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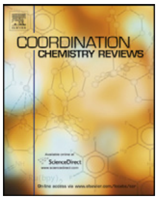

Review

Structural and electronic effects on the exchange interactions in dinuclear bis(phenoxo)-bridged copper(II) complexes

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ABSTRACT

Computational methods based on density functional theory have been employed to analyze the magnetic properties of dinuclear bis(phenoxo)-bridged Cu^{II} complexes. While the largest part of complexes in that family show antiferromagnetic coupling, we focus our study on those cases with distorted geometries that present ferromagnetic behaviour. The calculations reproduce such a magnetic behaviour, and a structural analysis reveals the main role played by several structural parameters, such as the Cu–O–Cu bridging angle. The out-of-plane shift of the phenoxo ring and the hinge distortion of the Cu_2O_2 central framework that are also important for similar hydroxo and alkoxo complexes. In this case the conformation of the phenoxo groups and the rotation of the phenyl rings can also play an important role. The last part of this work is dedicated to analyze the influence of the substituents of the phenoxo ring on the magnetic properties, which is especially important for structures with large out-of-plane shifted phenoxo rings. The presence of π electron releasing groups favours a ferromagnetic coupling.

1. Introduction

In the field of Molecular Magnetism [1], phenoxo bridged complexes are an important family of compounds. Phenoxo ligands have been employed in the synthesis of many complexes with different transition metals, among which the most frequent ones are those of copper(II). These copper(II) complexes also show remarkable non-magnetic properties, making them useful in metal extraction in hydrometallurgy [2], fluorescent sensors [3], heterogeneous catalysis [4], and show catechol oxidase activity [5]. For many years, all the phenoxo-bridged copper(II) complexes reported exhibited a relatively strong antiferromagnetic coupling. However, some strongly ferromagnetically coupled complexes have been obtained recently [6,7]. The magnetic properties of bridged dinuclear copper(II) complexes have been extensively

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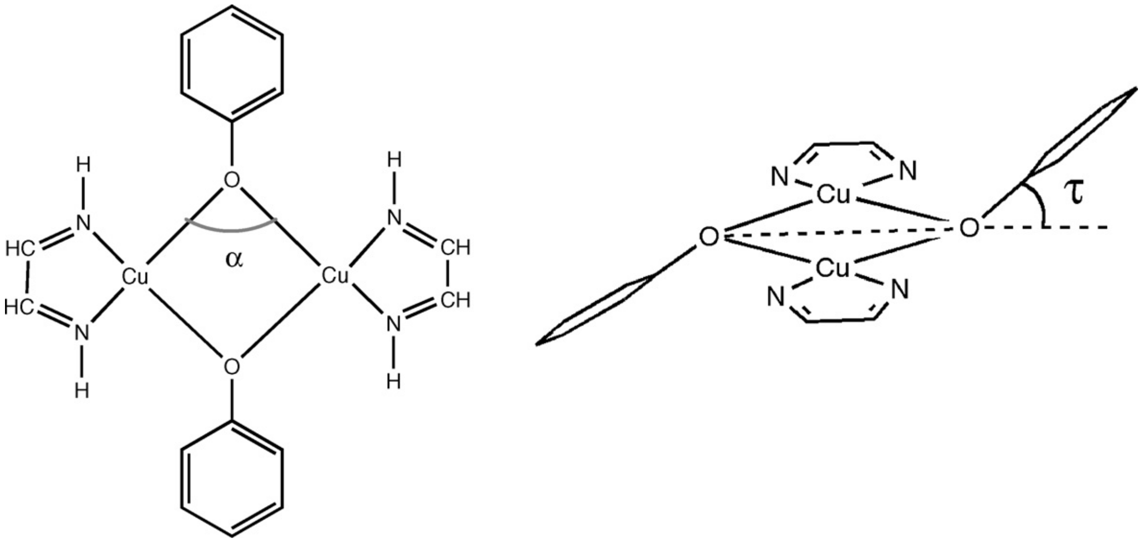
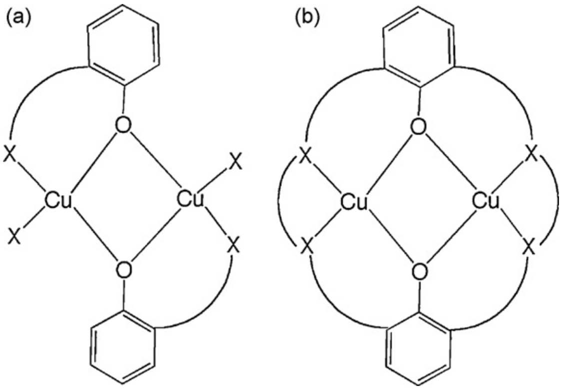


Scheme 1.

studied, since the copper(II) ions have an $S = 1/2$ spin, which makes them easier to deal with, from both the experimental and theoretical points of view [8]. Bleaney and Bowers derived a theoretical expression for the magnetic susceptibility of dinuclear copper(II) systems [9], making it possible to extract the exchange coupling constant (J) for each complex from the magnetic susceptibility curves. The wealth of available coupling constants allows the study of their relationship with structural parameters, in search for some trends that could lead to a rational design of new complexes with improved magnetic properties.

For the related bis(hydroxo) [10] and bis(alkoxo) [11] bridged copper(II) complexes, linear relationships between the Cu–O–Cu bond angle and the J values obtained from a fitting of the experimental magnetic susceptibility data have been reported. For instance, in the case of hydroxo complexes, a transition from antiferromagnetism to ferromagnetism is observed for Cu–O–Cu angles smaller than 97° [10]. This phenomenon is attributed to an "accidental orthogonality" of the orbitals bearing the unpaired electrons. Thus, to minimize electronic repulsions, the system adopts the high spin state that corresponds in this case to a triplet. From a molecular orbital point of view, Hoffmann [12] and Kahn [13,14] gave consistent explanations within the extended Hückel framework. More recently, the use of theoretical methods based on density functional theory (DFT) has made it possible to obtain remarkably good quantitative estimates of the J values for this kind of complexes, in spite of the small energy differences associated to these interactions. Ruiz et al. have earlier applied such an approach to the study of magnetostructural correlations in hydroxo- and alkoxo-bridged copper(II) complexes [15,16]. The results indicate that several structural parameters affect the J value, but the Cu–O–Cu angle (α),correlated with the phenyl out-of-plane shift angle (τ), plays a key role (see Scheme 1). Among other structural parameters, let us mention the bending of the Cu_2O_2 framework around the O···O hinge, that can also play an important role if it is sufficiently large.

All dinuclear bis(phenoxo) bridged Cu^{II} complexes belong to one of two general types, having two chelate ligands spanning terminal and bridging positions (Scheme 2a) or with the phenoxo groups incorporated into a multidentate macrocyclic ligand (Scheme 2b). The second family, known as Robson complexes, has been studied by Thompson et al. [17], who showed that the exchange coupling constant is correlated to the Cu–O–Cu bond angle. An important feature of the Robson-type macrocycles is that they are generally constrained to adopt a planar configuration. Thompson et al. also analyzed the effect of different electron withdrawing substituents on the value of the coupling constant. Theoretical studies of the different electronic effects of substituents on the magnetic exchange interaction between substituted dialkoxo Cu^{II} systems and substituted carboxylate Cu^{II} complexes were later published by Rodríguez-Fortea et al. [18]. The effects reported in those two publications correspond to substituents only one or two bonds away from the bridging oxygen atoms.



Scheme 2.

The goal of the present paper is to study the influence of different structural parameters on the nature and magnitude of the magnetic exchange interactions in dinuclear bis(phenoxo)-bridged Cu^{II} complexes (Scheme 1), as well as the long range effect of different *para* substituents on the phenyl rings characterized by their Hammett parameter [19]. We put special emphasis in unravelling the structural features that favour the presence of ferromagnetism in a few members of the dinuclear bis(phenoxo) bridged Cu^{II} family.

2. Computational details

The exchange coupling constant was evaluated by calculating the energy difference between the two possible spin states, a triplet ($S = 1$) and a singlet ($S = 0$), based on the phenomenological spin Hamiltonian:

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

We have employed the "broken-symmetry" approach [20,21] to estimate the $S = 0$ energy state using a single-determinant method

[8,22,23]. All calculations were performed under the density functional theory approach, using the hybrid B3LYP functional [24] and a triple-ζ all electron basis set for all atoms [25]. Total energy calculations were performed using the Gaussian03 program [26], with a convergence criterion of 10^{-7} a.u.. The structural models (see Scheme 1) used for the calculations are based on a previous study on hydroxo-bridged copper(II) complexes. Three different angles were varied for the magnetostructural study: the Cu–O–Cu bridging angle (α), the out-of-plane angle of the phenyl ring (τ), both sketched in **1**, and the hinge distortion of the central Cu_2O_2 framework. The copper centres in **1** are tetracoordinated, and their coordination spheres are formed by two phenoxo oxygen atoms and two nitrogen atoms from a diimine ligand. The use of the non-projected energy of the broken-symmetry solution as the energy of the low spin state within the DFT framework provides good results because it avoids the cancellation of the non-dynamic correlation effects as stated in previous studies [22,23]. Thus, the J value for a dinuclear transition metal complex can be obtained from the energies of the high spin state and the "broken-symmetry" wavefunction with the non-projected approach:

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

where S_1 and S_2 are the total spins of the two interacting paramagnetic centers and $S_1 > S_2$ is assumed for heterodinuclear complexes. The use of the original *broken-symmetry* approach, proposed by Noodlemann [20,21], provides an overestimation of the stability of the low spin states.

$$E_{HS} - E_{BS} = -2S_1S_2J \qquad (3)$$

For the orbital analysis of the magnetostructural correlations using either the Kahn–Briat (KB) model [13,14] or the Hay–Thibeault–Hoffmann model (HTH) [12], the empty orbitals have been employed because it is well known that they provide a better description of the "magnetic orbitals".

In order to evaluate the effect produced by different substituents at the phenoxo ring on the calculated value of the J, the hydrogen atoms in a *para* position relative to the oxygen atoms were substituted by the following groups: CH_3, Cl, $CONH_2$, CO_2H, CN and NO_2. The geometries of the substituents were optimized at the DFT B3LYP/6-31G* level, included in the Jaguar 5.5 code [27], leaving the rest of the molecule frozen. The total energy calculations were performed as described for the structural models in the above paragraph. The calculated magnetic exchange value were correlated with the Hammett parameters of the substituents [19].

3. Results and discussion

3.1. Analysis of the structural and magnetic data

A crystallographic structural database search (Cambridge Structural Database) [28] for dinuclear bis(phenoxo)-bridged Cu^{II} complexes produced 330 hits. The largest and smallest Cu–O–Cu angles found were 110.4° and 85.7°, respectively [29,30], although most compounds present angles between 90° and 105°. On the other hand, the out-of-plane shift of the phenoxo groups is represented by values of τ in the range 0–50°. A scatterplot of these two angles is represented in Fig. 1 for the 75 complexes with experimentally determined exchange coupling constant and four short bridging Cu–O bond distances (see Table S1) [4,6,7,17,31–83]. From Fig. 1, the same conclusions can be extracted as from the whole set of 330 complexes, i.e., that there is no clear correlation for the whole family of complexes between those two angles. However, it seems in many cases that large phenyl out-of-plane shift angles appear preferentially for small Cu–O–Cu angles. We observe a few exceptional complexes that present small values of both Cu–O–Cu and τ (CSD refcodes XIPBAZ **(2)**, NIGDUD **(3)**, and TIDLEY **(4)**) [6,7]. The remarkable feature of those complexes is that two of them **(2)** and **(3)**, present a relatively strong ferromagnetic coupling. Another compound that must be singled out is **(1)**, because it presents the strongest ferromagnetic coupling (+117 cm^{-1}) within the family, with a relatively large Cu–O–Cu angle (96.1°).

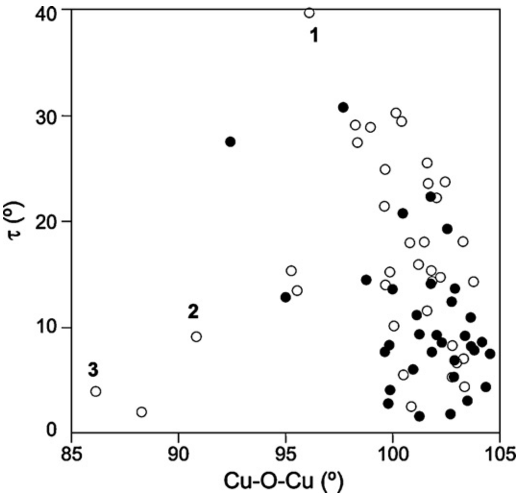


Fig. 1. Scatterplot of the phenyl out-of-plane shift (τ) and the Cu–O–Cu angle for the dinuclear bis(phenoxo)-bridged Cu^{II} complexes whose exchange coupling constants are known, and which possess four short bridging Cu–O bond distances [4,6,7,17,31–42,44,46–59,61–83]. Black circles correspond to the Robson-type complexes **2b**, white circles to structures with two independent bridging ligands **2a**. The three refcodes indicated correspond to the known ferromagnetic complexes.

A scatterplot of the exchange coupling constant and the Cu–O–Cu angle is shown in Fig. 2. The Robson-type complexes (black circles) usually adopt a flat structure with large Cu–O–Cu angles and relatively strong antiferromagnetic coupling. However, there are a couple of exceptions, that correspond to a weakly antiferromagnetically coupled complex **(5)** with a relatively small Cu–O–Cu angle of 92.4° and a large τ (27.6°), and a strongly antiferromagnetic complex (CSD refcode GALROB01 **(9)**) with $\alpha = 95.0°$ and a small τ (12.8°) showing a disordered structure [41]. However, the database lists a second structure for the last complex (CSD refcode GALROB **(9A)**) [84] with very different Cu–O–Cu and τ angles, 101.3° and 6.8°, respectively, hence it cannot be used in the discussion.

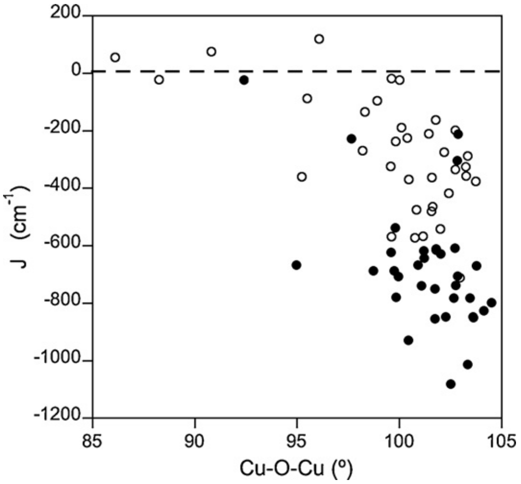


Fig. 2. Scatterplot of the experimental J values and the Cu–O–Cu angle for the dinuclear bis(phenoxo)-bridged Cu^{II} complexes of Fig. 1 [4,6,7,17,31–42,44,46–59,61–83]. Black circles correspond to the Robson-type complexes **2b**, white circles to structures with two independent bridging ligands **2a**.

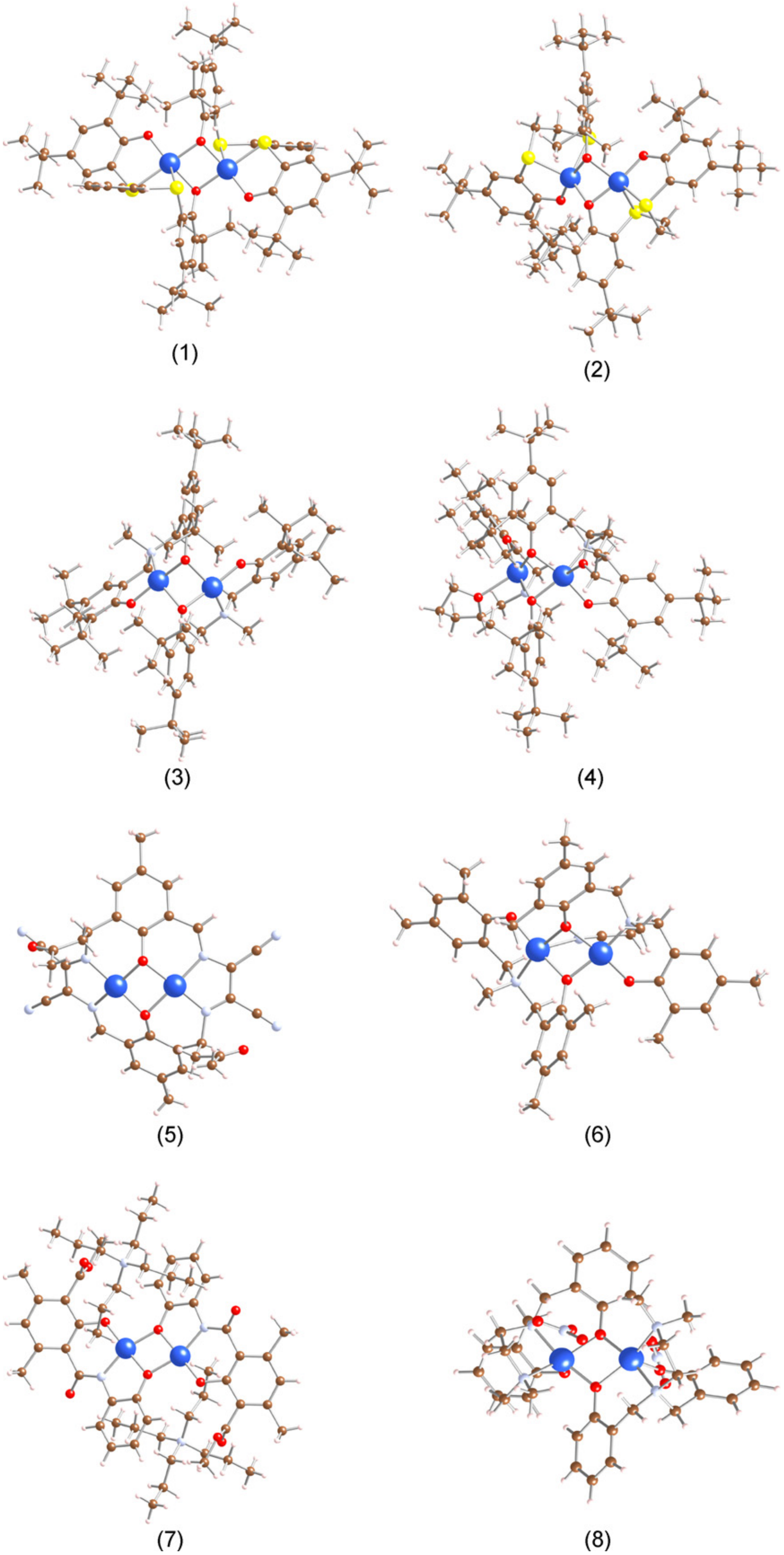


Fig. 3. Molecular structures of the eight dinuclear Cu^{II} complexes studied. Copper atoms are represented by large blue spheres, sulfur atoms by medium size yellow spheres and oxygen, carbon and nitrogen atoms by red, brown and blue spheres. **(1)** Bis(μ_2-1,2-bis(3,5-bis(t-butyl)-2-hydroxyphenylsulfanyl)benzene)-copper(II) [7]; **(2)** bis(μ_2-1,2-bis(3,5-bis(t-butyl)-2-hydroxyphenylsulfanyl)ethane)-copper(II) [7]; **(3)** bis(μ_2-N,N-bis(2-oxy-3,5-di-t-butylbenzyl)-N-methylamine-N,O,O,O′)-copper(II) [6]; **(4)** bis(μ_2-2-((bis(3,5-di-t-butyl-2-oxybenzyl)amino)methyl)-tetrahydrofuran-N,O,O′)-copper(II) diethyl ether solvate [70]; **(5)** (μ_2-7,18-bis(acetonyl)-10,21-dimethyl-23,24-dihydroxy-4,5,15,16-tetracyano-3,6,14,17-tetra-azatricyclo-(17.3.1.18,12)tetracosa-1(23),2,4,8,10,12(24),13,15,19,21-decene)-copper(II) acetone solvate [72]; **(6)** bis(μ2-N,N-bis(2-oxy-3,5-dimethylbenzyl)-N-methylamine-N,O,O,O′)-copper(II) acetonitrile solvate hemihydrate [6]; **(7)** bis(tetra-n-propylammonium) bis(μ_2-N-(2-hydroxyphenyl)-3- methoxycarbonyl-4,6-dimethylsalicylamide)-copper(II) [49]; **(8)** bis(μ_2-N-(2-hydroxybenzyl)-N-(2-oxybenzyl)-N′,N′-dimethylethylenediamine)-copper(II)dinitrate monohydrate [42].

Table 1

Experimental and calculated *J* values (in cm^{-1}) for eight selected dinuclear bis(phenoxo)-bridged Cu^{II} complexes. Average structural data are also provided for comparison (see whole family values, Table S1), the conformation of the phenoxo groups has been classified as *syn* or *anti*.

Compound	refcode	Cu–O–Cu (°)	τ (°)	Cu–O–Cu–O (°)	Phenyl conf.	Cu–O–C–C (°)	Cu–O (Å)	J_{exp}	J_{calc}	Ref.
1	XIPBED	96.1	39.6	0.0	*anti*	58.2	1.952	+117	+77	[7]
2	XIPBAZ	90.8	9.2	36.8	*syn*	58.1	1.975	+73	+25	[7]
3	NIGDUD	86.1	4.0	41.1	*syn*	57.2	1.975	+53	+6	[6]
4	TIDLEY	88.3	2.1	41.4	*syn*	59.2	1.986	–24	–46	[70]
5	TOPJAJ	92.4	27.5	17.0	*syn*	33.8	1.931	–25	–65	[72]
6	NIKXUB	98.2	29.1	25.9	*syn*	30.8	1.963	–271	–350	[70]
7	GIYZOD	103.8	14.3	0.0	*anti*	8.7	1.928	–378	–329	[49]
8	EGUGAO	103.0	6.7	13.2	*syn*	34.9	1.957	–714	–636	[43]

We have calculated the exchange coupling constants for several dinuclear bis(phenoxo)-bridged Cu^{II} complexes (Fig. 3 and Table 1), using the methodology described in Section 2. The studied compounds were selected in order to have a wide range of magnetic coupling constants and also to analyze some appealing magnetic behaviour. The calculated values correctly reproduce the nature (ferro- or antiferromagnetic) and the strength of the interactions. In this regard it is well known that the experimentally determined ferromagnetic coupling constants have a large uncertainty in comparison with the antiferromagnetic ones. Comparison of the Cu–O–Cu angles in the three ferromagnetic complexes with those in the antiferromagnetic ones indicates that this structural parameter cannot by itself account for the magnetic properties. The very large phenyl out-of-plane angle of **(1)** could be responsible of the strong ferromagnetic coupling. For this complex, the presence of large substituents in the ligand, and the fact that is not a Robson-type complex allowing more flexibility, results in such a distorted structure. For complexes **(2)** and **(3)**, the phenyl out-of-plane angle is relatively small but there is a large hinge distortion of the Cu_2O_2 framework, as indicated by a large Cu–O–Cu–O torsion angle. In order to show the difficulties found for rationalizing the dependence of the exchange interactions based on a few structural parameters, we can also mention that according to the very small Cu–O–Cu angle in **(4)** analogous to those found for the ferromagnetic complexes, a ferromagnetic coupling should be expected. However, it is weakly antiferromagnetic. A detailed analysis of the structure of this complex reveals a strong hinge distortion of the central Cu_2O_2 framework and also a large rotation of the phenyl groups that adopt a *syn* conformation (measured in Table 1 by the Cu–O–Cu–O and Cu–O–C–C torsion angles, respectively). Thus, for the dinuclear bis(phenoxo)-bridged Cu^{II} complexes the *J* value seems to be determined by an interplay of at least the different structural parameters collected in Table 1. Hence, we undertake in the subsequent sections a more detailed analysis of the effect of each of those structural parameters on the exchange coupling constant.

3.2. Magnetostructural correlations

In this section we analyze the dependence of the exchange coupling constant on several structural parameters. We will employ for that purpose model complexes (see Scheme 1), in which changes in the structural parameters (or group substitution in the phenyl ring) can be easily introduced to independently analyze their effect on the magnetic properties.

3.2.1. Role of the bridging angle and the out-of-plane shift of the phenyl group

The calculated values of the exchange coupling constant in a model compound as a function of the Cu–O–Cu bridging angle for two values of the phenyl out-of-plane angle ($\tau = 0°$ and 50°) are plotted in Fig. 4, together with the experimental data. All the experimental points of non-macrocyclic complexes (Scheme 2a) are within the region delimited by the calculated curves corresponding to the two τ angles considered. The Robson-type compounds (Scheme 2b), in contrast, have more negative *J* values. We must keep in mind, though, that very large antiferromagnetic coupling constants ($|J| > 600\,cm^{-1}$) are very difficult to determine, and consequently, there are large errors in the experimental values of *J*. For the planar system ($\tau = 0°$), the calculated *J* value is antiferromagnetic at all Cu–O–Cu angles considered (90–105°), and its absolute value increases with the Cu–O–Cu angle. In contrast, when the phenoxide is significantly shifted from the Cu_2O_2 plane ($\tau = 50°$), all the calculated J values are ferromagnetic, with a slightly parabolic dependence on α.

The behaviour observed for the dinuclear bis(phenoxo)-bridged Cu^{II} complexes is similar to that found previously by Ruiz et al. [15,16] for the bis(hydroxo)-bridged ones, in the sense that a large out-of-plane displacement of R (R = H, phenyl) favours a ferromagnetic behaviour. The variation of the calculated exchange coupling constant as a function of the Cu–O–Cu angle, is much more pronounced for the model with $\tau = 0°$ than with $\tau = 50°$ (Fig. 4).

In order to achieve a better understanding of the magnetostructural correlations obtained (Fig. 4), we have analyzed the theoretical results with the help of two qualitative orbital models, proposed by Kahn and Briat [13,14] and by Hay et al. [12]. The former relates the antiferromagnetic contribution to *J* with the square of the overlap integral between the two magnetic orbitals (S_{ab}), obtained here from the calculations of the broken-symmetry wavefunction. The latter relates the same contribution to the square of the energy difference between the two magnetic orbitals $(\varepsilon_1 - \varepsilon_2)^2$,

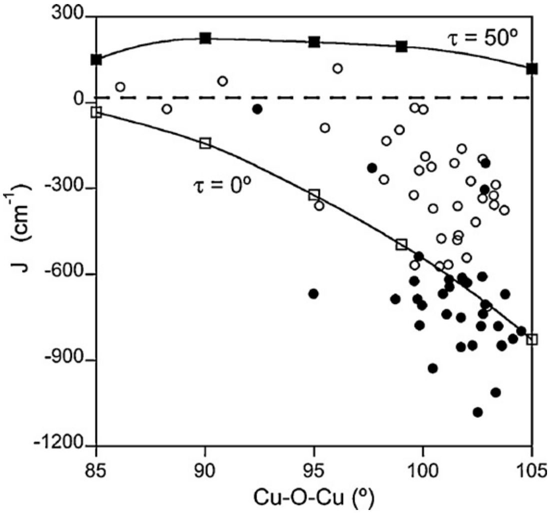


Fig. 4. Calculated *J* values for two model complexes (Scheme 1) with two different values of the phenyl out-of-plane angle, $\tau = 0°$ and 50°, indicated as white and black squares, respectively. Black circles correspond to the Robson-type complexes **2b**, white circles to structures with two independent bridging ligands **2a** [4,6,7,17,31–42,44,46–59,61–83].

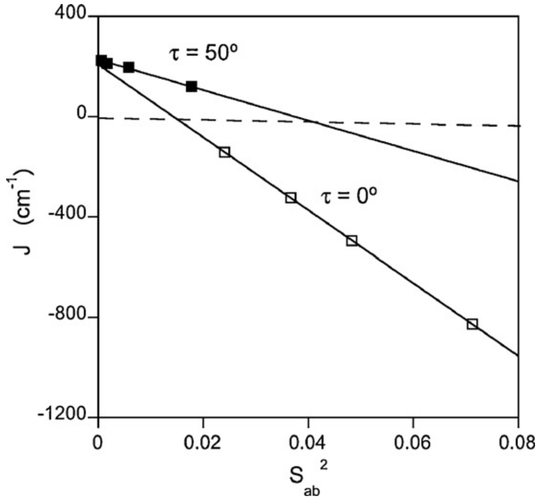


Fig. 5. Dependence of the J values calculated for model structures with $\tau = 0°$ and 50°, (white and black squares, respectively) on the square of the overlap integral of the magnetic orbitals.

extracted here from the calculations of the triplet state. In both cases we have used the β empty version of the magnetic orbitals, since they give better results than the occupied ones [85–87]. In Fig. 5 we see that J has a linear dependence on the square of the overlap, as predicted by the Kahn–Briat model. The overlap integral varies much less for the model with the phenoxide shifted from of the Cu_2O_2 plane ($\tau = 50°$), and it is therefore expected to present a coupling constant much less sensitive to changes in the Cu–O–Cu angle than for the in-plane situation. The results can be considered a textbook case, since the strongest ferromagnetism appears for a bridging Cu–O–Cu angle of 90° (see Fig. 4), for which we obtain the smallest S_{ab} overlap integral (black squares in Fig. 5).

To understand why the variation of J is so small when $\tau = 50°$, we can alternatively employ the Hay–Thibeault–Hoffmann model, illustrated by Fig. 6. In this case, the energy term $(\varepsilon_1 - \varepsilon_2)^2$ is negligible at a Cu–O–Cu angle of 90° (Fig. 6 above), resulting in ferromagnetic ($\tau = 50°$) or practically uncoupled ($\tau = 0°$) systems. If the Cu–O–Cu angle is smaller or larger than 90°, the $(\varepsilon_1 - \varepsilon_2)^2$ term becomes larger and, consequently the system is less ferromagnetic. The analysis of the magnetic orbitals of the triplet state indicates that with $\tau = 50°$ they present an energy crossover close to a Cu–O–Cu angle of 90° (black symbols in Fig. 6 above) while for $\tau = 0°$ the energy gap increases with the Cu–O–Cu angle (white symbols in Fig. 6 above). For both τ values, the energy of b_{2u} is practically independent of the Cu–O–Cu angle (Fig. 6, above), while that of the b_{1g} orbital increases due to its enhanced antibonding character at large Cu–O–Cu angles. It is worth noting the excellent agreement of the Kahn–Briat and Hay–Thibeault–Hoffmann models, reflected in the similarity of Figs. 5 and 6. The crossover of the two magnetic orbitals occurs at a different Cu–O–Cu angle depending on the position of the phenoxo group relative to the Cu_2O_2 plane: at 90° for $\tau = 50°$, but at of 85° for $\tau = 0°$.

3.2.2. Hinge distortion of the Cu_2O_2 framework and conformation of the phenyl rings

The results obtained in the previous subsection are in qualitative agreement with those obtained earlier for hydroxo and alkoxo bridging ligands [15,16]. In this section, we will analyze the effect of two structural parameters on the J value, the hinge distortion of the Cu_2O_2 framework, that was also studied previously for hydroxo and alkoxo complexes [15,16], and the role of the conformation and rotation of the phenyl rings. The calculated J values for a model complex show a strong dependence on the hinge distortion (Fig. 7).

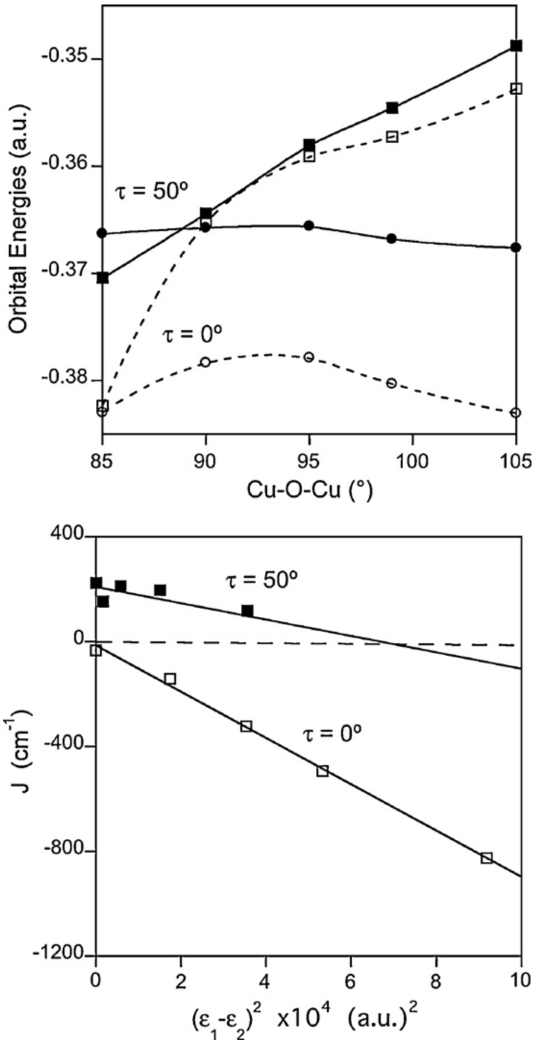


Fig. 6. *Above*: Energies of the two "magnetic" orbitals of the triplet state with $\tau = 0°$ and 50°, indicated as white and black symbols, respectively. Circles correspond to the b_{2u}, squares to the b_{1g} orbital (Scheme 3). *Below*: Dependence of the calculated J values on the square of the energy difference between the two magnetic orbitals.

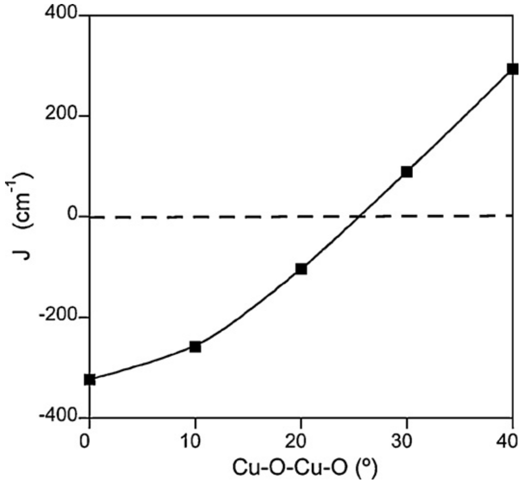


Fig. 7. Calculated J values for the model complex Scheme 1 as a function of the Cu–O–Cu–O torsion angle. The Cu–O–Cu bridging angle was fixed at 95° and the phenyl rings remain in the plane ($\tau = 0°$).

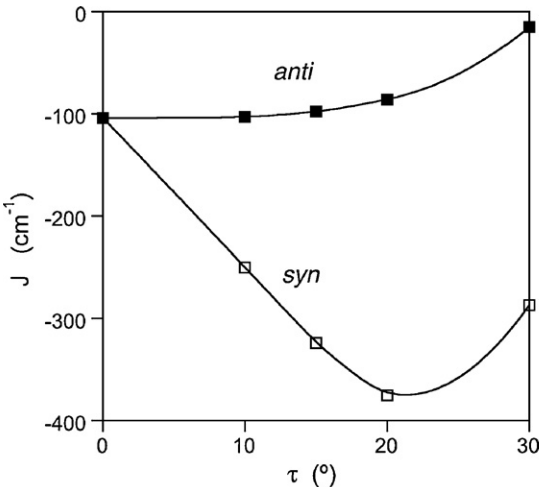


Fig. 8. Calculated *J* values for the model complex **1** as a function of the phenyl out-of-plane angle (τ), for a Cu–O–Cu bridging angle of 95° and a Cu–O–Cu–O angle of 20°. The white and black squares indicated the *syn* and *anti* conformations of the phenyl rings, respectively.

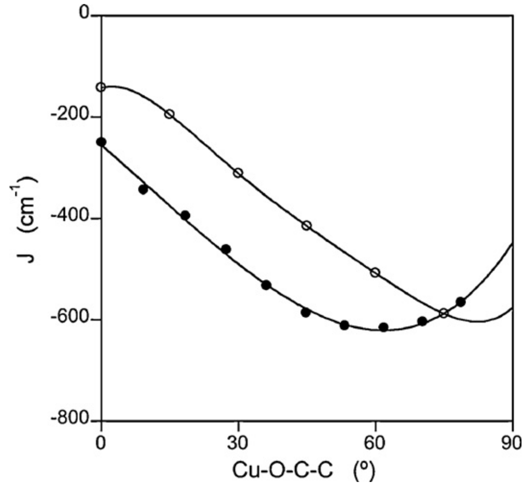


Fig. 9. Calculated *J* values for the model complexes (see **1**) versus the phenyl ring torsion angle Cu–O–C–C for two different models: (a) with Cu–O–Cu = 95°, Cu–O–Cu–O = 20° and the τ = 15° (black circles), and (b) with Cu–O–Cu = 90°, Cu–O–Cu–O = 0° and the τ = 0° (white circles). A Cu–O–C–C torsion angle of 0° corresponds to the coplanar situation and an angle of 90° to phenyl rings perpendicular to the central Cu_2O_2 framework.

Large distortions of the Cu_2O_2 framework result in an increase of the ferromagnetic contribution, as we had previously seen for the analogous hydroxo-bridged complexes.

The previous results suggest that either the out-of-plane shift of the phenyl ring or the hinge distortion of the Cu_2O_2 framework can increase the ferromagnetic contributions. The analysis of the structures of dinuclear bis(phenoxo)-bridged Cu^{II} complexes also reveals many cases of the phenyl rings rotation with respect to the Cu_2O_2 framework (see Table S1). Even if in most cases the two phenoxo ligands adopt an *anti* conformation, some compounds present a *syn* conformation, whereas a perfectly flat conformation has been found in only one case (CSD refcode FEYXIQ **(10)**) [47]. In most cases a *syn* conformation is associated with a large hinge distortion of the Cu_2O_2 framework. Now we will analyze the effects of the conformation and rotation of the phenoxo groups on the exchange coupling constant.

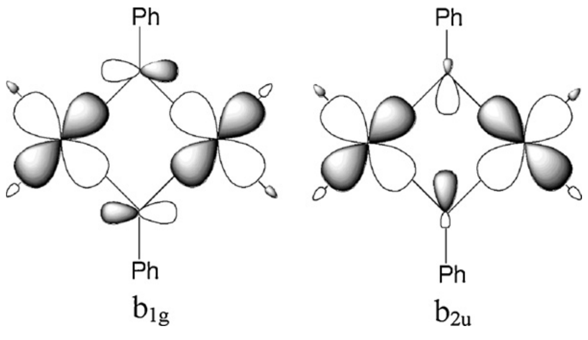
The dependence of the calculated *J* values for the model complex with *syn* and *anti* conformations of the phenyl rings at τ = 20° is represented in Fig. 8. This τ value was selected because it is representative of the experimental values in several complexes (Table 1) with the *syn* conformation, i.e. complexes **(5)** and **(6)** [6,72]. Surprisingly, in the *anti* conformation the out-of-plane shift of the phenyl groups has a minor effect on J, while in *syn* conformation the same shift strongly enhances antiferromagnetic coupling. The trend is inverted when the out-of-plane angles are large (τ > 20°, Fig. 8) and the Cu–O–Cu–O angle is 20°. This can be explained by the analysis of the magnetic orbitals (not shown). The maximum overlap between the oxygen and copper orbitals corresponding to the magnetic orbitals occurs for larger τ angle values. Thus, for the case with Cu–O–Cu–O angle equal to 0°, the largest overlap of the orbitals of copper and oxygen atoms is for the coplanar structure (τ = 0°), while if the central Cu_2O_2 framework has a hinge distortion the strongest antiferromagnetic coupling is found for an out-of-plane shift of the phenyl groups (see Fig. 8).

A glance at the structures collected in Fig. 3 tells us that the phenyl group presents variable degrees of rotation around the O–C bond (Cu–O–C–C torsion angle), from coplanar (0°) to perpendicular (90°) to the Cu_2O_2 core. Our calculations (Fig. 9) indicate that the rotation of the phenyl ring toward the perpendicular orientation strengthens the antiferromagnetic coupling. Such behaviour can be easily explained with the help of the orbitals bearing the unpaired electrons (Fig. S1). The energy of the b_{2u} orbital (Scheme 3) does not change with the rotation of the phenyl group while the b_{1g} orbital increases its energy with the rotation due to the participation of the π antibonding orbitals of the phenyl ring. Consequently, the phenyl rotation results in a larger $(\varepsilon_1 - \varepsilon_2)^2$ term, and in a stronger antiferromagnetic coupling. We have also performed calculations to analyze the influence of the rotation of the phenyl group around the C–O bond at different τ angles. The influence of the rotation of the phenyl on the calculated *J* values becomes smaller for large values of τ (40–50°). Thus, some complexes with large values of τ can be ferromagnetic even with significantly rotated phenyl rings.

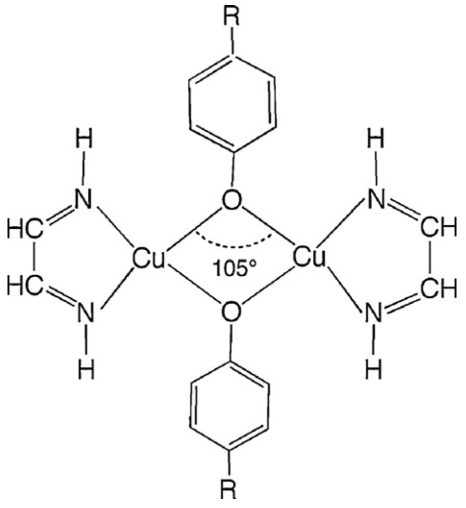
3.2.3. Effect of the substituents in the phenyl ring

The effect of different substituents at the *para* position of the phenoxo groups on the calculated *J* values for the model with α = 105° (Scheme 4) at two different values of τ (0° and 50°) is shown in Fig. 10.

The analysis of the results indicates that for the model complex with τ = 0° (white squares in Fig. 10) there is an almost perfect linear dependence of the *J* values with the Hammett parameter [19], moreover, the substituent effect is very small. It is possible to observe that electron withdrawing groups produce a very small decrease in the antiferromagnetic coupling. Hence, on going from a methyl (the most electron releasing group of the studied series) to a nitro substituent (the most electron withdrawing group of the studied series) the calculated *J* values changes only from −838 to −787 cm^{-1}. The *J* values for the model complex with τ = 50° (black squares in Fig. 10) present a feeble correlation with the Hammett parameter, although there is a dramatic change between the two



Scheme 3.



Scheme 4.

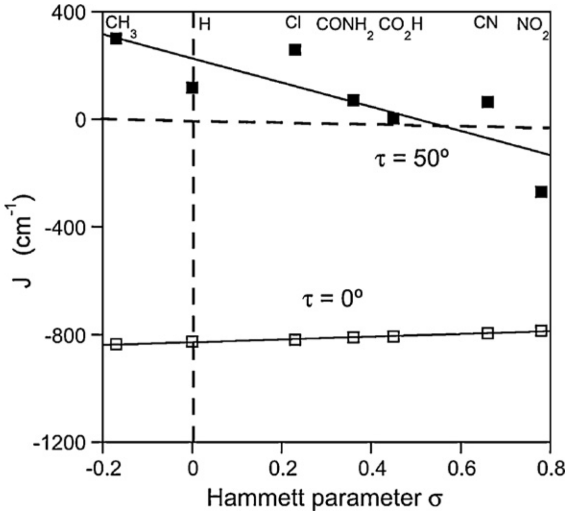


Fig. 10. Dependence of the calculated J values for the substituted model compound (Scheme 4) for $\alpha = 105^\circ$ and $\tau = 0^\circ$ or 50°, white and black squares, respectively, on the Hammett parameter. The R substituents are indicated at the top of the figure.

extremes of the series with the nitro group producing a strong antiferromagnetic coupling ($J = -270\,\text{cm}^{-1}$), while all the other calculated J values remain ferromagnetic. Therefore, the influence of electronic effects of the substituents is more evident when $\tau = 50^\circ$. The opposite effect found for the two positions of the phenoxo groups, is clearly reflected in the different sign of the slopes in Fig. 10. While at $\tau = 0^\circ$ the electron withdrawing groups enhance the antiferromagnetic coupling; at $\tau = 50^\circ$ the coupling becomes slightly more ferromagnetic.

We have performed an orbital analysis of the calculated J values for the substituted phenoxo dinuclear Cu^{II} complexes using the Kahn–Briat model. A nice correlation results between J and S_{ab}^2 (Fig. 11 left) at each value of τ. It is possible to observe that the overlap integral is much larger when the phenoxo group is in the plane ($\tau = 0^\circ$), yet the overlap is less affected by the substituents than when the bridge is shifted out-of-plane. If we look at the substituent effect from the point of view of the HTH model (Fig. 11 right), the results are amazingly similar.

The small influence of the substituent when $\tau = 0^\circ$ can be easily understood taking into account that the magnetic orbitals (Scheme 3) are of σ character, whereas the changes associated with the chemical substitution and measured through the Hammett parameter affect the π electron density of the phenyl ring. In contrast, when $\tau = 50^\circ$ a π orbital of the phenyl ring can mix with the σ orbitals of the central Cu_2O_2 framework, and consequently the change of the substituents considerably modifies the exchange coupling. A look at the shape of these orbitals for the methyl- and nitro-substituted complexes confirms that they are practically identical at $\tau = 0^\circ$ (Fig. S2, in Supporting Information). However, at $\tau = 50^\circ$ the low-lying magnetic orbital in the methyl-substituted complex incorporates significant contributions from the π system of the phenyl ring (Fig. 12left), resulting in a larger lobe at the bridging oxygen atom that induces a greater Cu–O antibonding character. As a result, this magnetic orbital is destabilized and the energy gap decreases, resulting in a smaller antiferromagnetic contribution.

Our results are in agreement with those of Thompson et al. [17], who concluded that the presence of electron withdrawing groups reduce the strength of the antiferromagnetic coupling, taking into account that the experimental cases that they considered are close to $\tau = 0^\circ$. An orbital explanation of this fact is difficult because the changes in the J values are very small (see Fig. 10) and no important changes appear in the magnetic orbitals involved (see Fig. S2).

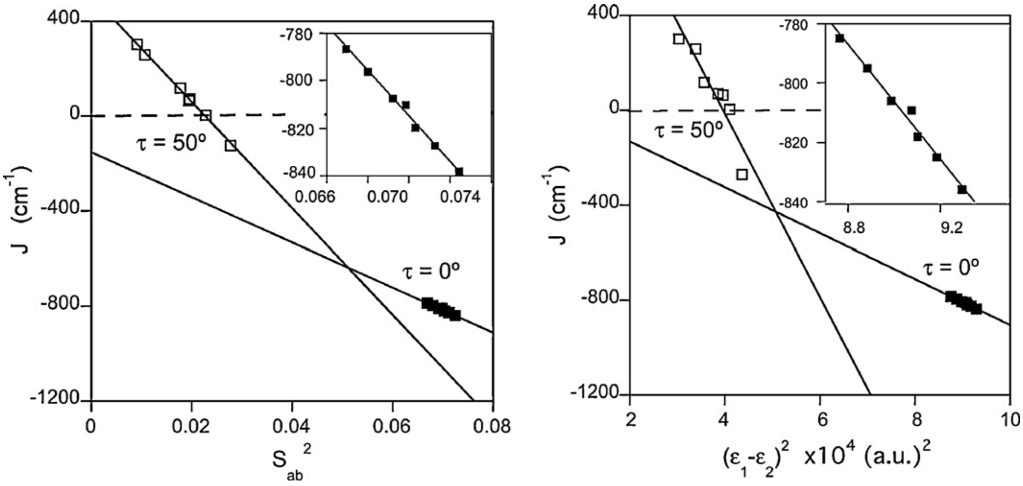


Fig. 11. Dependence of the calculated J values on the square of the overlap integral between the broken-symmetry magnetic orbitals (left) and on the square of energy difference between the magnetic orbitals of the triplet state (right) in substituted phenoxo model complexes with $\alpha = 105^\circ$ ($\tau = 0^\circ$ and 50°; black and white squares, respectively). The inset corresponds to a blow-up of the values at $\tau = 0^\circ$.

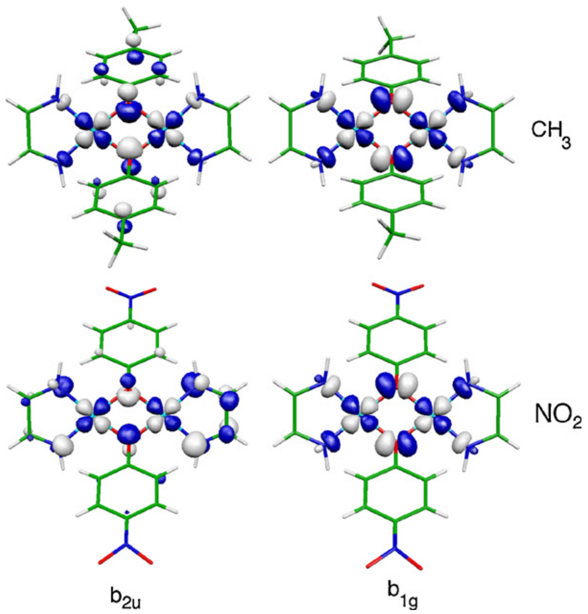


Fig. 12. Magnetic orbitals for the model structure **4** at $\tau = 50^\circ$ with to R = CH$_3$ (above) and NO$_2$ (below). The orbital with lower energy is represented on the left.

4. Concluding remarks

The *J* values calculated for some dinuclear bis(phenoxo)-bridged Cu^{II} complexes using density functional theory methods are in excellent agreement with the experimental data, reproducing the ferromagnetic coupling for the only three complexes for which such a behaviour has been observed, **(1)**, **(2)** and **(3)**.

The analysis of magnetostructural correlations for the dinuclear bis(phenoxo)-bridged Cu^{II} complexes shows a large dependence of the coupling on the bridging Cu–O–Cu angle, especially for the most common planar complexes. However, for complexes with a large out-of-plane shift this dependence is rather small. This fact can be understood due to the presence of an energy crossing of the two magnetic orbitals. Hence, the energy difference between them is always relatively small, and therefore the antiferromagnetic contribution is also small. Magnetostructural correlations can be accounted for by both the Kahn–Briat and the Hay–Thibeault–Hoffmann models giving very similar results with the two models.

We can draw some conclusions about the dependence of the *J* values on some structural parameters: (i) Large out-of-plane shifts for the phenoxo groups (τ angles) reduce the antiferromagnetic term and combined with the presence of small Cu–O–Cu angles can give ferromagnetic interactions. Moreover for large τ values, the ferromagnetic coupling is almost independent of the Cu–O–Cu angle (see Fig. 4). (ii) Large hinge distortions (i.e., Cu–O–Cu–O larger than 25°) cancel the antiferromagnetic contributions, and can lead to ferromagnetic coupling at small Cu–O–Cu angles (see Fig. 7). (iii) A *syn* conformation of the phenoxo groups favours the antiferromagnetic contribution (Fig. 8). (iv) For small τ angles, the rotation of the phenyl rings with respect to the Cu$_2$O$_2$ framework results in an increase of the antiferromagnetic contributions (see Fig. 9). However, for large τ angles, the influence of this rotation becomes smaller.

Applying these rules we can explain why **(1)**, **(2)** and **(3)** complexes are ferromagnetic [6,7] despite that they adopt crystal structures with large rotation of the phenyl rings and the *anti* conformation of **(1)** results in the strongest ferromagnetic coupling.

It is important to pay attention to the **(5)** and **(6)** complexes [6,72]. These complexes have relatively small Cu–O–Cu angles (92.4° and 98.2°, respectively), a relatively large out-of-plane shift of the phenyl group (27.5° and 29.1°, respectively), and large hinge distortion (17.0° and 25.9°, respectively). These three factors favour a very weak antiferromagnetic contribution, thus, their antiferromagnetic nature may seem surprising (Table 1). We note, however, that the *syn* conformation of the phenoxo groups is crucial in these two complexes to enhance the antiferromagnetic term, as was seen in Fig. 8. In summary, a prediction of the magnetism of the dinuclear bis(phenoxo)-bridged Cu^{II} complexes can be done with the help of Table 2.

Table 2
Relationship between the magnetic properties and the structural parameters for the different types of dinuclear diphenoxo-bridged Cu^{II} complexes.

Cu–O–Cu (°)	τ (°)	Cu–O–Cu–O (°)	Magnetism
Large (>99)	Small (<10)	Small (<10)	Strong AF
Large (>99)	Medium (~20)	Small (<10)	Moderate or weak AF
Small (<99)	Large (>30)	Small (<10)	FM
Small (<99)	Small (<10)	Large (>30)	Weak FM or AF
Small (<99)	Medium (~20)	Medium (~20)	Weak AF

FM: ferromagnetism, AF: antiferromagnetism.

Finally, the influence of substituents in the *para* position of the phenoxo ring on the exchange coupling constants has been analyzed. If the phenoxo ring is close to the plane of the Cu$_2$O$_2$ central framework (small phenyl out-of-plane shift), the electronic nature of the substituent does not affect the magnetic coupling, which is strongly antiferromagnetic in all cases. The electron withdrawing or releasing character of the substituent basically affects the π system of the ring while the magnetic orbitals have σ character. Thus, the influence is very small. However, if there is a large out-of-plane shift of the phenoxo group, there is a mixture of the π phenoxo orbitals with the magnetic orbital centred in the Cu$_2$O$_2$ central framework enhancing in the case of electron releasing groups the antibonding character of the more stable magnetic orbitals. Therefore, the energy difference of the magnetic orbitals becomes smaller for such electron releasing groups resulting in a stronger ferromagnetic coupling.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2010.04.003.

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