetic orbitals and a more antiferromagnetic coupling.[14, 38] Indeed, Tercero et al. already highlighted the disagreement between experimental results and theoretical predictions, being the former generally ferromagnetic while the latter predicted antiferromagnetic interactions. The authors suggested, by means of a theoretical experiment, that the chelating nature of the terminal ligands attached to the alkoxo bridge of the cubane structures might be the reason for the observed disagreement, since calculations were performed with a simpler non-chelating terminal ligand, while most of the examples found in literature included a chelating one. New calculations were carried out on two analogous structures, where the chelating terminal ligand attached to the alkoxo bridge was preserved in one, and theoretically broken in the other: the calculated magnetic exchange constant was substantially more ferromagnetic for the one with chelating nature. Considering that this terminal chelate introduces an additional exchange pathway between the two copper atoms, it seems reasonable that it can substantially affect the magnetic superexchange. In our case, both complexes **1** and **2** show a terminal ligand attached to the alkoxo bridge with a chelating nature. However the chelates are significantly different from a geometrical as well as from an electronic point of view. While the chelate shows a substituent of aliphatic nature in complex **1**, the substituent includes two alcohol groups in complex **2**. Additionally, the dihedral angle between the two planes formed by the atoms at the chelate ring (Cu-N-C-C-O) are quite different, being 45.64° and 32.60° for complex **1** and **2**, respectively. As for structural issues, it should be emphasized that complex **1** represents the first example where the tridentate Schiff bases assume a different configuration about the tetranuclear Cu_4O_4 core (see Figure 4), being the configuration of complex **2** (see Figure 3) the one always found for cubane systems previously reported in the literature. The different stereochemistry of complex **1** might also be behind the reasons for the antiferromagnetic behavior observed, compared to the ferromagnetic coupling usually encountered.

On the other hand, either negligible or antiferromagnetic values of J_2 have been obtained, in agreement with similar [4+2] cubane compounds previously reported.[39, 5e] Nevertheless, this parameter has been often observed to strongly correlate with the J_1 value in the fitting procedure, and thus the J_2 values obtained should be considered with caution.



Scheme 2. A) Structural arrangement of a [4+2] cubane structure like the one of complexes **1** and **2**, where short (equatorial) and long (axial) Cu-O bonds have been illustrated with thick and thin lines, respectively. B) Magnetic model used for the description of the structure represented in A, where J_1 and J_2 describe the magnetic exchange pathways through Cu(II) pairs showing short and long Cu-Cu distances, respectively

Conclusions

We have presented here the syntheses, single-crystal structures and magnetic behaviors of two new tetranuclear [Cu_4] copper(II) complexes (**1** and **2**) using polydentate Schiff base ligands, H_2L^1 and H_4L^2, respectively. Variable temperature magnetic susceptibility measurements in the range 2–300 K indicate overall antiferromagnetic exchange coupling in complex **1**, while ferromagnetic exchange coupling in complex **2**. The difference in magnetic behavior can be hardly ascribed to a specific or single structural parameter, but to a resulting different geometry derived from the combination of all of them: although both complexes show comparable closed-cubane like core structures, the arrangement of the ligands around the Cu_4O_4 core differs significantly, and this might be at the origin of such a different magnetic behavior.

Supplementary information. Experimental details, Tables for crystallographic and magnetic data, figures of NMR, IR and electronic absorption and fluorescence spectra are provided as supporting information.

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Keywords: Copper(II); Closed-cubane; Crystal structure; Magnetic properties

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Table 1. Bond lengths (Å) and angles (°) for complexes **1** and **2**.

	1	**2**
Cu-O(1)	1.894(3)	1.915(4)
Cu-O(2)	1.975(3)	1.947(4)
Cu-N(1)	1.926(4)	1.956(5)
Cu-O(2)'	1.994(3)	1.970(4)
Cu-O(2)"	2.349(3)	2.569(4)
Cu-O(6)	–	2.797(6)
O(1)-Cu-N(1)	92.92(16)	94.0(2)
O(1)-Cu-O(2)	177.12(12)	172.15(18)
O(2)-Cu-N(1)	84.22(16)	84.6(2)

O(1)-Cu-O(2)'	96.10(12)	94.68(17)
N(1)-Cu-O(2)'	155.62(14)	166.3(2)
O(2)-Cu-O(2)'	86.41(12)	88.21(18)
O(1)-Cu-O(2)"	104.50(12)	94.16(16)
N(1)-Cu-O(2)"	121.05(13)	117.4(2)
O(2)-Cu-O(2)"	77.35(11)	79.74(16)
O(2)'-Cu-O(2)"	78.39(11)	72.49(16)

Symmetry codes: for **1** (') –y+5/4, x–3/4, –z+1/4, (") y+3/4, –x+5/4, –z+1/4;
for **2** (') –y+5/4, x+1/4, –z+1/4, (") –x+1, –y+3/2, z.

Caption of figures:

Figure 1. Molecular structure of complex **1** (dotted lines indicate long Cu-O bond distances).

Figure 2. Molecular structure of complex **2** (dotted lines indicate long Cu-O bond distances). The water molecule bound at each copper ion (Cu-Ow = 2.797(6) Å) not shown for sake of clarity.

Figure 3. Complex **1** viewed down the S4 symmetry axis and a perspective side view (H-atoms and ethyl groups not shown).

Figure 4. Complex **2** viewed down the S4 symmetry axis and a perspective side view (H-atoms, methoxy and CH_2OH groups removed for clarity). The ligands arrangement is similar to that detected in all the complexes structurally characterized and reported to date.

Figure 5. Thermal dependence of the $\chi_M T$ for complexes **1** and **2**. Points indicate experimental data and straight lines represent the best fitting curves obtained.

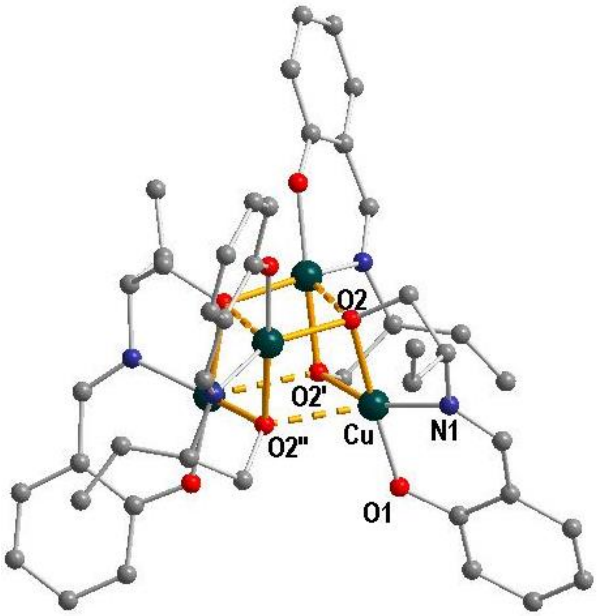


Figure 1. Molecular structure of complex **1** (dotted lines indicate long Cu-O bond distances).

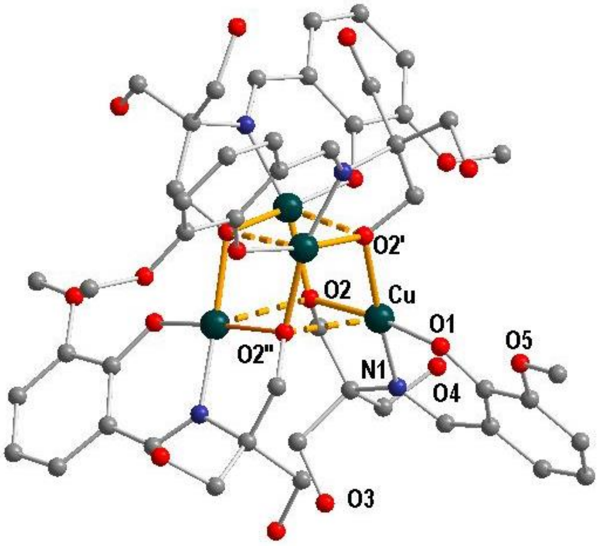
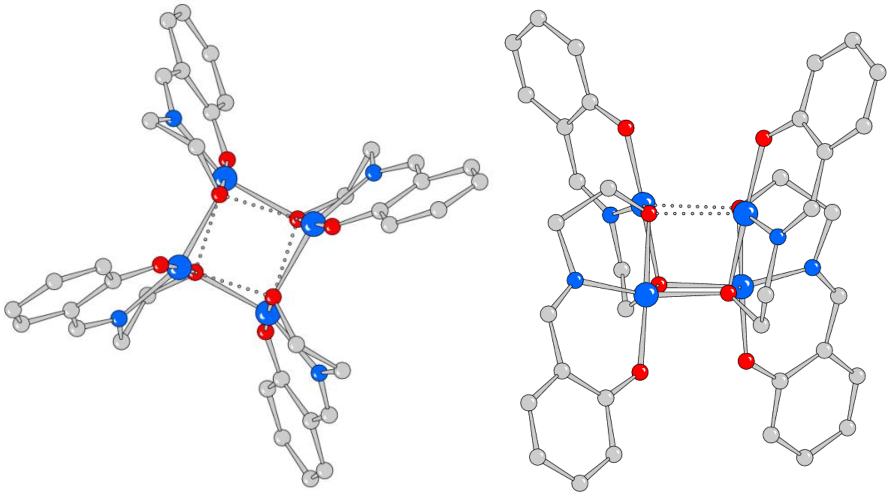
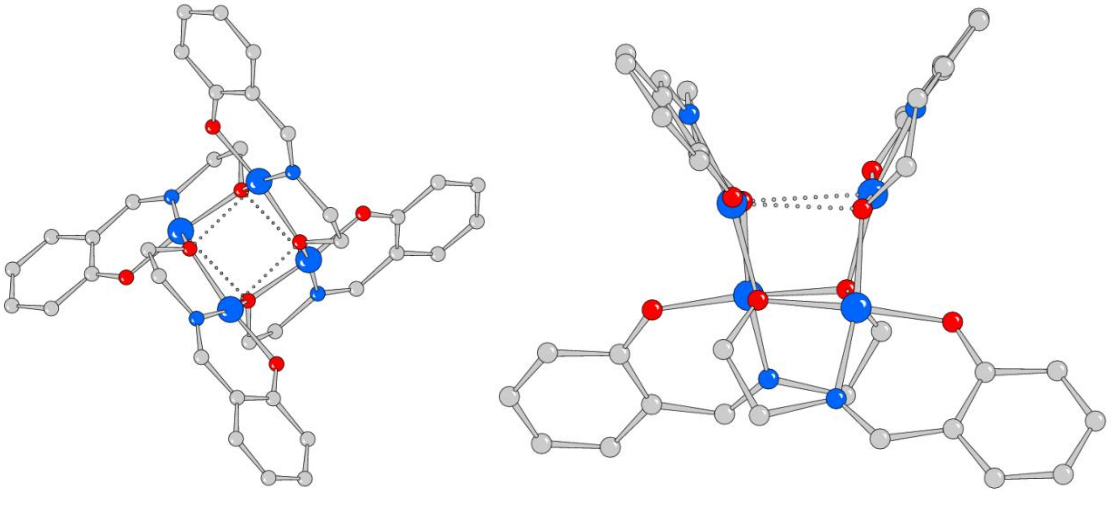


Figure 2. Molecular structure of complex **2** (dotted lines indicate long Cu-O bond distances). The water molecule bound at each copper ion (Cu-Ow = 2.797(6) Å) not shown for sake of clarity.



3a) **3b)**

Figure 3. Complex **1** viewed down the S4 symmetry axis and a perspective side view (H-atoms and ethyl groups not shown).



4a) **4b)**

Figure 4. Complex **2** viewed down the S4 symmetry axis and a perspective side view (H-atoms, methoxy and CH_2OH groups removed for clarity). The ligands arrangement is similar to that detected in all the complexes structurally characterized and reported to date.

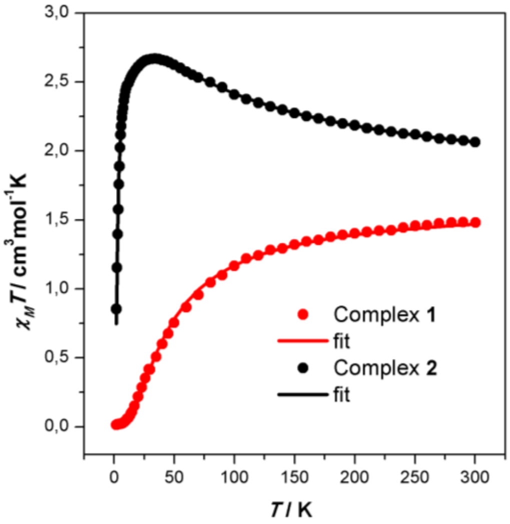


Figure 5. Thermal dependence of the $\chi_M T$ for complexes **1** and **2**. Points indicate experimental data and straight lines represent the best fitting curves obtained.