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ORIGINAL PAPER

Theoretical description of the magnetic properties of μ_3-hydroxo bridged trinuclear copper(II) complexes

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Abstract A theoretical study of the magnetic properties, using density functional theory, of a family of trinuclear μ_3-OH copper(II) complexes reported in the literature is presented. The reported X-ray crystal structures of $[Cu_3(\mu_3\text{-}OH)(aat)_3(H_2O)_3](NO_3)_2{\cdot}H_2O$ (*HUKDUM*), where aat: 3-acetylamine-1,2,4-triazole; $[Cu_3(\mu_3\text{-}OH)(aaat)_3(H_2SO_4)(HSO_4)(H_2O)]$ (*HUKDOG*), where aaat: 3-acetylamine-5-amine-1,2,4-triazole; $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(tchlphac)_2]$ (*HOHQUR*), where PhPyCNO: phenyl 2-pyridyl-ketoxime and tchlphac: acid 2,4,5-trichlorophenoxyacetic; $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(NO_3)_2(CH_3OH)]$ (*ILEGEM*); $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)_3(ClO_4)_2]$ (*QOPJIP*), where Hpz=pyrazole; $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)(Me_3CCOO)_2]\,2Me_3CCOOH$ (*DEFSEN*) and $[Cu_3(\mu_3\text{-}OH)(\text{8-amino-4-methyl-5-azaoct-3-en-2-one})_3][CuI_3]$ (*RITXUO*), were used in the calculations. The magnetic exchange constants were calculated using the broken-symmetry approach. The calculated J values are for *HUKDUM* $J_1=-68.6\ cm^{-1}$, $J_2=-69.9\ cm^{-1}$, $J_3=-70.4\ cm^{-1}$; for *HUKDOG*, $J_1=-73.5\ cm^{-1}$, $J_2=-58.9\ cm^{-1}$, $J_3=-62.1\ cm^{-1}$; for *HOHQUR* $J_1=-128.3\ cm^{-1}$, $J_2=-134.1\ cm^{-1}$, $J_3=-120.4\ cm^{-1}$; for *ILEGEM* $J_1=-151.6\ cm^{-1}$, $J_2=-173.9\ cm^{-1}$, $J_3=-186.9\ cm^{-1}$; for *QOPJIP* $J_1=-118.3\ cm^{-1}$, $J_2=-106.0\ cm^{-1}$, $J_3=-120.6\ cm^{-1}$; for *DEFSEN* $J_1=-74.9\ cm^{-1}$, $J_2=-64.0\ cm^{-1}$, $J_3=-57.7\ cm^{-1}$ and for *RITXUO* $J_1=-10.9\ cm^{-1}$, $J_2=+14.3\ cm^{-1}$, $J_3=-35.4\ cm^{-1}$. The Kahn-Briat model was used to correlate the calculated magnetic properties with the overlap of the magnetic orbitals. Spin density surfaces show that the delocalization mechanism is predominant in all the studied compounds.

Keywords Cu^{II} · DFT · Hydroxo-centered · Kahn-Briat · Trinuclear complex

Introduction

In the field of molecular magnetism, polynuclear transition metal complexes have been attracting much attention because of their interesting magnetic properties [1–3]. In the characterization of this kind of compounds, theoretical calculations permit to analyze different systems that are too complicated to be fitted with analytical expressions. Compared with the many theoretical studies on binuclear transition-metal complexes [4, 5], studies performed on polynuclear systems have been limited [6–8], since the coupling interaction mechanisms in these systems are more complicated, as more exchange pathways between the paramagnetic centers are present.

The use of theoretical methods such as density functional theory (DFT) has been applied to many research areas, for example magnetism [9, 10]. The good results obtained in the calculation of magnetic exchange constants in systems like dinuclear transition-metal complexes, and in many polynuclear

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compounds, have shown that the broken-symmetry approach is a powerful tool to be used in the evaluation of the magnetic properties [6]. In this way this type of calculation has become essential to study systems that are too complicated to evaluate with analytical methods, for example because of the numerous magnetic exchange pathways present in a given system. As one of the simplest polynuclear systems, the trigonal trinuclear oxo and hydroxo complexes are attracting much attention since these systems present spin frustration phenomenon [11, 12].

Some reports exist in the literature in which theoretical calculations have been done on trigonal Cu^{II} systems, like the work of Wang et al. [12], Yoon et al. [13] and Afrati et al. [14]. However, all these authors used model structures of the trigonal Cu^{II} system to describe the magnetic properties.

In the work of Wang et al. [12] a model structure, $[Cu_3(\mu_3\text{-}X)_2(pz)_3L_3]$ (where X=Cl, Br, O; L=Br, Cl and pz=pyrazole) was used to obtained a magneto-structural relation, which reveals that the magnetic coupling interaction is sensitive to the Cu-(μ_3-X)-Cu angle. With the angle changing from 76° to 120°, the magnetic coupling interaction is switched from ferromagnetic to antiferromagnetic.

The work of Yoon et al. [13], reported the use of a trigonal model structure to compare the magnetic properties between trinuclear μ_3O and μ_3OH Cu^{II} systems. The results of this work show that for $Cu_3(\mu_3\text{-}O)$ systems the ferromagnetic state is favored when the μ_3-O ligand is out of plane formed by the three Cu^{II} centers. Also this study shows that the DFT analysis permits to conclude that the difference in the magnitude of the magnetic exchange constant between μ_3O and μ_3OH arises from the large decrease in the Cu^{II}-oxo bonding interactions upon protonation. Consequently, the ferromagnetic contribution to the exchange coupling is reduced, which reflects the decrease in the spin density contributions from the orthogonal magnetic orbitals of the three metal centers to the bridging ligand.

The work of Afrati et al. [14] presents an experimental and theoretical study of trinuclear Cu^{II} systems. This work reports two experimental structures, which are used together with four model structures to calculate the magnetic properties of these systems, using a spin-projection method [15]. This approach has been used by many authors, but Ruiz et al. [10] have reported that the use of the non-projection method gives a more accurate evaluation of the magnetic exchange constant.

An interesting work published by Ghosh et al. [16] reports an experimental and theoretical study of trinuclear copper(II) μ_3-OH centered ferromagnetically coupled systems. The results found in this work show that there is not a clear relation between the magnetic exchange constant and the displacement of the hydroxo group from the plane of the copper centers of these highly distorted systems.

In this work we present the density functional study of the magnetic properties of seven trinuclear $Cu_3(\mu_3\text{-}OH)$ systems reported in the literature. The structures used in this work are $[Cu_3(\mu_3\text{-}OH)(aat)_3(H_2O)_3](NO_3)_2{\cdot}H_2O$ [17] (*HUKDUM*), where aat=3-acetylamine-1,2,4-triazole, $[Cu_3(\mu_3\text{-}OH)(aaat)_3(H_2SO_4)(HSO_4)(H_2O)]$ [17] (*HUKDOG*), where aaat=3-acetylamine-5-amine-1,2,4-triazole, $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(tchlphac)_2]$ [14] (*HOHQUR*) where PhPyCNO=phenyl 2-pyridyl-ketoxime and tchlphac=acid 2,4,5-trichlorophenoxyacetic, $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(NO_3)_2(CH_3OH)]$ [18] (*ILEGEM*), $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)_3(ClO_4)_2]$ [19] (*QOPJIP*), where Hpz=pyrazole, $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)(Me_3CCOO)_2]$ 2Me_3CCOOH [20] (*DEFSEN*), and $[Cu_3(\mu_3\text{-}OH)$(8-amino-4-methyl-5-azaoct-3-en-2-one)$_3][CuI_3]$ [21] (*RITXUO*). An orbital analysis using the Khan-Briat model is performed to evaluate the relation between the exchange constant and the overlap of the magnetic orbitals of these systems. Also the spin density surfaces are calculated to evaluate the spin distribution over the paramagnetic centers and over the coordination sphere.

Methods

Molecular models

For all the calculations the X-ray crystalline structures were obtained from the Cambridge Crystallographic Data Centre (CCDC). The CCDC codes for these compounds are $[Cu_3(\mu_3\text{-}OH)(aat)_3(H_2O)_3](NO_3)_2{\cdot}H_2O$ (*HUKDUM*), $[Cu_3(\mu_3\text{-}OH)(aaat)_3(H_2SO_4)(HSO_4)(H_2O)]$ (*HUKDOG*), $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(tchlphac)_2]$ (*HOHQUR*), $[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(NO_3)_2(CH_3OH)]$ (*ILEGEM*) $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)_3(ClO_4)_2]$ (*QOPJIP*), $[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)(Me_3CCOO)_2]$ 2Me_3CCOOH (*DEFSEN*), and $[Cu_3(\mu_3\text{-}OH)$(8-amino-4-methyl-5-azaoct-3-en-2-one)$_3][CuI_3]$ (*RITXUO*).

A discrete model was adopted consisting only of the $[Cu_3(OH)(L)]^{n+}$ unit, without considering any solvation molecule or counteranion Fig. 1. For *HUKDOG* the crystal structure of the trinuclear species was isolated with two coordinated sulphate anions. In order to keep the charge distribution on the sulphate groups, the oxygen atoms of these groups, which were coordinated to other copper centers, were used as protonated units (black circles, Fig. 2). The protons were optimized under DFT level, using TURBOMOLE 5.9.1 [22], keeping the rest of the structure frozen. For *QOPJIP* the crystal structure is formed by two trinuclear units linked together by a perchlorate anion; only one of these trinuclear units was considered for the calculations.

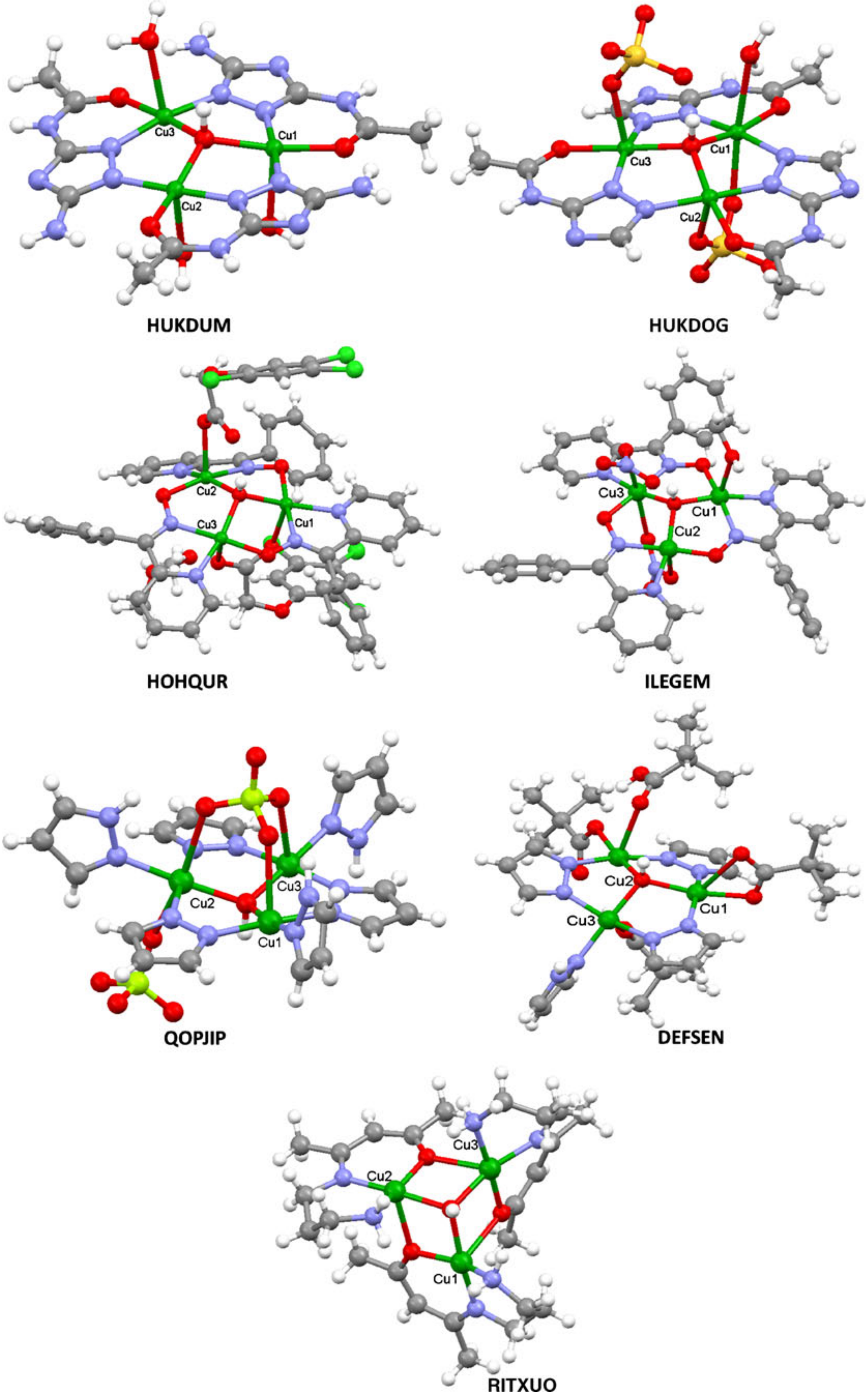


Fig. 1 Cationic structures ($(Cu_3\mu_3\text{-}OH)^{n+}$), used in the calculations of the intramolecular magnetic exchange constant, J

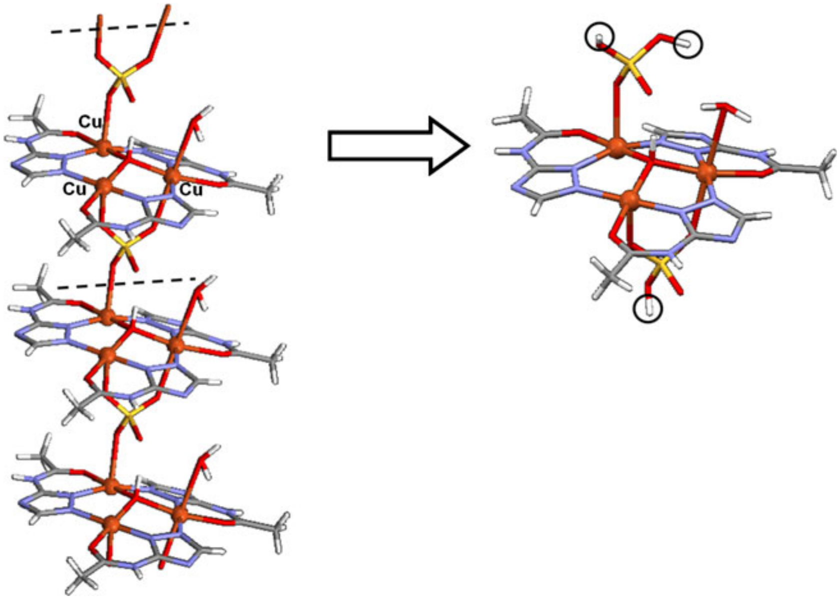


Fig. 2 Scheme of the fragmentation and protonation of structure *HUKDOG*, to obtain the trinuclear unit to perform the DFT calculations

DFT calculations of the magnetic properties

Spin-unrestricted calculations under the density functional theory approach were done, using the hybrid B3LYP functional [23] and a triple-ζ all electron basis set for all atoms [24]. A guess function was generated using Jaguar 5.5 code [25], a triple-ζ basis set was used for all the atoms. Total energy calculations were performed with the Gaussian09 program [26], using the quadratic convergence method with a convergence criterion of 10^{-7}a.u.. Mulliken spin densities were obtained from the Gaussian09 single point calculations.

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

$$\widehat{H} = -\sum_{i>j} J_{ij} S_i S_j, \tag{1}$$

where S_i and S_j are the spin operators of the paramagnetic centers i,j of the compound. The J_{ij} parameters are the magnetic coupling constants between the centers with unpaired electrons of the molecule. The Hamiltonian describing all the studied compounds is:

$$\widehat{H} = -J_1(S_1 \cdot S_2) - J_2(S_2 \cdot S_3) - J_3(S_3 \cdot S_1). \tag{2}$$

The four possible spin distributions for the studied systems were calculated, and the obtained total energy values permitted to build up a system of three equations, where the different exchange constants are the unknown parameters. Scheme 1 shows the geometric representation of the ferromagnetic solution and one of the possible broken-symmetry solutions. Table 1 shows the four different spin solutions used in the described methodology for all studied systems.

The utilization of the non-projected energy of the broken-symmetry solution as the energy of the low spin state within the DFT methodology gives good results because it avoids the cancellation of the non-dynamic correlation effects, as stated in studies carried out by other authors [27]. Thus, the J value is obtained using the non-projected method proposed by Ruiz et al. [10].

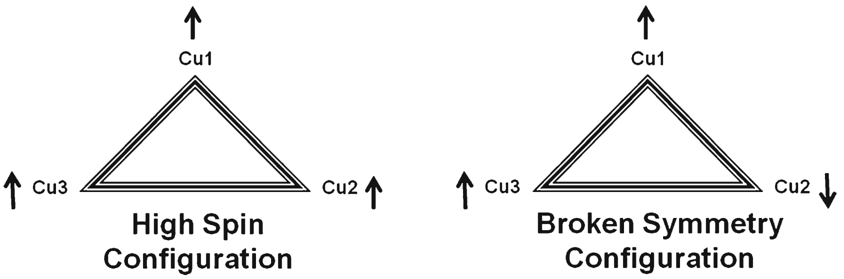
$$E_{HS} - E_{BS} = -(2S_1S_2 + S_2)J, \tag{3}$$

where S_1 and S_2 are the total spins of the two interacting paramagnetic centers with $S_1 \geq S_2$. It can also be mentioned that the use of the original broken-symmetry approach, proposed by Noodlemann [28] provides an overestimation of the stability of the low spin states.

The methodology used in the present work was developed, largely used and discussed by Alvarez and Ruiz. These authors have published many papers related to the use of DFT applied to magnetic phenomena of inorganic compounds ranging from dinuclear to spin Peierls. Ruiz et al. have tested several basis sets and functionals under the density functional theory and also showing that the HF methodology does not give good results [29–35].

It is important to stress that the so-called experimental J values, with which the calculated values are compared, are obtained by using analytical models based on several approximations. Therefore, the reported experimental J values cannot be considered as an absolute reference to be compared to the calculated ones. DFT calculations permit to obtain the total energy of all possible spin states of the molecule, completely isolated from the crystal lattice interactions.

Scheme 1 Geometric representation of two of the spin solutions for trigonal Cu^{II} systems



Results and discussion

Cu$_3$(μ_3-OH)(aat)$_3$(H$_2$O)$_3$](NO$_3$)$_2$·H$_2$O (*HUKDUM*)

The reported structure of *HUKDUM* presents a triangular moiety with three different Cu-Cu distances (3.347(2), 3.374(2), 3.393(2) Å), forming a scalene triangle. It can be mentioned that all the metal centers have square base pyramidal geometries, and the copper centers are bridged by the nitrogen atoms of the substituted triazole ligands in a μ_2-mode, while the μ_3-OH ligand is bridging the three copper centers (Table 2). The distance of the hydroxo group from the plane formed by the three copper centers is 0.435 Å. The calculated values of the three exchange constants are: $J_1=-68.6$ cm^{-1}, $J_2=-69.9$ cm^{-1}, $J_3=-70.4$ cm^{-1}. Table 2 summarizes the intermetallic distances and the different bridges between the copper centers. Even though the three exchange pathways present the same bridging ligands, the distortions in each pathway produce a difference in the intermetallic distances and therefore a change in the antiferromagnetic behavior (Table 3).

No analytical expression for a scalene triangle is available in the literature; therefore Ferrer et al. [17] used an approximation to estimate an average of the exchange constants with an analytical expression for an equilateral arrangement. The fit gave a J value of −194.6 cm^{-1}. The use of the described theoretical tools allows the evaluation of all three magnetic exchange constants present in this compound.

[Cu$_3$(μ_3-OH)(aaat)$_3$(H$_2$SO$_4$)(HSO$_4$)(H$_2$O)] (*HUKDOG*)

The crystal structure reported by Ferrer et al. [17] (*HUKDOG*) shows that the trigonal arrangement of the copper atoms forms an isosceles triangle, with Cu-Cu distances of 3.337(4), 3.337(5) and 3.364(4) Å. This system shows that two copper centers have the same intermetallic distance. However, from the magnetic point of view this interaction cannot be consider as equal since the bridging ligands are not the same. For Cu$_1$-Cu$_2$ a μ_2-triazole, a μ_2-sulphate and a μ_3-OH act as bridging ligands; for Cu$_2$-Cu$_3$ the bridging ligands are the μ_2-triazole and a

Table 1 Different spin solutions used for the calculations for the seven Cu^{II} systems

Cu1	Cu2	Cu3
α	α	α
β	α	α
α	β	α
α	α	β

Table 2 Metal distances between the copper atoms and the bridging ligands that link the metal centers, for all the structures studied

Atoms	Metal distances (Å)	Bridges
HUKDUM		
Cu$_1$-Cu$_2$	3.347(2)	μ_2-triazole; μ_3-OH$^-$
Cu$_2$-Cu$_3$	3.374(2)	μ_2-triazole; μ_3-OH$^-$
Cu$_1$-Cu$_3$	3.393(2)	μ_2-triazole; μ_3-OH$^-$
HUKDOG		
Cu$_1$-Cu$_2$	3.337(4)	μ_2-triazole; μ_2-SO$_4^{2-}$ μ_3-OH$^-$
Cu$_2$-Cu$_3$	3.337(5)	μ_2-triazole; μ_3-OH$^-$
Cu$_1$-Cu$_3$	3.364(4)	μ_2-triazole; μ_3-OH$^-$
HOHQUR		
Cu$_1$-Cu$_2$	3.210(2)	μ_2-ketoxime; μ_3-OH
Cu$_2$-Cu$_3$	3.153(2)	μ_2-ketoxime; μ_3-OH
Cu$_1$-Cu$_3$	3.135(2)	μ_2-ketoxime; μ_3-OH; μ_2-trichlorophenoxiacetate
ILEGEM		
Cu$_1$-Cu$_2$	3.225(1)	μ_2-ketoxime; μ_3-OH
Cu$_2$-Cu$_3$	3.152(1)	μ_2-ketoxime; μ_3-OH; μ_2-NO^{3-}
Cu$_1$-Cu$_3$	3.261(1)	μ_2-ketoxime; μ_3-OH
QOPJIP		
Cu$_1$-Cu$_2$	3.355(1)	μ_2-pyrazolate; μ_3-OH; μ_3-ClO^{4-}
Cu$_2$-Cu$_3$	3.368(1)	μ_2-pyrazolate; μ_3-OH; μ_3-ClO^{4-}
Cu$_1$-Cu$_3$	3.386(1)	μ_2-pyrazolate; μ_3-OH; μ_3-ClO^{4-}
DEFSEN		
Cu$_1$-Cu$_2$	3.384(1)	μ_2-pyrazolate; μ_3-OH
Cu$_2$-Cu$_3$	3.2503(9)	μ_2-pyrazolate; μ_3-OH
Cu$_1$-Cu$_3$	3.2950(9)	μ_2-pyrazolate; μ_3-OH
RITXUO		
Cu$_1$-Cu$_2$	3.243(1)	μ_3-OH; μ_2-Schiff-base
Cu$_2$-Cu$_3$	3.247(1)	μ_3-OH; μ_2-Schiff-base
Cu$_1$-Cu$_3$	3.255(1)	μ_3-OH; μ_2-Schiff-base

A summary of the calculated J values for the seven studied compounds is shown in Table 3

Table 3 Calculated intramolecular exchange constants for the trinuclear Cu systems

Molecule	J_1(cm^{-1})	J_2 (cm^{-1})	J_3 (cm^{-1})
HUKDUM	−68.6	−69.9	−70.4
HUKDOG	−73.5	−58.9	−62.1
HOHQUR	−128.3	−134.1	−120.4
ILEGEM	−151.6	−173.9	−186.9
QOPJIP	−118.3	−106.0	−120.6
DEFSEN	−74.9	−64.0	−57.7
RITXUO	−10.9	+14.3	−35.4

μ_3-OH (Table 2). The distance of the hydroxo group from the plane formed by the three copper centers is 0.511 Å. Structurally for *HUKDOG* the trigonal system is isosceles, but from the magnetic point of view this system should be considered as a scalene triangle. Three different magnetic exchange constants (J_1, J_2 and J_3) were defined. The calculated values of the magnetic exchange interactions are, J_1=−73.5 cm^{-1}, J_2=−58.9 cm^{-1} and J_3=−62.1 cm^{-1}.

The experimental magnetic data of this compound were fitted by Ferrer et al. [17] using an approximation with an isotropic model for an equilateral arrangement. The obtained J value of −185.1 cm^{-1} corresponds to an average of the three magnetic constants present in the studied compound. The fit of the experimental data with one J value is an over simplified model to explain the magnetic behavior of the system, and the DFT calculations permit a description of each magnetic exchange pathway.

$[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(tchlphac)_2]$ (*HOHQUR*)

The structure of the trinuclear arrangement of *HOHQUR* reported by Afrati et al. [14] presents three different intermetallic distances, 3.210(2), 3.153(2) and 3.135(2) Å, indicating that this structure should be considered as a scalene triangle. The three copper centers present square base pyramidal geometries, and the metal centers are bridged by the oxygen and nitrogen atoms of the ketoxime ligand in a μ_2-mode, and by a μ_3-OH ligand that coordinates the three metal centers. There is also a deprotonated anion of 2,4,5-trichlorophenoxiacetic acid that coordinates two copper centers, Cu_1-Cu_3 (Table 2). The distance of the hydroxo group from the plane formed by the three copper centers is 0.657 Å. The calculated values of the three exchange interactions are J_1=−128.3 cm^{-1}, J_2=−134.1 cm^{-1}, J_3=−120.4 cm^{-1}.

The experimental magnetic data of *HOHQUR* were fitted by Afrati et al. [14] using an equilateral model but this approximation is only appropriate for the high temperature range (100–300 K). The low temperature region was fitted independently (2–20 K) using a spin Hamiltonian that includes the isotropic phenomena and the antisymmetric exchange factor was taken into account.

$[Cu_3(\mu_3\text{-}OH)(PhPyCNO)_3(NO_3)_2(CH_3OH)]$ (*ILEGEM*)

The X-ray structure reported by Liu et al. [18] for this system shows that the trinuclear unit forms a scalene triangle with copper distances of 3.225(1), 3.152(1) and 3.261(1) Å. The copper atoms Cu_1-Cu_2 and Cu_1-Cu_3 are bridged by a μ_2-ketoxime ligand and by a μ_3-OH ligand, and Cu_2-Cu_3 are bridged by the same ligands mentioned above and also by a nitrate anion (Table 2). The distance of the hydroxo group from the plane formed by the three copper centers is 0.549 Å. Therefore, taking into consideration the metal distances and the different arrangements of the trinuclear unit, three magnetic exchange interactions were calculated, and the values obtained are J_1=−151.6 cm^{-1}, J_2=−173.9 cm^{-1}, J_3=−186.9 cm^{-1}.

The experimental magnetic data reported by Liu et al. [18] were fitted by the authors with an equilateral model. A poor fit of the experimental data was achieved; only the high temperature range (100–300 K) is relatively well defined by the use of this model. The fit of the experimental data with only one J value is an extremely simplified model to explain the magnetic behavior of the studied system. The DFT calculations allow for a better description of the magnetic phenomenon of this compound isolated from the crystal lattice.

$Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)_3(ClO_4)_2]$ (*QOPJIP*)

The analysis of the X-ray structure of *QOPJIP* reported by Zhou et al. [19] shows that the copper centers form a scalene triangle with metal distances for Cu_1-Cu_2 3.355(1) Å; Cu_2-Cu_3 3.368(1) Å; Cu_1-Cu_3 3.386(1) Å. The coordination environment around Cu_1 is octahedral, whereas for Cu_2 and Cu_3 is square base pyramidal. The metal centers are bridged by a μ_2-pyrazolate, a μ_3-OH ligand and by a μ_3-ClO_4^-. The distance of the hydroxo group from the plane formed by the three copper centers is 0.466 Å. The system presents three exchange pathways with the same bridging ligands. However, the distortions in each pathway produce a change in the copper-copper distances and three different J values are obtained. The DFT calculations for *QOPJIP* permitted to evaluate the three exchange constants independently, J_1=−118.3 cm^{-1}, J_2=−106.0 cm^{-1}, J_3=−120.6 cm^{-1}. Table 2 summarizes the intermetallic distances and the different bridges between the copper centers.

Zhou et al. [19] used an equilateral model to evaluate the mean intramolecular exchange interaction, J. It can be inferred that the authors used an approximated model to fit the magnetic data, since the system is a scalene triangle.

$[Cu_3(\mu_3\text{-}OH)(pz)_3(Hpz)(Me_3CCOO)_2(Me_3CCOOH)_2]$ (*DEFSEN*)

The structure reported by Zhou et al. presents three different intermetallic distances, Cu_1-Cu_2 3.384(1) Å; Cu_2-Cu_3 3.2503 (9) Å; Cu_1-Cu_3 3.2950(3) Å, forming a scalene triangle. The copper centers are bridged by a μ_3-OH and by μ_2-pyrazolate ligands (Table 2). The three copper centers present a pentacoordiante environment. The displacement of the hydroxo group from the plane formed by the three copper centers is 0.567 Å. Taking into consideration the three different metal distances and the distortions of each metal center in the trinuclear unit, three magnetic exchange interactions were calculated, $J_1=-74.9\ cm^{-1}$, $J_2=-64.0\ cm^{-1}$ and $J_3=-57.7\ cm^{-1}$.

The experimental magnetic data reported by Zhou et al. [20] were fitted with an isosceles model and considered the mean-field approximation. A good fit of the experimental data was achieved only in the temperature range of 50–300 K. The fit of the experimental data using an isosceles model, may result in an incorrect interpretation of the magnetic properties, since the system forms a scalene triangle. The DFT calculations allow for a better description of the magnetic exchange interactions of this system.

$[Cu_3(\mu_3\text{-}OH)(\text{8-amino-4-methyl-5-azaoct-3-en-2-one})_3][CuI_3]$ (*RITXUO*)

The trinuclear complex reported by Mukherjee et al. [21] forms a scalene triangle, with copper distances of 3.243 (1), 3.247(1) and 3.255(1) Å. The trinuclear unit is formed by the central μ_3-OH ligand and by three Schiff base ligands (Table 2). The metal centers are bridged by the μ_3-OH group and by an oxygen atom of the Schiff base ligand. It is important to stress that this structure was considered because it presents a very large displacement of the hydroxo group from the plane formed by the three copper centers, 0.794 Å. The calculated values of the three exchange constant for this system are $J_1=-10.9\ cm^{-1}$, $J_2=+14.3\ cm^{-1}$, $J_3=-35.4\ cm^{-1}$.

The fit of the experimental data with only one J value is a simplified model to explain the magnetic behavior of the system since the trinuclear unit forms a scalene triangle. The DFT calculations allow for a more exact description of the magnetic exchange interactions of this compound.

Figure 3 shows the correlation between the mean calculated magnetic exchange constants and the mean experimental values. All the calculated values are below the experimental ones. This can be due to the fact that the experimental J values have been obtained from bulk magnetic data that include other magnetic phenomena in the crystalline lattice. On the other hand, DFT calculations are able to isolate the magnetic phenomena from the molecular structure.

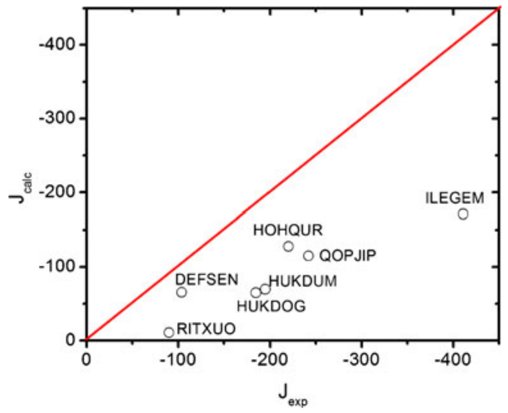


Fig. 3 Correlation of the mean calculated and experimental superexchange constants for the studied trinuclear systems. ($J_{av}=-194.6\ cm^{-1}$ [17]; $J_{av}=-185.1\ cm^{-1}$ [17]; $J_{av}=-220\ cm^{-1}$ [14]; $J_{av}=-411\ cm^{-1}$ [18]; $J_{av}=-241.9\ cm^{-1}$ [19]; $J_{av}=-104\ cm^{-1}$ [20]; $J_{av}=-89.9\ cm^{-1}$ [21])

The connectivity in the structures of *HUKDUM* and *HUKDOG* are very similar, since both present a μ_2-triazole and a μ_3-OH bridge between the copper centers. However, the calculated values of the exchange constant are different; this could be due to the distortions of the geometries and the presence of an extra bridge (SO_4^{2-}) in the case of *HUKDOG*. The overall antiferromagnetic phenomenon for *HUKDOG* is weaker than for *HUKDUM*, with an average J value for *HUKDUM* of $-69.6\ cm^{-1}$ while for *HUKDOG* of $-64.8\ cm^{-1}$. The magneto-structural behavior reported by Yoon et al. [13] indicates that a higher displacement of the hydroxo group from the plane of the copper centers produces a weaker antiferromagnetic phenomenon. The displacement of the hydroxo group is greater for *HUKDOG* (0.511 Å) than for *HUKDUM* (0.435 Å) which is in accordance with the reported magneto-structural correlation.

For *HOHQUR* and *ILEGEM*, the trinuclear units are very similar, because both present μ_2-ketoxime and μ_3-OH bridges. *HOHQUR* presents a μ_2-trichlorophenoxiacetate as a third bridging ligand and *ILEGEM* presents a NO_3^- as a third bridging ligand. The average J values of the exchange interaction shows that ILEGEM is more antiferromagnetic than *HOHQUR*, with J values of $-170.9\ cm^{-1}$ and $-127.6\ cm^{-1}$, respectively. The displacement of the hydroxo group from the plane of the copper centers is lesser for *ILEGEM* (0.549 Å) than for *HOHQUR* (0.657 Å), which is also in accordance to the magneto structural correlation reported by Yoon et al. [13].

For *QOPJIP* and *DEFSEN*, both compounds present a similar trinuclear structure with a μ_3-OH and μ_2-pyrazolates bridges. The average J value for *QOPJIP* is $-114.9\ cm^{-1}$ and for *DEFSEN* is $-65.6\ cm^{-1}$. It is important to indicate that *QOPJIP* also presents a μ_3-ClO_4^- ligand that coordinates the three copper atoms. On the other hand, the displacement of the hydroxo group from the plane of the three copper atoms is smaller for *QOPJIP* (0.466 Å) than for

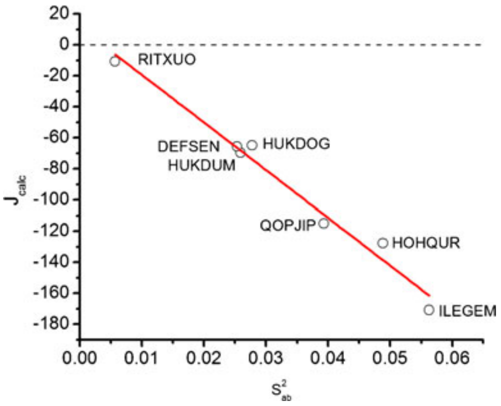


Fig. 4 Dependence of the calculated J values on the square of the overlap integral of the magnetic orbitals

DEFSEN (0.567 Å). In summary, the presence of an extra superexchange pathway and a smaller displacement of the hydroxo group from the copper atoms plane for *QOPJIP* produce a more antiferromagnetic phenomena for this compound, which is in accordance with the reported magneto-structural relation, reported by Yoon et al. [13].

The existence of one ferromagnetic exchange constant for *RITXUO* can be rationalized taking into account that this structure is the most distorted of all those studied. This system presents the greatest displacement of the hydroxo group from the plane of the copper centers of the studied family (0.794 Å). The work of Ghosh et al. [16] presents the theoretical study of the copper trinuclear system, showing that the highly distorted hydroxo centered unit presents ferromagnetic exchange phenomenon.

Orbital analysis

The magnetic exchange constant, J, can be decomposed into a positive ferromagnetic term, J_F, favoring the parallel alignment of the transition metal spins, and a negative antiferromagnetic term, J_{AF}, favoring the antiparallel alignment. This statement is valid using the sign convention $J \equiv E_{BS} - E_{HS}$, as stated by Mouesca [36]. The exchange effect is essentially mediated by the diamagnetic bridging ligand. This superexchange mechanism requires a covalent degree between the metal and the bridge. Therefore, a relation between the exchange energy constant and the mutual overlap is present. Following the valence bond interpretation of the exchange phenomena, Kahn and Briat [37, 38] proposed that the magnetic orbitals correspond to the highest occupied molecular orbitals and are not necessarily orthogonal. Among the conceptual tools used to compute J values, broken-symmetry methods were developed by Noodleman et al. [39, 40] and modified by Ruiz et al. [27]. This modified method constructs a broken-symmetry state as an outer

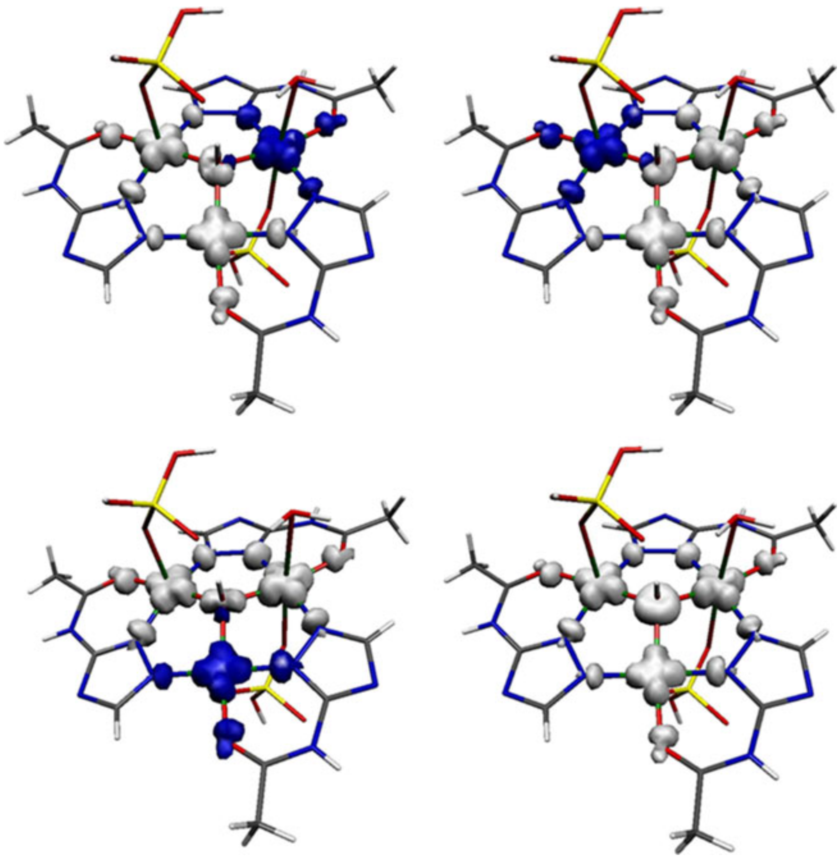


Fig. 5 Spin density surfaces for the trinuclear species *HUKDOG* of the antiferromagnetic configurations and the ferromagnetic one. Gray color corresponds to alpha spin density and blue color to beta spin density

product of the two natural magnetic orbitals. This last broken-symmetry state is not a pure spin state, but an artificial state of mixed spin symmetry and lower space symmetry, which turns out to be very useful for computational purposes. Finally the relation between exchange energy constant is approximately linear with the square of the overlap of the magnetic orbitals ($S_{ab}{}^2$) for the broken-symmetry approach [36].

A plot of the average J values of the seven studied complexes as a function of the square of the overlap is presented in Fig. 4. A linear relation can be observed for the seven complexes as expected from the Kahn-Briat overlap model. No linear relation exists between the displacements of the hydroxo group from the plane of the copper atoms with the square of the orbital overlap (see supplementary material, Fig. S1). Therefore it is possible to infer that the hydroxo group contributes, together with the other bridges to the exchange phenomenon.

Spin density distribution analysis

Mulliken spin density values were determined for all the studied compounds. The obtained values for the Cu^{II} atoms for all the structures are shown in Table S1 as supplementary material. All the calculated values are in the range of 0.60 e- to 0.68e-, as obtained for other studied Cu^{II} systems [5, 41–45]. These results reflect that most of the electron spin density is located on the metal centers, and the rest of the spin density appears over the atoms of the first coordination sphere, through a delocalization mechanism of the spin density.

Figure 5 presents the spin density surfaces for the ferromagnetic solution S_T=3/2 and three broken-symmetry solutions S_T=1/2 for *HUKDOG*. The same spin density surfaces for *HUKDUM*, *HOHQUR*, *ILEGEM*, *QOPJIP*, *DEFSEN and RITXUO* are shown as supplementary material, Fig. S2, S3, S4, S5, S6, S7). It is possible to observe that no polarization mechanism of the spin density is observed for the corresponding second coordination spheres.

Conclusions

The study using the density functional theory calculations of the reported magnetic properties of trinuclear hydroxo Cu^{II} complexes, permitted the calculation of the pure intramolecular exchange constants of the trinuclear units without any intermolecular of solid state magnetic phenomena. For the scalene arrangements it was possible to evaluate all three magnetic exchange interactions. No analytical model for scalene triangles exists in the literature.

An orbital study using the Khan-Briat model shows that for these systems there is a linear relation between the exchange constant and the overlap of the magnetic orbitals. The most antiferromagnetic systems are the compounds which present the ketoxime ligands, since these systems present the highest values for the overlap of the magnetic orbitals. No linear correlation between the overlap of the magnetic orbitals and the displacement of the hydroxo group is found. Therefore, the contribution to the exchange phenomena is due to all the bridging ligands and not only to the hydroxo group.

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