Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 285–294 **285**
DOI: 10.1021/ic902023u

Toward the Design of Ferromagnetic Molecular Complexes: Magnetostructural Correlations in Ferromagnetic Triply Bridged Dinuclear Cu(II) Compounds Containing Carboxylato and Hydroxo Bridges

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Received October 13, 2009

In the present work we present a comprehensive study of the magneto-structural correlations of a series of ferromagnetic triply heterobridged Cu(II) dinuclear compounds containing $[Cu_2(\mu\text{-}O_2CR)(\mu\text{-}OH)(\mu\text{-}X)(L)_2]^{2+}$ ions (where X = OH_2, Cl^-, OMe^- and L = bpy, phen, dpyam) which have the particularity of being all ferromagnetic. The present theoretical study, based on hybrid density functional theory (DFT) calculations, leads to strong conclusions about the role of the pentacoordination geometry of the Cu(II) ions (square base pyramidal (SP) or trigonal bipyramidal (TBP) coordination) and the nature of the third bridging ligand in determining the final value of the magnetic coupling constants in this series of compounds. These investigations point toward the existence of a maximum value for the ferromagnetic interaction and may offer some useful information to synthetic chemists aiming at obtaining new compounds with enhanced ferromagnetism.

Introduction

The search for molecular magnets with specific properties is a continuously challenging field for synthetic chemists.[1,2] The appropriate design of new compounds with improved features requires knowing magneto-structural correlations. Both experimental and theoretical viewpoints are extremely useful to successfully prepare the desired compounds with diverse structural and magnetic properties. Especially, compounds with ferromagnetism are of great interest for technological applications, and polynuclear Cu(II) compounds provide very useful models to disclose the relationship between molecular structure and magnetic properties. Among the different possible families of Cu(II) containing molecules, Cu(II) dinuclear complexes have been widely investigated since the early 1970s,[3] their magnetic behavior arising mostly from the Cu open-shell 3d orbitals in an effective $3d^9$ electronic configuration. This particular electronic structure with the spin density being strongly localized in the open shell 3d orbitals permitted Kahn et al.[1] to develop the concept of magnetic orbitals, a keystone in establishing and understanding useful magneto-structural correlations. A particular and special feature of Cu(II) dinuclear complexes is the ability of this ion to adopt diverse coordination geometries in different chemical environments and accepting a wide variety of bridging ligands. From the study of mono- and dibridged di-Cu(II) complexes, it has been established that the sign and magnitude of the magnetic coupling constant depends on the nature of the bridging ligands, the geometry of the dinuclear core, and the coordination environment of the metal atoms.[1] For heterodibridged systems, it has been reported that countercomplementary effects can arise between the ligands, where positive and negative contributions to the final value of the magnetic coupling constants (J), defining the observed ferro- or antiferromagnetic behavior, are competing.[4−6]

Another, yet different, family of Cu(II) complexes exists where the two metals are triply bridged. These compounds are of special interest because of their existence in a wide diversity of topologies, intramolecular magnetic exchange

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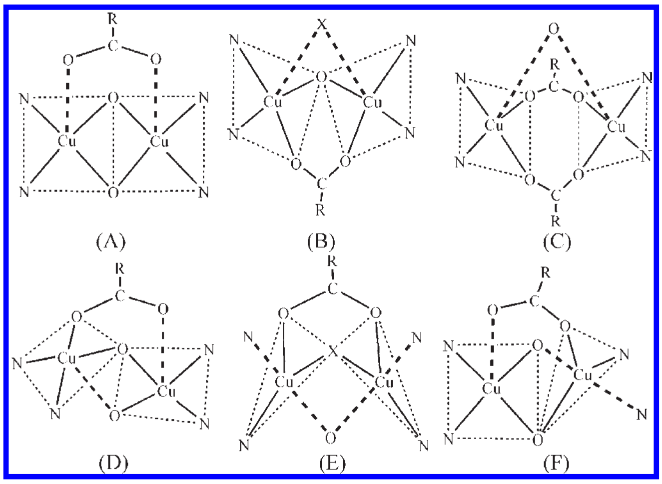

Figure 1. Representation of the structural features of the local environment of each of the Cu centers defining the A−F classes of triply bridged dinuclear complexes considered in this work. Notice that the dotted lines define the type of basis (square base pyramidal 4 + 1 coordination (SP) or trigonal bipyramidal 3 + 2 coordination (TBP)) and dashed lines indicate apical bond for SP and axial positions for TBP coordination.

pathways, and magneto-structural correlations.[6−10] In this series of Cu(II) compounds, the metal atoms exhibit a 5-fold coordination with a broad range of distorted geometries between regular trigonal bipyramid and regular square-based pyramid. The global topologies of these compounds can be described in terms of the relative arrangement of the two five-coordinate environments (square base pyramidal(SP) or trigonal bipyramidal (TBP) coordination), giving rise to different classes (A−F) of compounds as shown in Figure 1. These particular structural features are useful to further understand the relationships between molecular structure and the final value of the intramolecular magnetic exchange interaction in the triply bridged dinuclear unit. In this sense, it is worth to mention that class C compounds have been broadly studied and it is known that the magnetic coupling is dominated by the two carboxylato groups which, in general, lead to antiferromagnetic coupling. Consequently, this class will not be studied in the present work.

In a previous study, magneto-structural correlations have been investigated for some of these compounds by means of the simple Extended Hückel (EH) method, and a linear correlation has been found for class B compounds allowing a first step toward a proper understanding.[7] Nevertheless, the qualitative nature of the electronic structure description provided by the empirical EH method is of limited use for both interpretation and a quantitative description of magnetic systems. This is because the final value of the magnetic coupling is strongly dominated by subtle electron correlation effects, as shown by the landmark paper by de Loth et al.[11] and the subsequent analysis by Calzado et al.[12,13] Ideally, one can make use of mapping procedures and compute the magnetic coupling constants accurately via appropriate configuration interaction calculations[14] although, because of the extreme computational resources required, this is only possible for model systems with simplified ligands. Alternatively, one can make use of second order multiconfigurational approaches[15] or take advantage of recent advances in density functional theory (DFT) based methods.[16,17]

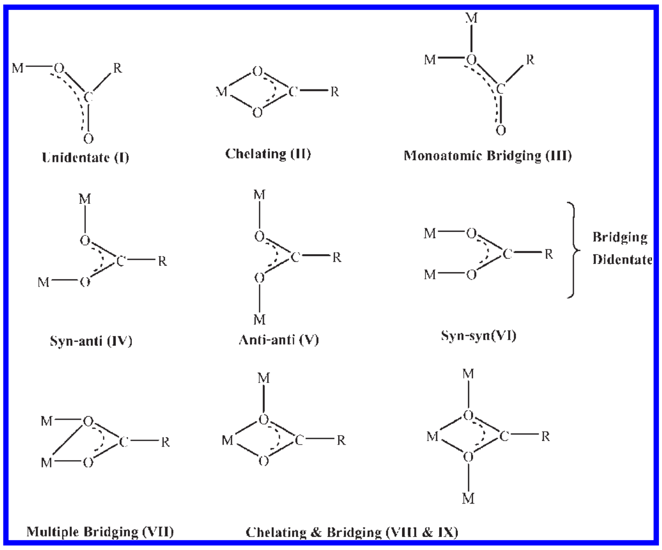

Figure 2. Topologies of the different bridging ligands contained in the molecules under study leading to the different nuclearity and variety of topologies as shown in Figure 1. Notice the presence of a π system involved in the different coordination modes.

In the present work we present a comprehensive study of the magneto-structural correlations of this extended series of triply bridged Cu(II) dinuclear compounds using state of the art hybrid DFT based calculations, and the results are compared to available data on similar dinuclear complexes. It is important to stress the fact that, while most of the Cu(II) dinuclear complexes exhibit an antiferromagnetic coupling, all compounds investigated in the present work have the particularity of being ferromagnetic thus making them more attractive for potential new technologies employing molecular magnets. In this sense, the present theoretical study allows one to extract strong conclusions about the role of a third bridging ligand in determining the final value of the magnetic coupling constants for a specific global topology in this series of compounds and may offer some useful information to synthetic chemists aiming at obtaining new compounds with enhanced ferromagnetism.

Brief Description of the Bridging Ligands and Crystal Structures

The bridging carboxylate ligands are extremely flexible with versatile coordination modes since each oxygen atom may act as a unidentate, chelate, monatomic bridge and triatomic bridge with *syn-syn*, *syn-anti*, *anti-anti* configurations.

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Table 1. List of the Dinuclear Triply-Bridged Copper(II) Compounds and Experimental Magnetic Properties[a]

compound	number	class	J (cm^{-1})	ref.
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)_2(dpyam)_2](ClO_4).H_2O$	**1**	A	112.7	[7]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(dpyam)_2](S_2O_8)$	**2**	B	not available	[7]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(bpy)_2](NO_3)_2$	**3**	B	not available	[7]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(phen)_2](BF_4)_2\cdot 0.5H2O$	**4**	B	120.8	[7]
$[Cu_2(\mu\text{-}O_2CCH_2CH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(phen)_2](NO_3)_2$	**5**	B	not available	[7]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(bpy)_2](ClO_4)_2$	**6**	B	38.6	[6]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(phen)_2](ClO_4)_2$	**7**	B	120.0	[8]
$[Cu_2(\mu\text{-}O_2CCH_2CH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(bpy)_2](ClO_4)_2$	**8**	B	148.9	[8]
$[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}Cl)(bpy)_2]Cl\cdot 8.5H_2O$	**9**	B	145.3	[7]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](ClO_4)\cdot 0.5H_2O$	**10**	E	79.1	[9]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$	**11**	E	79.7	[10]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)(dpyam)_2](ClO_4)$	**12**	E	62.5	[9]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)(dpyam)_2](PF_6)$	**13**	E	47.8	[10]
$[Cu_2(\mu\text{-}O_2CC_2H_5)(\mu\text{-}OCOC_2H_5)(\mu\text{-}OH)(dpyam)_2](ClO_4)$	**14**	D	24.1	[10]

[a] Note that positive J values correspond to a ferromagnetic ground state.

These features are able to generate complexes with different nuclearity and variety of topologies as shown in Figure 2 below and have been widely exploited in bioinorganic[18,19] and molecular magnetic materials chemistry (see refs 7−10 and references therein). Concerning the chelating ligands, 1,10-phenanthroline(phen), 2,2′-bipyridine(bpy), and 2,2′-bipyridylamine(dpyam) have been used in this work as a terminal didentate chelating ligand. The phen, bpy, and dpyam ligands represent a sequence of increasingly flexible chelating nitrogen ligands. The flexibility or/and the rigidity of these chelate ligands affect the dinuclear unit giving rise the variety of topologies discussed above (Figure 1). Additionally, the crystal lattice of dinuclear complexes may be stabilized by a variety of intermolecular non-covalent interactions; the more flexible dpyam chelate ligand is usually available to present the intra/intermolecular H-bonding from back H atom, while, more rigid bpy and phen ligands prefer to generate intra/intermolecular $\pi-\pi$ stacking and CH$\cdots\pi$ interactions between pyridine groups. Consequently, the differences in the crystal packing interactions may give rise to a wide range of topologies on the dinuclear unit although the molecular entity remains. Hence, magnetic coupling depends on the global topology of the dinuclear unit and on the local Cu(II) environment, not on the crystal packing although intermolecular interactions can induce significant structural distortions.

The global topologies of the dinuclear triply bridged copper(II) compounds considered in the present work reveal the 5-fold coordinated complexes containing a carboxylato bridge which can be classified in four different families, namely, classes A, B, E, and D for compounds **1**, **2**−**9**, **10**−**13**, and **14**, respectively: Class A compound reveals the coplanar bases with a square pyramidal geometry for both Cu(II) environments with two hydroxo bridges linked in the equatorial positions. On the other hand, class B compounds display non-coplanar bases with a square pyramidal geometry for both Cu(II) ions. Here, the triatomic carboxylato and hydroxo bridges are arranged in the basal positions. Class E compounds show non-coplanar bases with a trigonal bipyramidal geometry for both Cu(II) ions and one hydroxo bridge in an axial−axial configuration. Finally, the only class D compound displays non-coplanar bases with a square pyramidal geometry for both Cu(II) ions but with the hydroxo bridge displaced to an equatorial−equatorial configuration and two carboxylato (monatomic and triatomic) bridges are displaced to an axial−equatorial configuration.

The list of dinuclear triply bridged Cu(II) compounds considered in the present work and the available magnetic data are reported in Table 1.

Description of Magnetic properties

For dinuclear Cu(II) systems exhibiting magnetic interactions between the two paramagnetic ions, the magnetization versus temperature curves describing the magnetic behavior of these compounds can be approached, at first order, by the Bleaney−Bowers expression[20] which takes into account both the phenomenological Landé g-factor and the magnetic coupling constant J. For the model Heisenberg spin Hamiltonian as in eq 1

$$\hat{H} = -J\hat{S}_1\cdot\hat{S}_2 \tag{1}$$

the J value coincides with the energy difference between the singlet and triplet spin states of the corresponding dinuclear complex arising from the allowed combinations of the local doublet states of each one of the Cu ions in the d^9 electronic configuration. This energy gap can be related to the energies of the frontier orbitals: the larger their energy separation, the stronger the antiferromagnetic contribution to J is. In turn, the singly occupied molecular orbitals (SOMOs) can be approached as the symmetric and antisymmetric combinations of the magnetic orbitals of each center, which consists of the antibonding combination of the metallic atomic orbitals which holds the unpaired electron with the adequate molecular orbitals of their coordinated ligands.

The singlet−triplet energy gap can be estimated using appropriate wave function methods or DFT based methods.[14] In the latter, one must realize that the commonly used Kohn−Sham implementation based on the use of a single Slater determinant for the reference system of non-interacting electrons does not allow to describe open-shell singlets.[21−23] The broken symmetry procedure suggested

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earlier by Noodleman[24-26] and by Yamaguchi[27-29] for the SCF-Xα and UHF methods, provides a way to approach these states provided spin symmetry is recovered by proper spin projection;[30] in this case, the singlet−triplet gap is just twice the energy difference between the high-spin (approximate triplet) and the broken symmetry solution. Alternatively, one can make use of the Restricted Open Shell Kohn−Sham (ROKS) or Restricted Ensemble Kohn−Sham (REKS) formalisms.[21-23]

It is also important to note that the final value of the calculated magnetic coupling constant depends on the choice of the exchange-correlation potential (i.e., the DFT method chosen). It is well-known in solid state chemistry that pure LDA and GGA functionals provide poor descriptions of magnetic systems such as transition metal oxides and halides (NiO, cuprates, manganites, etc.) which belong to a large class of compounds denoted as strongly correlated materials.[14] The typical inconsistency of the LDA or GGA descriptions of the electronic structure and magnetic properties of many of these materials consists in an incorrect description of the insulating character (the magnitude and the nature of the calculated gap is too small or zero and usually of d-d type), poor spin localization (low spin states are almost close shell in nature), and showing important differences between high spin and low spin charge/spin distribution leading to strongly overestimated ferro or antiferromagnetic coupling constants. A very poor correlation with available experimental magnetic data does not allow one to confer predictive utility to these kinds of approaches. In the case of molecules, a similar behavior is observed regarding the spin and charge localization (i.e., too strong charge/spin delocalization) that also leads to a strong overestimation of either ferro or antiferromagnetic interactions and a very different nature of magnetic solutions with useless predictive utility. However, widely used hybrid functionals have shown to provide a much better and consistent description of solids and molecules and, more important, the estimated values of different properties including magnetic coupling constants are of enough predictive accuracy to provide useful magneto-structural correlations (see ref 14 and references therein).

In general, more elaborated hybrid potentials such as the M06 family or the range-screened hybrid functionals provide significantly better results,[16,17] although all strongly depend on the amount of non-local Fock exchange chosen.[14] Therefore, we rely on simpler hybrid functionals which are known to provide excellent magneto-structural correlations[31] even if the calculated J value may differ from experiment by an almost constant factor.[14,30,32]

In the following we summarize the most salient magnetic features of each class of triply bridged Cu(II) dinuclear compounds considered in the present work.

Class A Compounds. In class A compound (**1**) both metal atoms exhibit a distorted square base pyramidal 4 + 1 coordination (SP), with the basal planes defined by the coordinating atoms of the terminal ligand and the hydroxo bridges at the squares, strongly bonding the Cu(II) ions located at their centers. For compound **1**, the apical positions are occupied by the oxygen atoms of the formato bridge in a *syn,syn* conformation, but the Cu−O apical bonds are considerably weaker than the basal ones as can be argued from the longer distances, 2.34 Å versus 1.95−2.01 Å, respectively. The tight basal bonds place the unpaired electron of the d^9 of each metal center in a $d_{x^2-y^2}$ orbital pointing directly to the basal donors so the main magnetic exchange pathways go through the hydroxo bridges. This is clear from the calculations described below since their oxygen atoms accommodate the highest spin densities (0.095 au) while the formato oxygen atoms are almost free of it (0.0002 au). The fact that the hydroxo bridges follow almost exactly the Hodgson and Hatfield's linear relationships[6,33] between the singlet−triplet gap and the Cu−O−Cu angle (moderate ferromagnetism from +115 to +123 cm^{-1} expected versus the +112 cm^{-1} experimental value or the +125 cm^{-1} BHHLYP calculated value, see below) confirms the secondary role of the formato bridge in the magnetic exchange for this class A compound.

Class B Compounds. Compounds in class B (**2**−**6**) show experimental moderately ferromagnetic coupling constants in the 120−150 cm^{-1} range except for **6** which displays a smaller value (+38.6 cm^{-1}). Their dinuclear core is also formed by two 4 + 1 SP Cu(II) ions sharing three bridging ligands, but in this case there are one hydroxo and one carboxylato bridges at basal positions, and one water molecule (or a chloride anion for **9**) in the apex. As found in compound **1**, the apical bonds are clearly longer than the basal ones (2.34−2.46 Å for aquo and 2.63−2.66 Å for chloro ligands compared to the distances in the 1.92−2.03 Å range for basal atoms) and therefore similar magnetic orbitals evolve. This suggests again that the apical bridge should not contribute significantly to the magnetic exchange between the metal atoms (spin densities on the oxygen atoms of the water bridges were found to be almost zero in all calculations). Hence, in these dinuclear systems one can interpret the resulting magnetic behavior as being mainly due to exchange interactions through the hydroxo and carboxylato ligands. In such a case, a countercomplementary effect is expected between the hydroxo bridge, which generates ferromagnetic interaction due to the orbital orthogonality, and one triatomic bridge in *syn-syn* configuration which usually contributes a weak antiferromagnetic interaction.[6]

For class B complexes it is possible to trace a correlation between structure and experimental magnetic exchange interaction using available data for compounds **4**, **7**, **8**, and **9** (see Figure 3). We excluded compound **6** from the list because the published J value was obtained from a

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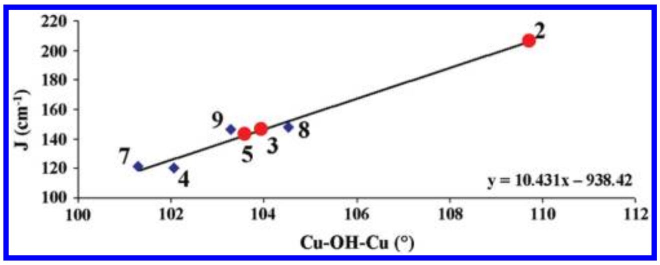


Figure 3. Plot of experimental J (cm^{-1}) versus Cu−OH−Cu angle (degrees) for class B compounds **4**, **7**, **8**, and **9**. The points corresponding to compounds **2**, **3**, and **5** (red circles) are as predicted from this linear correlation and, obviously, fit perfectly on the line.

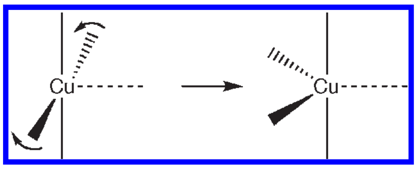
partial high temperature zone (50−200 K) fitting of the experimental data,[6] which introduces a high uncertainty on the estimated coupling constant that lies far away from the trend line. Figure 3 shows a clear linear correlation between the experimental J value and the Cu−OH−Cu angle. This correlation indicates that the larger this structural parameter, the larger the J value (one could predict J values for compounds **2**, **3**, and **5** as +205.2, +146.1, and +142.0 cm^{-1}, see below). However, a larger number of the detailed structures and their magnetic properties are required for a clear correlation to be observed. In fact, this correlation has to be taken with caution as it will be clear from the calculated values and magnetostructural correlations discussed in the forthcoming sections using the more elaborated hybrid DFT approaches that include electron correlation effects.

Class C Compounds. This class is the most frequently studied and the magnetic coupling is dominated by the two carboxylato groups which, in general, lead to antiferromagnetic coupling and have been broadly studied. Consequently, this class will not be further commented.

Class E Compounds. Class E compounds **10**−**13** show a weaker ferromagnetic interaction (from +47 to +80 cm^{-1}). They can be described as two trigonal bipyramidal (TBP) coordinated Cu(II) centers where the axial positions are occupied by a nitrogen atom of the chelating terminal ligand and the oxygen atom of the hydroxo bridge, the latter involving the strongest bridging bonds (1.90−1.92 Å). Further, an oxygen atom of the carboxylato bridge occupies one equatorial position of each metal and shows moderately strong Cu−O bonds (2.15−2.20 Å, slightly longer than for B-class compounds), and the remaining nitrogen atom of the dpyam terminal ligands holds the second equatorial position.

For compounds **10** and **11**, the third bridging ligand is a chlorine anion that occupies the remaining equatorial positions at 2.45−2.48 Å from the metal centers, the longest coordination bond distances although considerably shorter than in B-class complex **9**: the participation of this chloro bridge on the magnetic exchange seems not so negligible. On the contrary, for compounds **12** and **13** these positions are occupied by a methoxo bridge, considerably more basic than the chlorine anion, and thus showing stronger bonds to the metal (2.13−2.17 Å), comparable to those of formato. From this analysis it is hard to argue whether all three bridges will not be magnetically active.

Scheme 1



Previous work based on simple Extended Hückel arguments assigned the “*superexchange*” mechanism for these compounds to orbital orthogonality between the Cu magnetic orbitals and oxygen p-orbital via Cu−OH−Cu unit allowing two unpaired electrons spins to be coupled high spin.[7] This allows one to assume that the dominant ferromagnetic interaction increases with increasing bridging angle (compounds **10**−**12**) up to a certain maximum value and then decreases (compounds **10**−**13**). However, no clear correlation has been observed for class E compounds reported in the literature. Hence, it is clear that more detailed structures and magnetic properties are required to study the magneto-structural correlation in this class of compounds. DFT results in the present work provide a more general framework to understand the origin of ferromagnetism in these compounds and for a new magnetostructural correlation.

Note that the metal coordination environments for B and E class compounds can be related to each other through the Berry pseudo-rotation mechanism, that allows the transformation of a SP to a TBP through small movements of the ligands around a pivot atom (the apical one) as shown in Scheme 1.

This transformation can be monitored with the use of the τ parameter proposed by Addison et al.[34] which is 0.0 for a perfect SP and 1.0 for a TBP. This allows one to relate B and E class compounds by calculating the τ parameter for each metal center of each dinuclear compound and to quantitatively classify the B and E-class complexes according to the sum of the τ values of both Cu(II) ions. Thus a value close to 2.0 indicates that the two Cu(II) have a TBP environment, a value close to 0.0 indicate that the two metal atoms have a SP coordination whereas a value near 1.00 will indicate that the two coordination of the metal centers is just intermediate between SP and TBP. In Figure 4 the molecular structure of two representative complexes and the expected magnetic orbitals are depicted for clarity. In this figure compounds **5** and **11** are shown as representative of the two limiting SP-SP and TBP-TBP structures for which the expected $d_{x^2-y^2}$ or d_{z^2} magnetic orbitals arising from the local d^9 atomic configuration of the Cu(II) centers are suggested (see discussion below).

Classes D and F Compounds. Let us now briefly comment on the role of dpyam as blocking ligand instead of bpy or phen. This ligand favors the TBP geometry because of the formation of a 6-membered chelate ring that yields a higher bite angle (90−91° compared to 80−82° for the α-diimines), necessary to bind the metal through an axial and one equatorial interaction. The only exception to this rule is the Cu(II) coordination sphere in the class-D compound **14**. For this complex, both metal

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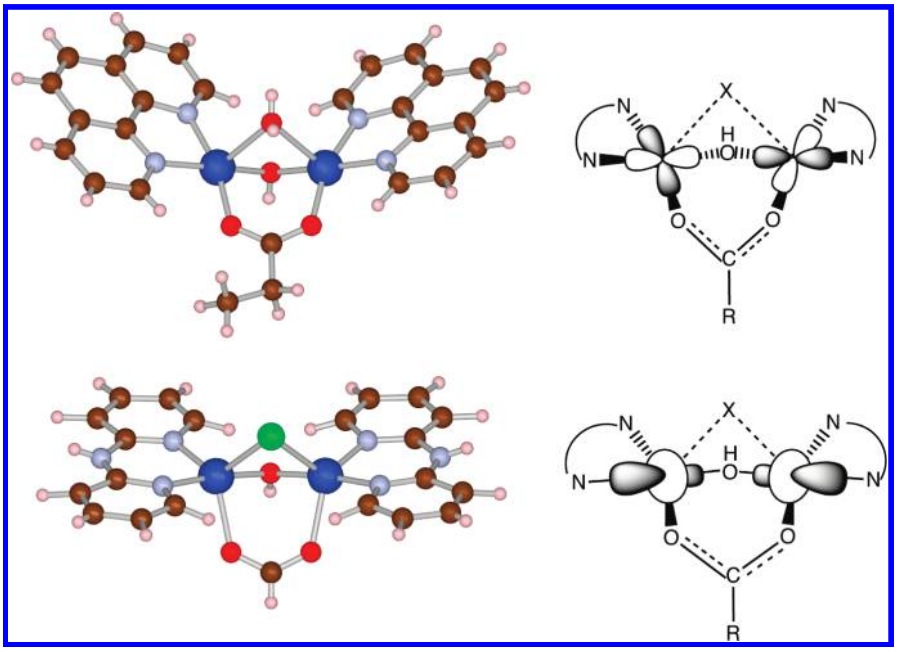

Figure 4. Molecular structure of compounds **5** (top) and **11** (bottom) as representative of the two limiting SP-SP and TBP-TBP structures. Besides the diagrammatic representation of the $d_{x^2-y^2}$ or d_{z^2} magnetic orbitals expected from the local environment of the Cu(II) centers are shown.

centers undergo noticeable distortions that are not fully accounted for by the Berry pseudo-rotation model. The Cu(1) atom can be considered in a mainly SP environment (τ = 0.22) with the O(4) atom of the monodentate bridging propionate anion occupying the apical position at 2.32 Å. The high value of the dpyam bite angle (90.4°) is compensated by both a tetrahedral distortion of the basal plane (dihedral angle between the O(1)−Cu(1)−O(3) and N(1)−Cu(1)−N(2) planes of 25.7°) and a bending of the ligand (24.7° angle between the heterocyclic rings of the Cu(1)-chelating ligand). For Cu(2), the coordination environment is severely distorted from SP which is considered to be intermediate between SP and TBP (τ = 0.43), although the O(5) atom of the monodentate bridging propionate lies at 2.80 Å from the metal atom, thus suggesting a very weak interaction that causes the O(4)−Cu(2)−N(5) equatorial angle to widen up to 146.2°. In addition, the equatorial bond between the Cu(2) atom and the O(2) has a long length (2.24 Å) comparable to an apical SP bond which corresponds to that typical of TBP. Because of these factors, compound **14** has the most asymmetrically coordinated magnetic centers.

It is possible to extrapolate the trends exhibited by either class B (the two Cu(II) in SP) or class E compounds (the two Cu(II) in TBP) to class F compounds which have one of the Cu(II) metal centers in SP and the other one in TBP coordination. In spite of its magnetic interest, the number of representative compounds belonging to this class is rather limited and according to the previous correlations with rather weak coupling.[35]

Computational Details

Hybrid DFT calculations have been carried out to extract the magnetic coupling constants for all the complexes and to investigate magneto-structural correlations. The spin polarized formalism based on a single determinant description has been considered to describe the open shell electronic states of lowest energy that correspond in all cases to the triplet ground state (described by means of a $S_z = 2$ solution, denoted as FM solution) and the first excited state that corresponds to an open shell singlet (described by means of a suitable $S_z = 0$ broken symmetry solution, denoted as BS solution). As described in section III, using the broken symmetry approach the relation between the energies of high spin and low spin solutions and J is given by $J = E(\mathrm{BS}) - E(\mathrm{FM})$ if the spin Hamiltonian corresponds to the expression in eq 1.

The two hybrid DFT based schemes used are the well-known and widely used B3LYP functional[36,37] and a simplified Becke Half-and-Half functional[38] defined as

$$E_{xc}^{BHandH} = 0.5\cdot E_x^{HF} + 0.5\cdot E_x^{LSDA} + E_c^{LYP}$$

and denoted as BHHLYP. These DFT methods have been shown to predict reasonable estimates for the magnetic coupling constants of antiferromagnetic compounds[14] although the information concerning ferromagnetic coupling is rather scarce.[16] Recently developed hybrid functionals such as M06 or the range separated hybrids have shown to provide accurate estimations of magnetic coupling constants[16,17] of dinuclear magnetic complexes and strongly correlated solids. In particular, the long-range separated hybrid functionals provide calculated J values in excellent agreement with experiment.[17] These recent developments are becoming accessible in the new versions of commonly used general quantum codes but still are of limited accessibility. Therefore, in this work we have chosen two standard functionals, namely, B3LYP and BHHLYP, because of their general availability for practical applications and, also, because of the consistency of the results observed in a large amount of theoretical studies to provide meaningful magnetostructural correlations.

Standard all electron Gaussian Type Orbitals (GTO) basis sets have been used to represent the electronic density of the

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dinuclear Cu(II) complexes described in the previous section with a molecular structure extracted from the experimentally determined crystallographic structures reported in the references included in Table 1. For Cu(II) ions, a 6-3111+g basis set[39,40] extended with an f-function ($\zeta = 0.528$) has been used (corresponding to a [14s9p5d1f/9s5p3d1f] contraction) whereas a 6-31g* basis set has been used for the remaining atoms (corresponding to a [4s/2s] contraction for H atoms, a [10s4p1d/3s2p1d] contraction for C, N, and O atoms[41] and a [16s10p1d/4s3p1d] contraction for Cl atoms.[42] Single-point energy evaluation runs were carried out for the crystallographic structures of the isolated dinuclear ions without further geometry optimization. This prevents mixing structural and electronic effects and introducing errors in the magnetic coupling constants arising from errors in the structure optimization. In two cases, compounds **12** and **13**, the H atom belonging to the OH bridging group was adjusted to a position close to that corresponding to the remaining systems since, on the one hand, the available crystallographic positions were not consistent with the typical bridging mode of this group and, on the other hand, the calculated data clearly indicate a deviation from the trend exhibited by the whole series of compounds. Hence, we used d(O−H) = 0.90 Å with the O−H bond forming an angle of ~40° with the vector normal to the Cu−O(H)−Cu plane and closer to the carboxylate group whereas the Cu−O distances and all the remaining structure has been fixed to the crystallographic data. All calculations were carried out using the Gaussian03 suite of programs.[43]

We end this section by noting that spin contamination is rather small, and in line with results found in previous studies. For all the systems and methods considered in this work, the expected values for the square of the total spin operator ($\langle S^2 \rangle$) are in the [2.004−2.006] range for the ferromagnetic (or high spin) solution and in the [0.989−1.005] range for the low spin (broken symmetry) solutions, that is, a maximum deviation of +0.006 from the $\langle S^2 \rangle = 2.000$ value for a triplet state and a maximum deviation of −0.011 from the $\langle S^2 \rangle = 1.000$ value for a perfect 50% singlet−triplet mixing state expected for a single Slater determinant broken symmetry description of a localized open-shell singlet. These values are, in our opinion, small enough to trust the J values obtained from this spin polarized single determinant approximation to the singlet−triplet energy gap.

Results and Discussion

Table 2. Calculated J and Addison τ Values (Aggregate and Compontents) for the Dinuclear Triply-Bridged Copper(II) Compounds Listed in Table 1[a]

compound	τ (τ_1+τ_2)	J_{calc} BHHLYP	J_{calc} B3LYP	J_{exp}
1		125.5	220.3	112.7
2	0.86 (0.43 + 0.43)	53.2	120.9	
3	0.40 (0.21 + 0.19)	79.6	166.3	
4	0.37 (0.21 + 0.16)	80.4	166.6	120.8
5	0.27 (0.08 + 0.19)	85.6	181.4	
6	0.37 (0.21 + 0.16)	83.2	169.0	38.6
7	0.34 (0.20 + 0.14)	80.5	169.7	120.0
8	0.37 (0.21 + 0.16)	87.0	176.7	148.9
9	0.69 (0.41 + 0.28)	69.4	146.8	145.3
10	1.34 (0.67 + 0.67)	83.6	185.7	79.1
11	1.44 (0.72 + 0.72)	78.3	161.3	79.7
12	1.28 (0.64 + 0.64)	82.4	162.6	62.5
13	1.14 (0.57 + 0.57)	34.2	108.1	47.8
14	0.65 (0.22 + 0.43)	57.6	99.2	24.1

[a] Note that positive J values correspond to a ferromagnetic ground state.

At first sight, comparing the experimental and calculated magnetic coupling constants for compounds **2**−**14** is quite frustrating (Table 2) since, contrarily to broad experience for antiferromagnetic compounds,[14,31] the overall agreement between calculation and experiment is rather poor although, except for compound **6** (see above discussion), the experimental singlet−triplet value is always between the two sets (BHHLYP and B3LYP) of calculated values. At this point one may wonder whether the experimental measurements are accurate enough or the calculations are failing. Two comments are appropriate here. First, magnetic measurements for ferromagnetic compounds are more delicate than for antiferromagnetic complexes because they are strongly influenced by remaining paramagnetic impurities and because the interaction between the ferromagnetic molecules cannot be neglected as it is currently done in the models used to fit magnetic susceptibility to experiments. For instance, for the present compounds, the fitting procedures leads to antiferromagnetic zJ' mean field parameters in the −0.2 to −0.9 range and a 6% content of paramagnetic impurities.[2] Moreover, the published J value for compound **6** was obtained from a partial high temperature zone (50−200 K) fitting of the experimental data, which introduces even more uncertainty to the estimated coupling constant. Second, there is a large body of evidence that hybrid DFT calculations are able to properly describe the trends for antiferromagnetic and ferromagnetic compounds and, depending on the exchange-correlation potential used, even to accurately reproduce the experimental values.[16,17,31] Hence, one may suggest to trust the calculated values, at least in what concerns the main trends, and inspect the information provided by the calculations in detail. To this end it is convenient to make use of the structural parameter τ introduced by Addison et al.[34] and discussed in the previous section. In Figure 5, the BHHLYP calculated J values of class B and class E compounds are plotted with respect to the sum of the τ values for each metallic centers obtained by the PLATON code.[44] This plot reveals interesting magnetostructural correlations which are not apparent from the experimental values only. In addition and in spite of the different values predicted by BHHLYP and B3LYP, the experimental values lie in the range of values

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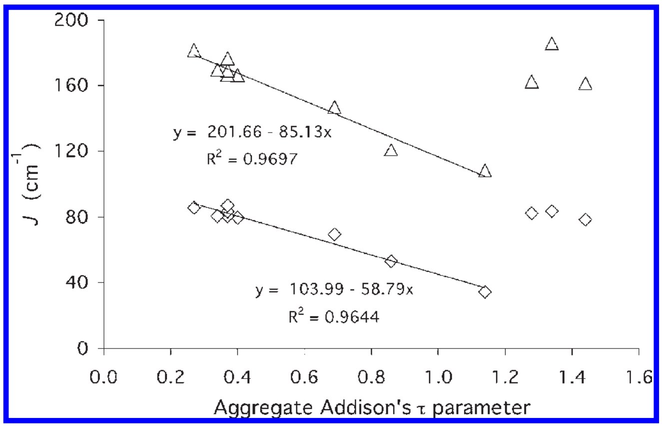

Figure 5. Plot of the B3LYP (triangles) and BHHLYP (diamonds) calculated J values (in cm^{-1}) versus the aggregate Addison's τ parameter for classes B (**2**−**9** plus **13**) and for E compounds (**10**−**12**).

predicted by both methods and both methods predict the same trends. However, one must warn that available structural data from measurements on the complexes of interest in the present work do not cover a broad enough range of aggregate τ values to firmly confirm the trends predicted above. In any case, results in Figure 5 clearly show that the proposed magnetostructural relationships discussed above are meaningful.

In fact, it appears that for class B compounds **2** to **9**, the calculated J values, predicted by the BHHLYP (or by the B3LYP functional), correlate reasonably well with the sum of the experimental τ parameters corresponding to each Cu atom. However, this result is opposite to the observations by Kahn[1] and Journaux[45] for the antiferromagnetic J coupling constants for several oxalato dinuclear Cu(II) complexes with pentacoordinated environments. These authors found that the closer the coordination to SP, the larger the antiferromagnetic interactions (more negative J values) whereas Figure 5 reveals that for the class B compounds examined in the present work, the closer the coordination to SP, the larger the ferromagnetic interactions (more positive J values). This is because the oxalate system and the present class B compounds exhibit different topologies and different magnetic behavior. Interestingly enough, compound **13**, which according to the structural data and also to the τ value has been classified as belonging to class E, follows the correlation above for class B. This is because the τ value is very close to the lower bound of τ values defining class E and, therefore, the calculated J value and the magnetostructural correlation above seem to provide a more solid argument than those from simple structural data. Accepting that compound **13** behaves as class B leaves us with only three compounds in class E with the subsequent difficulty to obtain a meaningful magnetostructural correlation. Nevertheless, the plot in Figure 5 shows that J also correlates with the aggregate τ parameter although with a much smaller slope.

Kahn[1] and Journaux[45] interpreted the enhancement of the antiferromagnetic coupling as arising from the increasing in the overlap of the metal magnetic orbitals, mainly the $d_{x^2-y^2}$ atomic orbital of the d^9 metal atom, with the bridging ligand with a concomitant intensification of the coupling pathway through the basal positioned bridges, whereas the distant apical ligands are not involved in magnetic exchange. On the contrary, for TBP environments the magnetic orbital is d_{z^2} in nature, in such a way that the exchange pathways through the bridging ligands would be less intense but magnetic interaction is now spread across all five ligand atoms and involves all three bridges. For the triply bridged complexes studied in the present work, the arguments above are illustrated in Figure 4 along with two representative structures studied in the present work. However, one must recall that magnetic interactions are strongly dominated by electron correlation effects and, hence, simple orbital interpretations may be misleading, especially for ferromagnetic interactions. A proper interpretation would require a deep analysis of configuration interaction wave functions such as those reported by Cabrero et al.[12,13] for model systems.

Next, we analyze the magnetostructural correlation shown in Figure 5 in depth. For B-class compounds, the magnetic orbitals are located on the basal plane pointing directly toward the oxygen atoms of the hydroxo and carboxylato bridges (Figure 4, top), which have short bond distances and hence are effective in coupling the exchange interactions between the two paramagnetic ions. From orbital arguments, the resulting moderately large ferromagnetic interaction can be explained invoking the countercomplementary effect,[6] except for the above commented compound **6**. Note that the apical aqua ligand (third bridge) do not contribute to the magnetic exchange, as their spin density is negligible in both triplet and BS solutions for all calculations. However, it is worth mentioning that the B3LYP calculations for complex **9** on the triplet state lights up some spin density on the chlorine bridge (0.7% versus 0 in the BS singlet). Interestingly enough, all calculations show an increase of spin density in the oxygen atom of the hydroxo bridge in the triplet state which is even larger than for the Cl bridge suggesting an active role of this bridging ligand in the magnetic interactions.

Next, let us focus on the E-class complexes where the metal contribution to magnetic orbitals is d_{z^2} (Figure 4, bottom) with the axial lobe pointing toward the shortest Cu-bridge distances (1.90−1.92 Å) which correspond to the hydroxo bridge. This strongly suggests that the hydroxo bridge is the responsible one for the most intense exchange pathway, which is confirmed by the high spin density values for the oxygen atom of the hydroxo group (∼9% and ∼17% in the BHHLYP and in B3LYP triplet calculations, respectively). Both equatorial bonds are weaker but, contrarily to what is found for class B, they are of comparable strength, indicating an active participation in the magnetic coupling. In fact, the spin density on the oxygen atoms of the carboxylato ligands is similar to that found in class B, but now the third bridge (chlorine atom for compounds **10** and **11**) lights up in the triplet state with a non negligible spin density of 3% from BHHLYP and 7% upon B3LYP. This is clear from the spin density plots[46] for the ferromagnetic ground state of compound **11** (the compound with largest aggregate τ) and also for compound **5** (the compound with smallest aggregate τ) shown in Figure 5. Note, that the magnetic orbitals arising from these calculated spin density plots is in agreement with the qualitative arguments depicted in Figure 6 and evidence the large spin polarization of the hydroxo groups. This explains that the calculated value for compounds **10** and **11**

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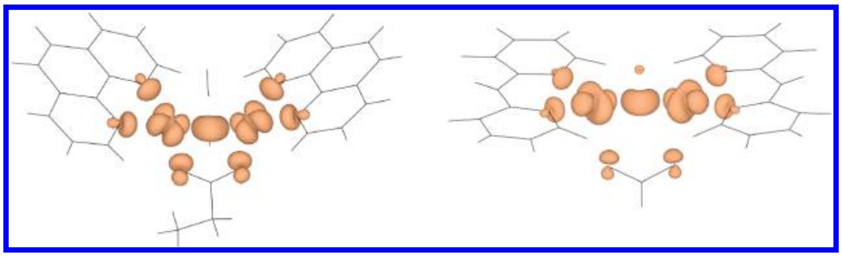

Figure 6. Spin density plots for the ferromagnetic ground state of compounds **5** (left) and **11** (right). Notice that these correspond to the two compounds with smallest and largest aggregate τ value, respectively.

corresponds to ferromagnetic couplings larger than expected from the magnetostructural correlation found for class B compounds (including **13**) based on the aggregate τ parameter (see Figure 5). This evidences the important role played by Cl (or methoxo in **12**) as the third bridge. This behavior may be due to the higher σ- and π-donor character of chloro ligands compared to water. These interactions are similar to those occurring for the hydroxo bridge, but because of its weaker field and higher covalency, chloro bridging ligands are able to allow further magnetic interactions between the Cu atoms with a reduced Cu−Cl−Cu angle (over 75 degrees) which, according to Hatfield's trends,[33] seems to favor ferromagnetic exchange. Nevertheless, experimental coupling constants for compounds **10** and **11**, together with the dubious value for compound **6**, are below $+100$ cm^{-1} indicating that the magnetic activity of the chloro bridge does not compensate the overall bond weakening because of the TBP geometry of the metals.

Compounds **12** and **13** belong to class E and have the peculiarity that the third bridge is a methoxo ligand. They have the same chemical formula for the dinuclear cation and only differ in the counterion which is percholate for **12** and hexafluorophosphate for **13**. This chemical difference leads to two structurally similar dinuclear ions, with differences induced mostly by the crystal packing. The most important variations are 0.1 Å in the Cu−Cu distance, 5° in the Cu−O(H)−Cu and Cu−O(CH$_3$)−Cu angles, and differences in the aggregate τ parameters for the Cu(II) ions, 0.64 and 0.57 for **12** and **13**, respectively. Noticeably, the magnetic coupling constant for **12** is 30% larger than for **13**. For these two compounds all attempts to carry out DFT calculations using the original crystal structure failed to converge. This has been attributed to an inaccurate assignment of the position of the hydrogen atom of the hydroxo bridge in these crystallographically symmetric compounds, that resulted in a rather strange trigonal-planar geometry for the oxygen atom. To achieve a more chemically sound nearly tetrahedral configuration, we then moved the hydrogen atom of the OH bridging ligand toward the carboxylato bridge. This small variation in the atomic position of this H atom lead to calculations that easily converge and to reasonable magnetic coupling values, which are the ones included in Table 2. It is important to point out that **12** and **13** exhibit the characteristic feature of the triplet state spin density "lighting on" over the oxygen atom of the hydroxo bridge (similar values to that reported for **10** and **11**), but here also over the oxygen atom of the methoxo bridge with similar contribution (from 0 to 6 or 17% in BHHLYP and B3LYP methods). This result suggests that the methoxo bridge contributes to the ferromagnetic exchange in a strength comparable to that of the hydroxo bridge. Nevertheless, the dominating factor for the magnetic coupling in both compounds seems to be the coordination geometry of the copper atoms: the τ values for the Cu(II) ions in **13** is 0.57 (1.14 aggregate), very close to that of Class B compounds, in such a way that their calculated J value is in accordance with that expected for the class B magnetostructural correlation above commented. On the contrary, calculated and experimental J values for complex **12** align better to the ones found for the remaining E class compounds as the τ values for **10**, **11**, and **12** are not so different compared to compound **13** although here the number of compounds is too small to extract a meaningful correlation.

Complex **14** belongs to class D compounds where, like in class B, the metal atoms lie in a mainly SP coordination although the environment of the Cu(2) with $\tau = 0.43$ corresponding to a nearly intermediate geometry is considerably more distorted than the one corresponding to Cu(1) where $\tau = 0.22$. In this case, the pyramids do not share the same bridging ligand at the apical positions (Figure 1). For this complex, the basal planes accommodating the $d_{x^2-y^2}$ metallic contribution to the magnetic orbitals are almost perpendicular, and the hydroxo bridge is the only one sharing both basal planes and is tightly bonded to both Cu(II) ions. The O(3) and O(2) atoms from the $\mu^2(\eta^1, \eta^1)$-bridging carboxylate occupy one Cu(1) basal and one Cu(2) apical positions, respectively, and the O(4) atom of the $\mu^2(\eta^2)$-carboxylate lies at the apical position of Cu(1) and one basal position of Cu(2). In this complex, only the O(1) atom of the hydroxo ligand changes significantly its spin density from singlet to triplet states (from almost zero to 9% or 16% for BHHLYP and B3LYP, respectively). Presumably this is the only bridge that plays a noticeable role in the magnetic exchange and, consequently, a small ferromagnetic interaction is expected because of the topological orthogonality of the magnetic orbitals.[1]

Next, we discuss possible magnetic exchange pathways for class D compound **14**. A first possibility involves a single Cu−OH−Cu (101.8°) unit which links Cu(II) centers in an basal−basal configuration. This structure can occur because of the nearly intermediate geometry ($\tau = 0.43$) of one of the Cu(II) centers. Consequently, another possible pathway is the triatomic carboxylato bridge, and the small J value ($+24.1$ cm^{-1}) may result from a countercomplementary effect between the monatomic bridge, with a small bridging angle which usually contributes the ferromagnetic interaction due to the orthogonality between the Cu magnetic orbitals and the oxygen p-orbital, and the triatomic carboxylato bridge which usually contributes to an antiferromagnetic interaction.

Conclusions

In this work we used hybrid DFT calculations to investigate the magnetic coupling and magnetostructural correlation of a series of Cu(II) dinuclear complexes which have the common particularity, over other well-known families of Cu(II) dinuclear complexes, of incorporating a third bridging ligand, resulting in three different bridging ligands. The addition of this ligand is not innocent since it turns out to largely favor ferromagnetic interactions, as opposed to the broad class of Cu(II) dinuclear complexes with one or two bridging ligands which usually result in an antiferromagnetic compound.

Comparison of calculated and experimental values of the isotropic magnetic coupling constant J is not as straightforward as it may seem because, on the one hand, the calculated results depend strongly on the amount of Fock exchange used in the exchange correlation functional and, on the other hand, the accuracy of the measured values is not as good as for antiferromagnetic compounds. The good news is that calculated values (BHHLYP and B3LYP) lead to a range of values where almost all experimental data fit. However, analysis of the experimental data and comparison to structural data does not reveal any meaningful correlation. Assuming that the calculated values are good enough to provide a meaningful trend allows one to unravel a very interesting magnetostructural correlation for class B compounds, namely, that the magnitude of the calculated magnetic coupling constant correlates almost quantitatively with the sum of the Addison's τ parameter of each Cu(II) cation. The existence of this correlation opens the way for the guided synthesis of new complexes with higher ferromagnetic character that may in turn lead to important technological applications.

Concerning the relationship between J and the Cu−OH−Cu angle discusse above, one must advert that it fits the experimental data on the set of compounds **4**, **7**, **8**, and **9** only and not for the rest of compounds investigated in the present work. Nevertheless, we must realize that for this set, the aggregate τ range is very narrow (between 0.34−0.37). Therefore, the almost constant value of this coordination parameter implies that variations of J can be attributable to the Cu−OH−Cu angle. For fixed τ, this empirical correlation does not show up from the calculated values although a dispersion of the J values in a restricted J interval ($\sim$10 cm^{-1}) is observed. More experimental data on compounds having diverse combinations of aggregate τ and Cu−OH−Cu angles are needed to properly investigate this double dependency.

To conclude, using ligands favoring the square based pyramidal coordination on each Cu(II) atom in a triple bridge is the key to obtain complexes with enhanced ferromagnetic character. Available data for class E compounds also indicate that this enhancement can also be achieved by using a third ligand favoring the interaction through the d_{z^2} orbitals. In addition, the theoretical correlation indicates that there is an upper limit of +200 cm^{-1} (when aggregate τ is 0) for the ferromagnetic coupling in this kind of hetero-triply bridged compounds, and this fact must be accounted by the experimentalists.

Acknowledgment. Financial support has been provided by the Spanish MICINN (Grant FIS2008-02238), Generalitat de Catalunya (Grants 2009SGR1041 and XRQTC) and The Thailand Research Fund (Grant BRG5280012). The Thai Center of Excellence for Innovation in Chemistry (PERCH−CIC), Commission on Higher Education, Ministry of Education and Khon Kaen University are also gratefully acknowledged. Part of the computational time provided by the Centre de Supercomputació de Catalunya (CESCA) is also gratefully acknowledged.