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ARTICLE TYPE

Solvent Switchable Nuclearity of Cu^{II} Complexes with 2,6-bis((2-(acetylamino)phenylimino)methyl)-4-*tert*-butylphenol (H_3L) Ligand

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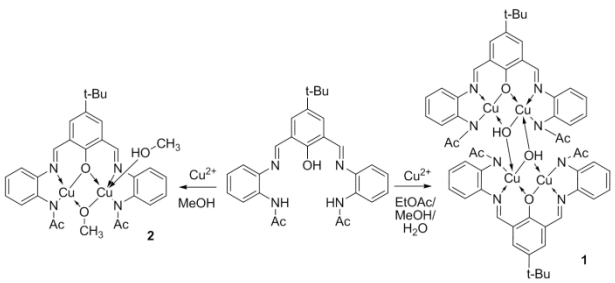
A new tetranuclear complex Cu_4, $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ **(1)**, with the functionalized Schiff base ligand 2,6-bis((2-(acetylamino)phenylimino)methyl)-4-*tert*-butylphenol (H_3L) has been obtained and characterized in the solid state by X-ray diffraction. The formation of the tetranuclear species is solvent dependent; the presence of water being determinant in its isolation. Based on the mass-spectrometric evidence, the behaviour of the H_3L/Cu^{II} system in the presence of water was constructed. Namely, water can switch the nuclearity of the Cu^{II} cluster from dinuclear to tetranuclear. The redox behaviour of this species in DMSO solution, showing two cathodic metal-centred peaks at E_P = -0.80 and -1.35 V, and an irreversible ligand-centred anodic peak at E_P = 1.03 V, was found to be similar to that of a pristine dinuclear complex. The tetranuclear species was also characterized in the solid state by magnetic measurements, showing a dominating bulk antiferromagnetic behaviour, with a singlet ground state at approximately 2 K. DFT calculations permitted to estimate the strong intradimer antiferromagnetic exchange interaction (J_1 = - 440 cm^{-1}), together with two weak interdimer ferromagnetic exchange interactions (J_2 = + 0.5 and J_3 = + 1.7 cm^{-1}).

Introduction

The compartmental ligands have the ability to bind two or more cations in a close proximity. Among these, Schiff base ligands which are functionally substituted, and therefore bear additional donor atoms, represent an important group of heteropolydentate ligands in coordination chemistry. The organic precursor derived from 4-X-phenol-2,6-dicarbaldehyde (X= methyl or *tert*-butyl), when condensed with different primary amines, provides both the imine donor groups and an auxiliary oxygen donor atom; the latter acts as a bridge between the metal centres. If a [2+1] condensation reaction in mild synthetic conditions is performed, this leads to the formation of the corresponding acyclic ligand.[1-3] This type of Schiff base ligands are good precursors for the formation of the desired dinuclear complexes.[4-6] In this way, if paramagnetic ions are bonded, the complex species will present intramolecular magnetic interactions between the metal centres, due to the existence of the endogenous phenoxido oxygen bridge.[7-13] However, the final coordination environment around the metal centres will be influenced by such parameters as donor atoms of the ligand, counterions, pH, solvent, and temperature. Among these, the solvent used may have an important impact on the metal coordination, and different solvents or mixture of solvents can produce different species, since they control the final stability of the isolated compounds.[14] The use of protic solvents, such as methanol or water, permits to obtain solvent derived species such as hydroxide, which can help the aggregation and act as bridging ligands, inducing magnetic pathways in the obtained polynuclear species.[15] On the other hand, the capacity of the Cu^{II} ion to complete the fifth position of its first coordination sphere, by binding an apical ligand, permits the assembly of square planar dinuclear Cu_2 units into polynuclear complexes.

In this paper we report the isolation and characterization of a tetranuclear Cu^{II} complex Cu_4, $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ **(1)**, formed by the functionalized Schiff base ligand, LH_3: 2,6-bis((2-(acetylamino)phenylimino)methyl)-4-*tert*-butylphenol. This new tetranuclear complex is an example of a Cu_4 moiety, which forms in the presence of water, by the assembly through hydroxido bridges of two dinuclear Cu^{II} species (Scheme 1). The solid state and solution properties, together with the switching between the dinuclear and tetranuclear complex species are discussed.



Scheme 1. Preparation of the tetranuclear **(1)** and dinuclear **(2)** Cu^{II} complexes.

Experimental Section

The elemental analysis (carbon, hydrogen and nitrogen) of the complex was obtained from Thermo Flash EA 1112 series analyzer. NMR spectra were measured on a BRUKER AVANCE-400 MHz NMR-spectrometer at 24°C. IR spectra were recorded on a Nicolet FT-IR spectrometer in Nujol or KBr. Mass spectra were obtained on a MALDI-TOF Reflex 3 instrument (BRUKER) in the positive ion mode (UV laser, 337 nm). The ESI mass spectra were registered on the Finnigan LCQ Advantage tandem dynamic mass-spectrometer (USA), equipped by octapole ion trap mass analyzer with the Surveyor MS pump and the nitrogen generator Schmidlin-Lab (Germany). The data collection and treatment was fulfilled using the program X Calibur version 1.3. The temperature of the heated capillary was 150 ºC, electric potential 4.5 kV, the solvent phase flow rate was 25 mL/min, nitrogen was the spraying and drying gas. Acetonitrile of the Merck Company was used for the gradient analysis.

Synthesis of 2,6-bis(2-acetylaminophenyl)iminomethyl)-4-tertbutylphenol, LH_3.

To a solution of 974 mg (4.7 mmol) of 2,6-diformyl-4-tert-butylphenol in 8 ml of dry methanol, a solution of 1.42 g (9.5 mmol) N-acetyl-o-phenylenediamine in 2 ml of dry methanol was added. The resulting red solution was stirred for six hours. The formed reddish precipitate was filtered off, washed with small portions of cold dry methanol, and dried in air.

The yield of the ligand LH_3 was 2.24 g (98%). M.p.193–194 °C. Anal. Found: C, 71.44; H, 6.48; N, 11.94%. $C_{28}H_{30}N_4O_3$; Calc.: C, 71.47; H 6.43; N, 11.91% ; FTIR: ν_{max} (KBr)/cm^{-1}: 1624, 1668, 3326, 3377 and 3226; ν_{max} (Nujol)/cm^{-1}: 1622, 1668, 3321, 3390 and 3172. ^{1}H-NMR: δH(400 MHz; $(D_3C)_2CO$; Me_4Si): 1.42 (9 H, s, CH_3), 2.17 (6 H, s, CH_3), 7.17 (2 H, t, J 7.2, CH), 7.28 (2H, t, J 7.8, CH), 7.34 (2H, d, J 7.8, CH), 8.19 (2H, s, CH), 8.25 (2H, d, J 7.2, CH), 8.98 (2H, br s, NH), 9.04 (2H, s, CH=N) and 13.51 (1H, s, OH); ^{13}C-NMR: δC(400 MHz, $(D_3C)_2CO$, Me_4Si) 23.50, 30.05, 34.04, 117.86, 121.31, 121.68, 124.24, 127.17, 130.97, 133.41, 135.96, 139.85, 141.96, 159.42 and 167.88. M.S.: m/z (EI) 469 $(M\text{-}H^+$, 100%), 440 (35, $M\text{-}2CH_3)^+$, 427 (75, $M\text{-}3CH_3)^+$ and 383 (20, M-2Ac-H)$^+$.

Synthesis of the tetranuclear complex $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ (1).

To a solution of water containing methanol-ethylacetate (1:4) of 500 mg (1.0 mmol) of 2,6-bis(2-acetylaminophenyl)iminomethyl)-4-tert-butylphenol, a solution in the same solvent mixture of 400 mg (2.0 mmol) of cupric acetate dihydrate was added. After stirring for 24 hours at room temperature the solution was left overnight, and a greenish-brown crystalline solid was separated (M.W. $C_{58}H_{66}Cu_4N_8O_{11}$ 1305.52; yield 440 mg; 72%). Crystals were obtained by crystallization of the crude compound from a methanol-dichloromethane solvent mixture. These crystals were used for X-ray diffraction and magnetic susceptibility measurements. (Found C, 54.5; H, 4.9; N, 8.8. $C_{58}H_{66}Cu_4N_8O_{11}$. Calc.: C, 53.31; H, 5.05; N, 8.57%); FTIR: ν_{max} (KBr)/cm^{-1}: 1629, 1689, 3301 and 3266. M.S.: m/z (ESI(+)) [acetonitrile]: 1205 (100, $(LCu_2)_2OH)^+$.

Structure Determination.

Data collection for the tetranuclear complex was performed on a Bruker Smart Apex diffractometer. Reflection indexing, Lorentz-polarisation correction, peak integration and background determination were carried out with the Bruker SAINTPLUS[16] program. Empirical multiscan absorption corrections using equivalent reflections were performed with the program SADABS.[17] The structure was solved and refined against F2 by full-matrix least-squares techniques using SHELXTL software package.[18] Hydrogen atoms were calculated after each cycle of refinement using a riding model, with C—H = 0.95 or 0.98 Å and U_{iso}(H) of 1.2 or 1.5 U_{eq}(parent), except the H atom corresponding to the hydroxyl group of the ligand, which was located in the final difference Fourier map, and subsequently refined isotropically with the O—H distances restricted to be 0.84 Å. During the last stage of structure completion by Difference Fourier Synthesis the presence of residual density was evident. It was interpreted as arising from one of the two methanol molecules, and then modelled using two disordered positions (labels A and B), with 50/50 occupancies. The carbon to oxygen distance inside each part of the methanol molecule was restricted to be 1.50 Å.

Crystallographic data and details on data collection are listed in Table 1. The Structure drawings were carried out with DIAMOND-3.2i, supplied by Crystal Impact.[19]

Table 1. Crystal data and structure refinement for $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ (1)

Empirical formula	$C_{58}H_{66}Cu_4N_8O_{11}$
Formula weight	1305.52
Temperature/K	152(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	31.183(7)
b/Å	9.097(2)
c/Å	21.277(5)
α/°	90.00
β/°	117.262(3)
γ/°	90.00
Volume/Å^3	5365(2)
Z	4
ρ_{calc} mg/mm^3	1.614
m/mm^{-1}	1.636
F(000)	2688.0
Crystal size/mm^3	0.23 × 0.10 × 0.06
2Θ range for data collection	2.94 to 54°
Index ranges	-39 ≤ h ≤ 39, -11 ≤ k ≤ 11, -27 ≤ l ≤ 27
Reflections collected	16085
Independent reflections	5861[R(int) = 0.0522]
Data/restraints/parameters	5861/3/397
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.1059
Largest diff. peak/hole / e Å^{-3}	0.54/-0.39

Electrochemical Measurements.

Voltammetric experiments were performed using an IPC-Win potentiostat, in one-compartment cell of 10 ml. The working electrode was a Pt disk with an active surface area of 0.049 cm^2. A platinum wire counter electrode and $Ag/AgCl/KCl_{aq}$ reference electrode (RE) were used. All potential values are referred to this RE. The formal potential of the ferrocene couple (Fc/Fc^+) versus RE is about 0.49 V in dry DMSO/Bu_4NBF_4.

All solutions were thoroughly deaerated by bubbling Ar through the solution prior to the experiments and above the solution during the measurements; 0.05 M Bu_4NBF_4 was used in all experiments as the supporting electrolyte.

Magnetic Susceptibility Measurements.

The magnetic properties were studied using a SQUID-magnetometer (MPMS XL7, Quantum Design). For the measurements, a polycrystalline sample was filled into a pre-calibrated quartz tube. Susceptibility data were taken at 0.1 kOe in a temperature range of 1.8 to 320 K. The susceptibility data were corrected for the sample holder previously measured under the same conditions and for the diamagnetic contributions of the sample using Pascal´s constants.[20]

Computational Details.

Spin-unrestricted calculations under the Density Functional Theory approach were done, using the hybrid B3LYP functional[21] and a triple-ζ all electron basis set for all atoms.[22] A guess function was generated using Jaguar 5.5 code.[23] Total energy calculations were performed with the Gaussian09 program,[24] using the quadratic convergence method, with a convergence criterion of 10^{-7} a.u.. Mulliken spin densities were also obtained from the single point calculations.

The Heisenberg-Dirac-van Vleck spin Hamiltonian was used to describe the exchange coupling in the polynuclear complex, equation 1:

$$\hat{H} = -\sum_{i>j} J_{ij} S_i S_j \qquad (1)$$

where, S_i and S_j are the spin operators of the paramagnetic centres i,j of the compound, and the J_{ij} parameters correspond to the magnetic coupling constants.[25]

Molecular Models.

For the theoretical calculation of the magnetic properties, the X-ray crystalline structure of compound **(1)** was used (Figure S1). A discrete model was adopted consisting only of the tetranuclear unit, deleting all the solvation molecules.

The five possible spin distributions for the studied compound were calculated, and the obtained total energy values permitted to build up a system of equations, where the different exchange constants are the unknown parameters.

Results and Discussion

Synthesis of complex (1).

The reddish ligand H_3L was synthesized at ambient temperature by simply stirring a methanolic solution of 2,6-diformyl-4-*tert*-butylphenol and *N*-acetyl-*o*-phenylenediamine for several hours. Ligand H_3L easily produces a dinuclear copper complex by the reaction with copper trimethylacetate dihydrate in dry methanol (Scheme 1, complex **(2)**).[26,27] However, a tetranuclear metal complex **(1)** can be obtained by mixing copper(II) acetate dihydrate with the ligand, H_3L, at room temperature in a non-dried solvent mixture of methanol: ethylacetate (1:4) (Scheme 1). The structure of the newly synthesized complex **(1)** was determined by single crystal X- ray diffraction and characterized by usual physicochemical methods. The possibility of different assemblies of the H_3L/ Cu^{II} system was explored by using mass-spectra experiments.

The mass spectra (ESI-MS) of complexes **(1)** and **(2)**, obtained from water containing acetonitrile solution are quite similar, and show a peak of high intensity (1205 m/z), which corresponds to the tetranuclear complex of composition $[(Cu_2L)_2OH]^+$ (Figures1a and 1b). Both of the observed peaks at 1205 m/z have the same structure of the isotopic pattern, which is typical for Cu_4 systems. The fragmentation of both $[(Cu_2L)_2OH]^+$ ions were studied by the tandem ESI-MS experiment, and this showed the same fragmentation scheme for both complexes. The peak at 1163 m/z corresponds to the deacetylation of the initial 1205 m/z ion. The peak pattern at 674 and 672 is identified as the trinuclear copper complex $(Cu_3L)O$, which is generated from complex $(Cu_2L^{63})(Cu^{65}CuL^{63})OH$ (1205 m/z) by elimination of a ligand and one copper atom

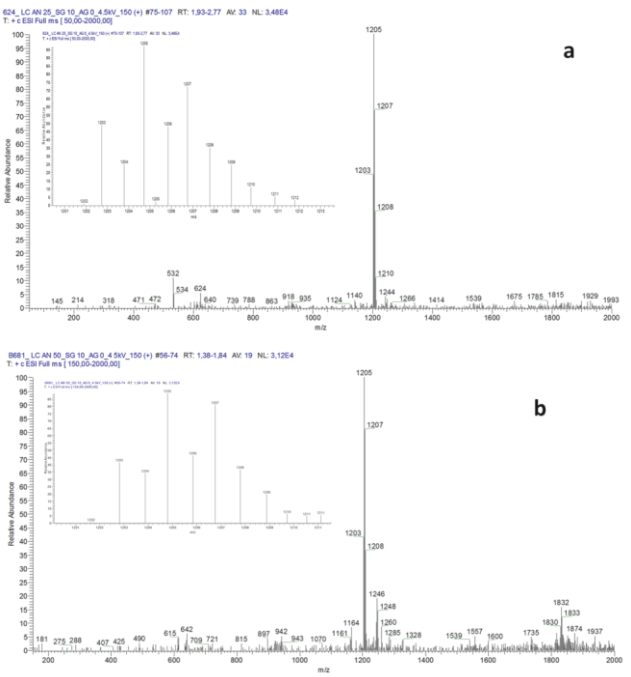


Figure 1. (a) The ESI-MS mass spectrum for the dinuclear complex **(2)** in acetonitrile (water) solution. The insert represents the isotopic pattern for peak 1205 m/z.(**b)** The ESI-MS mass spectrum for the tetranuclear complex **(1)** in acetonitrile (water) solution. The insert represents the isotopic pattern for peak 1205 m/z.

Structural Description.

Compound (**1**) crystallizes in the monoclinic system with space group *C2/c*. The symmetry point group of the tetranuclear

complex is C_i, therefore (**1**) presents an inversion centre.

Crystal data and structural refinement details are shown in Table 1, while interatomic distances and angles are given in Tables S1 and S2. Figure 2 shows a scheme of the tetranuclear unit, which can be described as formed by two identical dinuclear species. The Cu-Cu distance in the dinuclear moiety is 3.039(1) Å (Cu1-Cu2 and Cu1^i-Cu2^i). The Cu_2O_2 unit is almost planar, as the deviation of the O1, O4, Cu1, Cu2 atoms from the least squares plane is 0.1050(31), 0.1713(37), -0.0047(6), -0.0049(6) Å, respectively. The two planes defined by N1, N2, Cu1, O1, O4, and N3, N4, Cu2, O1, O4, form an angle of 13.9 (1)°.

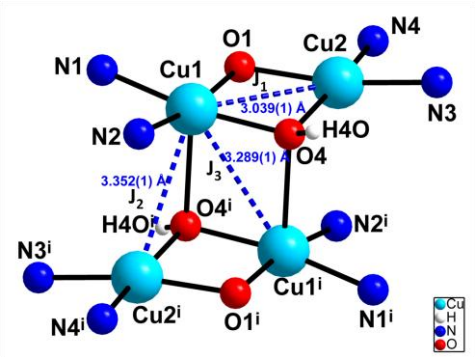


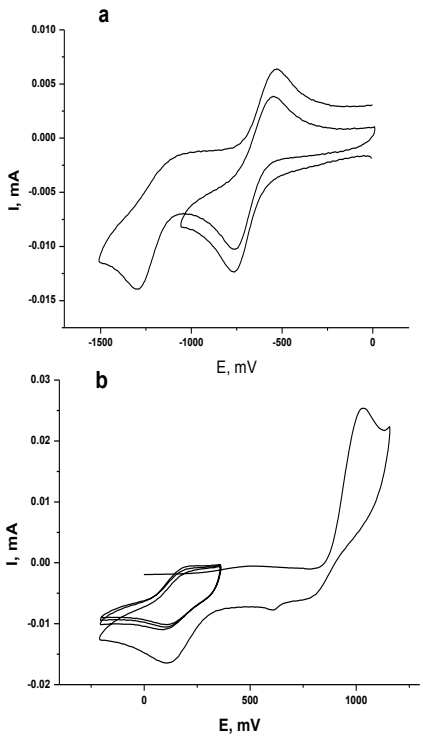
Figure 2. Schematic view of the copper(II) tetranuclear moiety. Symmetry code: (i) 1/2-x, 3/2-y, 1-z

Each dinuclear unit presents one tetracoordinated Cu^{II} centre in a square planar environment (Cu2 or Cu2^i), and one pentacoordinated Cu^{II} centre in a square pyramidal environment (Cu1 or Cu1^i). The square planar Cu^{II} centre has a coordination sphere formed by the phenoxido oxygen atom, the two nitrogen atoms from the acyclic ligand (imine and deprotonated amide nitrogen atoms), and an oxygen atom from the hydroxido group. The pentacoordinated Cu^{II} centre has the same donor atoms in the plane, and the fifth position is occupied by the oxygen atom of the hydroxido group from the neighbouring dinuclear unit (O4^i for Cu1 and O4 for Cu1^i). The distances between neighbouring copper atoms of the two dinuclear moieties are 3.352(1) Å for Cu1-Cu2^i and 3.289(1) Å for Cu1-Cu1^i.

Electrochemical properties.

The investigation of the electrochemical behaviour of the tetranuclear copper(II) cluster $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ **(1)** in dry DMSO was done in order to compare it to that of a similar complex $[Cu_2L(OCH_3)]$ **(2)**, having the same tridentate ligand.[26] This complex $[Cu_2L(OCH_3)]$ contains a Cu_2O_2 butterfly core, but with a methoxy bridge instead of the hydroxo bridging ligand present in the complex under study. This comparison was done to elucidate whether the tetranuclear structure is retained in solution. The voltammetric curves resulted almost identical to those obtained for the dinuclear copper analog.[26] Two successive one-electron peaks were observed in the cathodic region (Figure 3a). The first peak, corresponding to the formation of the mixed-valence species is quasi-reversible with the peak current ratio Ia/Ic equal to 0.87, the peak separation value being of 215 mV. However, contrary to the dicopper complex $[Cu_2L(OCH_3)]$, the second reduction peak is almost irreversible at a potential scan rate of 100 mV/s. An increase of the scan rate to 750 mV/s allows to observe the corresponding re-oxidation peak with Ia/Ic= 0.42. This indicates a low stability of the double-reduced complex. The formal peak potential values obtained for the tetranuclear Cu^{II} cluster in DMSO solution are very close to the values measured for $[Cu_2L(OCH_3)]$ complex[26] (for comparison: Epc1 = -0.80 V, Epc2 = -1.35 V in the former, and Epc1 = -0.81 V, Epc2 = -1.34 V in the latter case vs. Ag/AgCl/KCl).

The electrochemical oxidation peaks observed for the tetranuclear $[Cu_2L(OH)]_2$ complex (Figure 3b) were also similar to the voltammetric curve of the dinuclear analog $[Cu_2L(OCH_3)]$. The oxidation is a two-electron ligand-centered process (the phenol moiety is involved) and irreversible.[28,29] In the reverse scan a new reversible redox pair corresponding to Cu^{2+} reduction was observed at a potential of 0.18/0.11 V, thus indicating the destruction of the core. The comparison of peak potential values measured for solutions of $[Cu_2L(OH)]_2$ and $[Cu_2L(OCH_3)]$ complexes, revealed their similarity (for comparison: Epa = 1.03 V in the former, and Epa = 1.01 V, in the latter case, vs. Ag/AgCl/KCl).



Figures 3. Cyclic voltammetric curve obtained for a dry DMSO solution of $[Cu_2\ L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ **(1)** in the **(a)** cathodic region, and in the **(b)** anodic region.

The experimental electrochemical results discussed above do not allow to make an unequivocal conclusion about the stability of the tetranuclear Cu^{II} cluster $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ in DMSO solution. The qualitative and quantitative similarity of the voltammetric responses of the two complexes might be attributed to two reasons. On one hand, it might correspond to a dissociation of the tetranuclear cluster to dinuclear moieties. Our previous investigation showed[26] that the influence of the nature of

the bridging ligand (OCH_3 or OH), as well as the type of the N-substituent in the o-phenylenediamine moiety of the tridentate ligand (Ac or Boc), on the peak potential values of Cu_2O_2 complexes is negligible. Hence, it is not surprising that the peak potential values obtained for $[Cu_2L(OCH_3)]$ and $[Cu_2L(OH)]$ (after dissociation) would be similar. On the other hand, the structure determination of the tetranuclear Cu^{II} cluster $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ revealed a long distance between the copper centres belonging to different dimeric units, and therefore a weak interaction between the two dinuclear units can be expected. So, if the tetranuclear species persists in DMSO solution, it might be expected to behave as a dinuclear unit from the electrochemical point of view.

Magnetic Properties.

Magnetic properties of the complex $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ were investigated by magnetization measurements with an applied field of 0.1 kOe, at variable temperature in the range of 1.8-300 K. The experimental magnetic data are shown in Figure 4, as the temperature dependence of $\chi_M T$. Figure 4 shows that the $\chi_M T$ values decrease monotonically from a value of 0.64 $cm^3mol^{-1}K$ at 300 K to approximately 0 at 1.8 K. The value at 300 K is lower than the expected for four non-interacting Cu^{II} ions with $S = 1/2$ ($g = 2.0$, $\chi_M T = 1.50$ $cm^3mol^{-1}K$), indicating the presence of strong bulk antiferromagnetic interactions at room temperature.[30-32]

The magnetic interactions mediated by apical-equatorial bridges are known to be much weaker than those mediated by equatorial-equatorial bridging ligands. [33-35] Therefore from a magnetic point of view, the tetranuclear complex can be described in a first approximation as formed by two non-interacting dinuclear units, in which the two Cu^{II} ions are linked through phenoxido and hydroxido equatorial-equatorial bridges. The analysis of the magnetic data was done by using the Bleaney-Bowers equation, with the isotropic Heisenberg Hamiltonian ($H = -J_1 S_1{\cdot}S_2$, with $S_1 = S_2 = 1/2$, equation 2).[36] The presence of residual paramagnetic impurities was taken into account, together with the temperature independent paramagnetism (TIP).

$$\chi_M T = 2(1-\rho)\frac{2N\beta^2 g^2}{k_B}\frac{1}{\left(3+\exp\left(-\frac{J_1}{k_B T}\right)\right)} + \rho\frac{N\beta^2 g^2}{2k_B} + TIP \qquad (2)$$

In equation 2, N, χ_M, β, g, k_B, ρ and TIP have their usual meaning. The best fit of the temperature dependence of the $\chi_M T$ data in the temperature range of 2 to 300 K was obtained with a g value of 2.05; $\rho = 0.001$, TIP = $5.0{\cdot}10^{-4}$, and a J_1 value of -550 cm^{-1} (Figure 4a). Considering that interdinuclear interactions should be evident at very low temperatures, a second fit in the 50 to 300 K was done. In this case the best fit was obtained with a g value of 2.0; $\rho = 0.058$, TIP =$7.9{\cdot}10^{-4}$, and a J_1 value of -480cm^{-1} (Figure 4b). As it can be seen from the two fitting procedures, the obtained J_1 values for the intradimer interaction are not very sensible to the set of parameters used, however both are in the range of the expected values for phenoxido-hydroxido bridges in dinuclear Cu^{II} complexes.[33-35,37-42] The reported complexes present strong intramolecular magnetic interactions, with J values ranging from -630 to – 336 cm^{-1}.

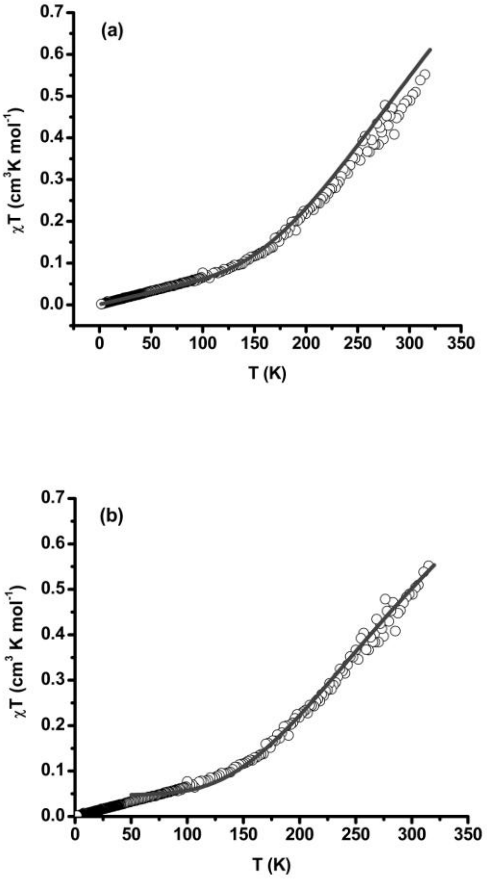


Figure 4. Temperature dependence of the susceptibility ($\chi_M T$) plot for Cu_4. Fit of the experimental data in the 2 -300 K **(a)** and 50 – 300 K **(b)** range with Bleaney-Bowers equation.

In the tetranuclear unit, each dinuclear unit presents two different exchange magnetic pathways, which are defined by the phenoxido (Cu1-O(Ph)-Cu2 : 100.12°) and hydroxido (Cu1-O(H)-Cu2 : 105.23°) bridges. Literature data for this kind of complexes reports that the type and magnitude of the exchange interaction is dependent of the structural parameters, such as distortion of the coordination geometry and the coplanarity of the copper ion and the bridging ligands. Therefore, strong antiferromagnetic exchange interactions require both good σ-bonding orientation of the magnetic orbitals (i.e., the orbitals that contain the unpaired electrons) and good superexchange pathways provided by the bridging atom orbitals.[43-46] In the reported complex, the $d_{x^2-y^2}$ corresponds to the magnetic orbital, which is localized in the same plane of the bridging ligands, presenting both phenoxido and hydroxido ligands in an equatorial-equatorial coordination mode. This structural feature promotes the observed strong antiferromagnetic interaction between the Cu^{II} ions.

In order to describe in a more detailed way the magnetic phenomenon, due to the different exchange pathways present in the tetranuclear system, DFT calculations were performed. The calculation of the magnetic exchange interaction present between

the copper atoms in the dinuclear unit that are linked by the phenoxido and hydroxido bridges gave the following *J* value: J_{1calc} = -440 cm^{-1} (Cu1 - Cu2) and ($Cu1^{i}$ - $Cu2^{i}$). This is the dominant magnetic interaction in the system, and is related with the quasi-planarity of the Cu_2O_2 plane.

The magnetic interactions through the hydroxido bridges in the equatorial-axial coordination mode were also estimated. Two exchange pathways are formed by the μ_3-OH, thus two magnetic exchange constants were calculated, J_{2calc} = +0.5 cm^{-1} (Cu1-$Cu2^{i}$ and $Cu1^{i}$-Cu2); and J_{3calc} = +1.7 cm^{-1} (Cu1-$Cu1^{i}$). These weak ferromagnetic values of the exchange constants are in agreement with the existing internuclear coordination.

In order to validate the calculated electronic structures, Mulliken spin density values were determined for the tetranuclear structure. The values obtained in the calculation for the Cu^{II} atoms are in the range of 0.60 to 0.64e-, as reported previously for other studied Cu^{II} systems.[47,48] Most of the calculated spin density is located on the metal centres, with the rest of the density appearing over the atoms of the first coordination sphere; this occurs through a delocalization mechanism. As an example, two different spin density surfaces of this system are shown in Figure S2; (a) one of the antiferromagnetic singlet states, S_T = 0, and (b) the ferromagnetic quintuplet state S_T = 2.

Conclusions

A polytopic flat ligand H_3L in the reaction with Cu^{II} ions leads to the dinuclear complex when the reaction is done in dry methanol, while the same reaction done with a water containing methanol - ethyl acetate solvent mixture, results in the formation of a tetranuclear species. This behaviour permits to isolate a tetranuclear complex, $[Cu_2L(OH)]_2{\cdot}2CH_3OH{\cdot}H_2O$ **(1)**, which was structurally and magnetically characterized in the solid state.

This dualism of the complex nuclearity is also present when complex **(1)** is dissolved in dry and water containing solvents. In electrochemical experiments using dry DMSO solution, the tetranuclear complex $[Cu_2L(OH)]_2$ **(1)** behaves as a dinuclear moiety of similar structure, $[Cu_2L(OCH_3)]$, as can be inferred from the voltammetric data. Contrary, the dissolution of the dinuclear complex $[Cu_2L(OCH_3)]$ in water containing solvents, such as acetonitrile or methanol, produces a mass-spectrum characteristic for tetranuclear species $[Cu_2L(OH)]_2$.

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† Electronic Supplementary Information (ESI) available: Supporting Information: Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Centre, CCDC 930542. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre; Postal Address : CCDC, 12 Union Road , Cambridge CB21EZ, UK, Telephone: (44) 01223 762910, Fax: (44) 01223 336033, e-mail: deposit@ccdc.cam.ac.uk.. See DOI: 10.1039/b000000x/

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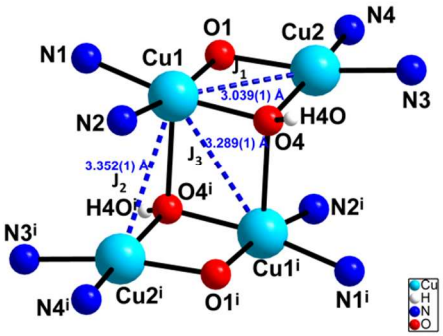

Dinuclear/tetranuclear interconversion of a magnetically coupled copper(II) Schiff base complex driven by water rich solvents.