Exchange Coupling in Carboxylato-Bridged Dinuclear Copper(II) Compounds: A Density Functional Study

Antonio Rodríguez-Fortea,[a] Pere Alemany,*[a] Santiago Alvarez,[b] and Eliseo Ruiz[b]

Abstract: A computational study of the exchange coupling is presented for a selected sample of carboxylato-bridged dinuclear copper(II) compounds. Model calculations have been used to examine the influence of several factors on the coupling constants: a) the electron-withdrawing power of the bridging ligands; b) the nature of the axial ligands; c) the number of bridging carboxylato groups; d) some structural distortions frequently found in this family of compounds; and e) the coordination mode of the carboxylato bridge. Coupling constants calculated for some complete structures, as determined by X-ray diffraction, are in excellent agreement with experimental data, confirming the ability of the computational strategy used in this work to predict the coupling constant for compounds for which experimental data are not yet available.

Keywords: coupling constants • density functional calculations • magnetic properties • magnetostructural correlations • transition metals

Introduction

In transition metal complexes containing more than one metal atom with unpaired electrons, the observed magnetic behavior often differs from the predicted sum of the properties of the component units. This phenomenon is due to a coupling of the electron spins and is termed intramolecular antiferromagnetism or ferromagnetism, depending upon whether antiparallel or parallel spin coupling, respectively, is found in the ground state. Much experimental and theoretical work in recent decades has been done on the mechanism of this exchange coupling in polynuclear complexes, leading to the now well-established field of molecular magnetism, that is, the synthesis and study of the magnetic behavior of materials based on molecular entities.[1–5]

One of the most striking features in molecular magnetism is the ability of some polyatomic ligands to provide pathways for exchange coupling between atoms that are not directly bonded. Intramolecular spin coupling was discovered in 1951 by Guha;[6] Bleaney and Bowers[7] then found it in a compound known at that time as copper(II) acetate monohydrate, which was revealed by further studies to be dimeric with four acetate ligands bridging the two copper atoms[8] (Figure 1). The copper(II) ions, each with one unpaired electron, are in square-pyramidal environments, with oxygen atoms from the acetato groups in the basal planes and water molecules occupying the apical positions. The magnetic susceptibility of this compound exhibits a broad maximum as a function of temperature and becomes negligible below 100 K.[9] This behavior can be rationalized through a phenomenological Heisenberg Hamiltonian $\hat{H}$ [Eq. (1)] that describes

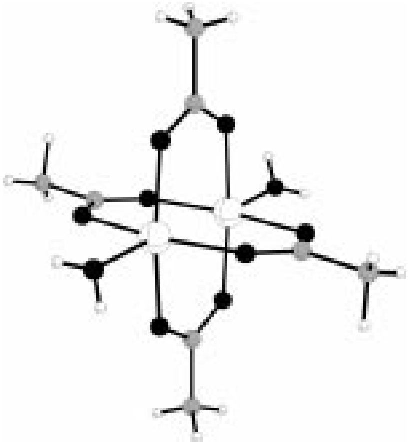

Figure 1. Crystal structure of $[Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2]$. Structural parameters were taken from reference [91].

$$\hat{H} = -J\vec{S}_A\vec{S}_B \qquad (1)$$

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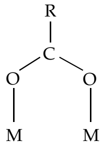
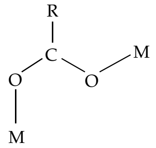
the exchange interaction between the two paramagnetic centers. S_A and S_B are the total spins on each metal ion ($S_A = S_B = 1/2$ in copper(II) acetate) and J is the coupling constant. Positive values of J indicate a ground state with parallel spins, that is, a ferromagnetic interaction, whereas negative values correspond to an antiferromagnetic coupling, with antiparallel spins. The experimental data show that the two electron spins in copper(II) acetate are antiferromagnetically coupled[3] with $J = -296\ \mathrm{cm}^{-1}$.

The study of intramolecular exchange interactions has since been extended to a large number of binuclear and polynuclear compounds with a great variety of bridging ligands (such as carboxylato, hydroxo, azido, oxalato).[3, 5, 10, 11] Among these, the copper(II) carboxylates form a large family with many structurally characterized compounds for which magnetic properties have been measured.[12–20] This wealth of experimental information permits detailed study of the influence of various factors on the exchange interaction between the two unpaired electrons. The different coordination modes of the carboxylato group (**1**–**4**), together with the choice of the substituent (R) at the bridging ligand, the axial ligand (L), and the number of bridging ligands, give rise to many tools for designing new compounds with desired magnetic properties. However, a key step in this process is a detailed knowledge of the mechanism of spin coupling in these compounds and how it is affected by the nature of the bridging and axial ligands and by the coordination geometry around the copper atoms. Although theoretical work on exchange coupling in carboxylato-bridged copper(II) dinuclear compounds has shed light on some of these aspects,[21–25] there is still no comprehensive study of all the factors mentioned above. The aim of the present work is to examine the exchange coupling phenomenon in carboxylato-bridged copper(II) binuclear compounds by applying a recently developed computational strategy that, as shown in previous work,[26–33] is able to reproduce quantitatively the coupling constants for a great variety of compounds with different bridging ligands and/or paramagnetic centers.



syn–syn

1



syn–anti

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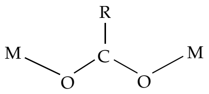

anti–anti

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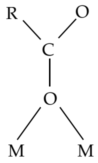


monoatomic

4

Abstract in Catalan: *En aquest treball es presenta un estudi computacional de l'acoblament magnètic en compostos dinuclears de coure(II) amb ponts carboxilat. S'han realitzat càlculs amb compostos model per estudiar la influència que tenen els factors següents sobre les constants d'acoblament: a) la capacitat atractora d'electrons dels lligands pont; b) la naturalesa química dels lligands terminals; c) el nombre de ponts carboxilat; d) algunes de les distorsions estructurals més freqüents en aquesta família de compostos; i e) el mode de coordinació dels lligands carboxilat pont. Les constants d'acoblament calculades per a les estructures completes determinades per difracció de raigs X d'alguns compostos representatius d'aquesta família estan en molt bon acord amb les dades experimentals, confirmant la fiabilitat de l'estratègia computacional emprada en aquest treball per predir la constant d'acoblament per a compostos dels quals no es disposa encara d'informació experimental.*

Computational Methodology

Since detailed descriptions of the computational strategy adopted in this work can be found elsewhere,[26–33] we will limit our discussion here to its most relevant aspects. The magnetic behavior of a dinuclear exchange-coupled compound is usually analyzed by using a phenomenological Heisenberg Hamiltonian [Eq. (1)]. In the case of copper(II) dimers, for which $S_A = S_B = 1/2$, the coupling constant J is directly related to the energy difference between the resulting triplet and singlet states by Equation (2).

$$E_S - E_T = J \tag{2}$$

Positive values of J indicate a triplet ground state (that is, ferromagnetic coupling), while for negative values the singlet state is lower in energy (antiferromagnetic coupling). The calculation of J by Equation (2) is made difficult by the fact that the singlet state cannot be expressed as a single determinant. To avoid this problem, Noodleman et al.[34–39] suggested the use of a broken symmetry (BS) wavefunction which is not a spin eigenstate, although it has $M_S = 0$. The energy of the BS solution can easily be related to the energies of the singlet and triplet states by Equation (3). Combination of Equation (3) with Equation (2) leads to Equation (4), which has been used by several authors within the framework of various quantum chemical methods to calculate exchange coupling constants.[37, 38, 40–76]

$$E_{BS} = \frac{1}{2}(E_S + E_T) \tag{3}$$

$$J = 2(E_{BS} - E_{BT}) \tag{4}$$

In recent work,[26–28, 30–33] however, we have found that, when density functional theory (DFT)-based wavefunctions are used, the coupling constant can be approximated simply by Equation (5).

$$J = E_{BS} - E_T \tag{5}$$

Experience has shown that this equation, in which the energy of the singlet state is estimated directly from the energy of the broken symmetry solution without performing any spin projection, leads to a good agreement with experimental data for a large variety of compounds with exchange-coupled electrons. The use of Equation (5) instead of Equation (4) has led to some controversy in the recent literature.[30, 77–80] For wavefunction-based methods, such as UHF, it is clear that the spin projection procedure that leads to Equation (4) is indeed the right way to tackle the problem. However, in density functional calculations the problem is somewhat different. In DFT, the wavefunction that is calculated in the Kohn–Sham method is only a tool for obtaining the ground-state electron density from which the energy is calculated. The use of spin projection techniques applied to the wavefunction constructed from the Kohn–Sham orbitals has been questioned recently in the literature. Wittbrodt and Schlegel[81] have discussed the influence of spin projection on potential energy surfaces, finding that its application certainly improves UHF and UMP2 results, whereas the best results from DFT methods are obtained with the energy values of the broken symmetry state without projection. In this context it is also interesting that Perdew et al.[82, 83] observe that the broken symmetry function describes the electron density and the on-top electron pair density with remarkable accuracy even if it gives an unrealistic spin density distribution. These authors conclude that the broken symmetry function is indeed the correct single-determinant solution for the Kohn–Sham equations for these systems. The adequacy of using broken symmetry solutions to estimate the energy of the singlet-state energy in organic biradicals has also been discussed recently by Gräfenstein et al.[84] Earlier papers give a more thorough discussion of this topic.[26–33]

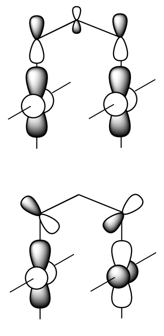
At a practical level, for the evaluation of the coupling constant of each compound, two separate calculations are carried out using DFT, one for the triplet state and another one for the low-spin, broken symmetry state. The hybrid B3LYP method,[85] as implemented in Gaussian 94, has been used in all calculations,[86] mixing the exact Hartree–Fock exchange with Becke's expression for the exchange[87] and using the correlation functional proposed by Lee et al.[88] The double-ζ quality basis set proposed by Schaefer et al.[89] has been adopted for all atoms except copper ones, which have been described using the triple-ζ basis set proposed by the same authors.[90]

Results and Discussion

Exchange coupling in copper(II) acetate: When the carboxylate ions bridge two copper atoms in *syn–syn* mode (**1**) the most usual case is that of four bridging ligands, giving compounds with an overall molecular symmetry close to D_{4h} as in the case of copper acetate described above (Figure 1). We will describe first the exchange coupling in this compound, to investigate afterwards the effect on this phenomenon of changes in either the bridge (R) or the axial ligand (L).

Our calculations using the experimental structure[91] of $[Cu_2(\mu\text{-}CH_3CO_2)_4(H_2O)_2]$ predict a moderate antiferromagnetic coupling for this compound, $J = -308\ cm^{-1}$, in excellent agreement with the experimental determinations available ($J = -296\ cm^{-1}$ obtained from magnetic susceptibility data and $J = -298\ cm^{-1}$ from inelastic neutron scattering on a deuterated sample).[3, 92, 93] It is extremely important to use a good crystal structure determination in order to reproduce the coupling constant properly, since deviations in the geometrical parameters can induce large changes in the calculated coupling constant. For instance, we have calculated the coupling constant of copper acetate using the geometry taken from an earlier structural determination.[8] Although the Cu···Cu distance from both structural determinations is practically the same, other geometrical parameters differ significantly from the usually accepted values (for example, the O-C-O angle varies from 107° to 125°). As a consequence of these structural changes the calculated coupling constant is strongly affected: its value ($-127\ cm^{-1}$) is in strong disagreement with the experimental one and significantly smaller than that found using the more accurate structural data.

The unpaired electron on each copper atom occupies an $x^2 - y^2$-like orbital oriented toward the four oxygen atoms of the acetato bridges. Although the relatively short Cu···Cu distance (2.62 Å) suggests a through-space interaction between the two unpaired electrons, it is now evident that the δ overlap between d orbitals is too small and superexchange has been found to be the dominating mechanism for coupling in this type of compound. The symmetric and antisymmetric combinations of the $x^2 - y^2$-like orbitals on both paramagnetic centers interact with the symmetry-adapted combinations of lone-pair acetate orbitals to give the two singly occupied molecular orbitals (SOMOs), with the symmetric combination above the antisymmetric one (**5**).



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Effect of the nature of the bridging ligand: Changing the nature of R, the group bonded to the carbon atom in the carboxylato bridge, in compounds with four bridges has a dramatic effect on the coupling constant. When the methyl group in acetate is replaced by CCl_3 the coupling constant is reduced from -296 to less than $-200\ cm^{-1}$.[14, 94, 95] A more spectacular change is obtained if $R = SiR'_3$, enhancing the antiferromagnetic coupling to a strong value ($J \approx -1000\ cm^{-1}$).[96] The experimental value for a given bridging ligand is not unique since the compounds that have been magnetically characterized with different axial ligands have slightly different structural data.[12, 14, 96] The experimental average values for the coupling constant with various carboxylato bridges (Table 1) seem to indicate that the effect of electron-withdrawing groups is to reduce the strength of exchange coupling, although the case of trifluoroacetato compounds, with a coupling constant very similar to that

Table 1. Calculated coupling constants [cm^{-1}] for [$L_2Cu_2(\mu\text{-}RCOO)_4$]. Experimental data indicated in the last row are average values for compounds with slightly different geometries and/or axial ligands.

	R = SiH_3	R = H	R = CH_3	R = CF_3	R = CCl_3
L = H_2O	− 806	− 417	− 299	− 254	− 158
L = NH_3	− 749	− 393	− 284	− 241	− 152
experimental	− 1000	− 550	− 300	− 300	− 200

found for acetato bridges and higher than that of trichloroacetate, may cast doubt on this simple explanation.

To avoid possible effects of small structural changes on the calculated coupling constant we have adopted the same $Cu_2(OCO)_4$ core in all our calculations (for geometrical details of this model structure, see Methods of Calculation). Agreement between calculated and experimental coupling constants for model compounds with H_2O and NH_3 as axial ligands (Table 1) is good, showing the same trends for J with respect to the electron-withdrawing power of the R groups. Since possible variations in J due to small changes in the structural parameters cannot be claimed for the computed coupling constants, the anomaly found for the trifluoroacetate ion can be unambiguously assigned to the nature of the bridging ligand.

The trends shown by the calculated coupling constants can be analyzed using the qualitative model developed by Hay, Thibeault, and Hoffmann (HTH)[97] to relate the magnetic properties of an exchange-coupled dinuclear complex to its electronic structure. For a system with two metal atoms each bearing one unpaired electron, the magnetic coupling constant according to this model is given by Equation (6), where ε_1 and ε_2 are the energies of the two SOMOs and K_{ab}, J_{aa}, and J_{ab} are two-electron integrals involving orthogonal localized molecular orbitals constructed from these SOMOs.

$$J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}} \qquad (6)$$

Combining this qualitative model with our calculated coupling constants, we analyze below the effect of various factors on the magnetic behavior of carboxylato-bridged dinuclear compounds. A plot of J versus the square of the orbital energy gap is shown in Figure 2a for different compounds with four carboxylato bridges (the coupling constants for the same compounds in Table 1 were calculated by using slightly different geometries; see the section on magnetostructural correlations below for details). The deviation of the correlation between J and $(\varepsilon_1 - \varepsilon_2)^2$ from the linear behavior predicted from Equation (6) could be expected from the fact that the two-electron terms, K_{ab} and $J_{aa} - J_{ab}$, for compounds with different bridging ligands are not expected to be equal. The overall trend seen in Figure 2a indicates nevertheless that the energy splitting of the two SOMOs is indeed the key factor in determining the magnitude of J in these compounds: antiferromagnetic coupling increases with the square of the energy gap, while changes in the two-electron terms introduce only small modifications for each type of bridge which are responsible for the departure from linearity found for the whole set of data.

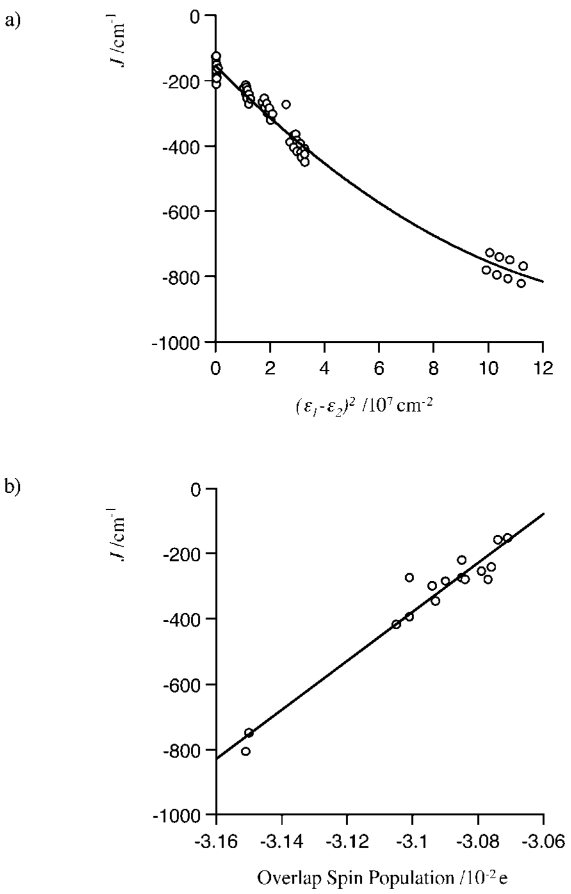


Figure 2. Exchange coupling constants calculated for [$L_2Cu_2(\mu\text{-}RCOO)_4$]: a) as a function of the squared energy gap between SOMOs; b) as a function of the Cu–O overlap spin population.

Previous studies suggest a correlation between J and the electronegativity of the atom directly bonded to the carbon atom of the carboxylato group.[12, 14, 98] If one considers an average value for acetato, trifluoroacetato, and trichloroacetato bridges, this correlation seems to indicate that the more electronegative this atom, the weaker is the coupling. According to this trend, compounds with haloformiato bridges should be those with the weakest coupling. To confirm this prediction we have evaluated the coupling constant for our model structure with R = F, Cl, and Br, each with NH_3 as axial ligands. The calculated J values (− 86, − 22, and − 37 cm^{-1}, respectively) confirm this general trend. A more detailed analysis shows, however, that the case of fluoroformiato bridges is again anomalous, with a stronger antiferromagnetic coupling than for the other two cases. Moreover, spin coupling is more complicated in these three cases: the participation of metal atoms in the SOMOs is much greater than in compounds with less electronegative atoms directly bonded to the carbon atom in the bridge. This situation implies an inversion in their relative energies and a greater participation of direct exchange in the coupling mechanism that make comparison with other cases difficult. Our results show that the correlation between the magnetic behavior and the electronegativity of the atom bridged to the carbon atom is in general valid, but caution is needed when very electronegative atoms are taken into consideration.

The effect of the electronegativity of atoms that are not directly bonded to the carbon atom of the bridge (for example, acetate, fluoroacetate, and chloroacetate bridges) is more difficult to analyze, but the same trend is found, with the fluoroacetato compound having an anomalously strong coupling. To test further the influence of the electron-withdrawing power of the R group on the coupling constant we have also studied the series of model compounds with R = CH_3, CH_2Cl, $CHCl_2$, and CCl_3, each with NH_3 as axial ligands. As expected, an increase in the number of chlorine atoms in R leads to a decrease in the coupling constant. The calculated J values (-284, -273, -220, and $-152\,cm^{-1}$, respectively) decrease almost linearly with the number of chlorine atoms in the bridge. These results are in good agreement with the experimental trends, which show that replacement of hydrogen by halogen atoms in the acetato bridge decreases the antiferromagnetic coupling.[13, 14, 99]

A replacement of R induces changes in the electron distribution of the bridging atoms that might be expected to affect the superexchange mechanism. The most evident change that could be related to the variation of the coupling constant is the covalency of the eight Cu–O bonds that hold the molecular framework together. A search for a possible dependence of the the coupling constant on the Cu–O overlap population, however, is unsuccessful because this parameter is influenced by all the electrons involved in the Cu–O bonds, not just by the unpaired electrons involved in the exchange coupling. If one restricts the analysis to these two electrons, the corresponding overlap spin population shows an excellent correlation with the calculated J values (Figure 2b): the more negative the overlap spin population (a negative sign indicates the Cu–O antibonding character of the SOMOs) the more negative (antiferromagnetic) is the coupling constant. The trend found for this magnitude is in agreement with that found for the energy gap between the SOMOs (Figure 2a): more negative spin overlap populations indicate a stronger (antibonding) interaction between the metal and the ligand orbitals which results in a larger energy gap between SOMOs and in a greater superexchange coupling.

Effect of the nature of the axial ligand: A change in the axial ligands induces smaller variations in the coupling constant. Replacement of H_2O by NH_3 reduces the strength of the antiferromagnetic coupling by about 5% (Table 1). Different trends have been established for replacement of terminal ligands, not directly involved in the superexchange pathway, in other compounds. For oxalato-bridged compounds,[27] an increase in the electronegativity of the donor atoms in the equatorial terminal ligands results in stronger antiferromagnetic coupling. The effect is inverted, however, when the substitution takes place at the axial position. In hydroxo-bridged compounds,[31] the strength of the antiferromagnetic coupling shows the same trend as the basicity of the ligand, whereas this trend is reversed for oximato-bridged compounds.[33] In each case a detailed analysis of the SOMOs is needed to explain the observed shifts in the coupling constant and no general rules can be established.

The variation of J observed in the carboxylato-bridged compounds when the axial ligands are replaced is specially interesting since it cannot be rationalized by using qualitative models like that proposed by Hay et al.[97] One of the key approximations of this model is to consider only the effect of the unpaired electrons, neglecting all possible influences on the exchange phenomena from the rest of the electrons in the molecule (active electron approximation). Within this approximation, all changes in the coupling mechanism introduced by modifications of the molecular framework can be interpreted in terms of changes in the SOMOs. In the case of carboxylato-bridged compounds, however, participation of the orbitals of the axial ligands in the SOMOs is forbidden by symmetry because of their δ character. Hence, the observed change, even if small, should be attributed to indirect effects associated with interactions of the unpaired electrons with lower lying electrons.

Effect of the number of bridging ligands: Exchange coupling between two paramagnetic centers that are not directly bonded is frequently rationalized by adding the contributions of the different superexchange pathways mediated by the bridging ligands.[3] Since dimers with four, three, two, and one carboxylato bridges have been structurally and magnetically characterized,[15, 100–107] this family of compounds offers an excellent opportunity to confirm the validity of such an approach. For this purpose we have built model compounds with three, two, or one bridges by progressively replacing carboxylato bridges by water molecules, retaining in this way the same coordination sphere for the two copper atoms in all four models. The Cu···Cu distance taken for these models is the average distance found in compounds with four, three, two, or one bridges (2.82 Å) and is somewhat greater than that used for complexes with four bridges studied in the previous section (2.62 Å). The variation of J with the Cu···Cu distance will be analyzed in the next section.

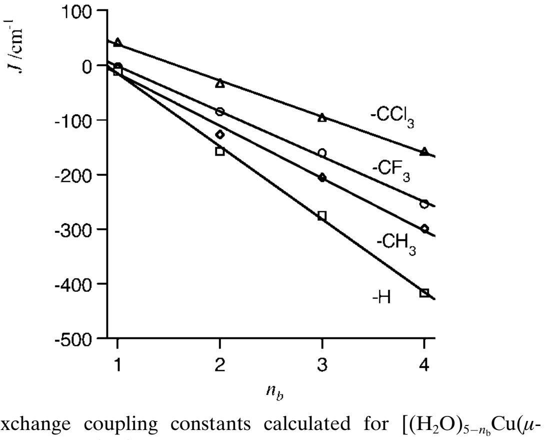


Figure 3. Exchange coupling constants calculated for $[(H_2O)_{5-n_b}Cu(\mu\text{-}RCOO)_{n_b}Cu(H_2O)_{5-n_b}]^{(4-n_b)+}$ as a function of the number of bridging carboxylato ligands, n_b.

Figure 3 shows the variation of the coupling constant with the number (n_b) of carboxylato bridges (R = H, CH_3, CF_3, CCl_3) having water as axial ligand. For all four cases a linear behavior is observed [Eq. (7)]. J^F can be regarded as a

$$J = J^F + n_b J^{AF} \tag{7}$$

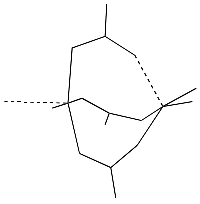
ferromagnetic contribution to the coupling constant that does not depend on the number of bridges, and J^{AF} as an antiferromagnetic contribution per bridge (Table 2).

Table 2. J^F and J^{AF} values [cm^{-1}] obtained for $[L(H_2O)_{(4\text{-}n_b)}Cu(\mu\text{-}RCOO)_{n_b}Cu(H_2O)_{(4-n_b)}L]^{(4-n_b)+}$ with $n_b = 1-4$ by least squares fitting of the calculated coupling constants to Equation (7).

R	L = H_2O J^{AF}	J^F	L = NH_3 J^{AF}	J^F
H	– 139	127	– 138	151
CH_3	– 102	91	– 98	94
CF_3	– 88	90	– 94	124
CCl_3	– 72	115	– 66	101

The linear dependence of J on the number of carboxylato bridges can be rationalized within the qualitative HTH model [Eq. (6)], according to which the ferromagnetic contribution to J corresponds with the exchange term $2K_{ab}$. Since the local coordination environment of the copper atoms is not changed when carboxylato bridges are substituted by water molecules, one does not expect great changes in K_{ab} with the number of bridges, even for the hypothetical case in which all four bridges have been removed. The ferromagnetic contribution, J^F, found from the linear least-squares fits presented in Figure 3, can thus be associated with the $2K_{ab}$ term. Within the HTH model, the dominating antiferromagnetic contribution to J is given by the ratio of the squared energy gap between the two SOMOs and the difference between the two-electron integrals. Taking these two parameters from our calculations on the triplet state, $(\varepsilon_1 - \varepsilon_2)^2$ is found to change as the square of the number of bridges, $n_b{}^2$, while $(J_{aa} - J_{ab})$ is found to decrease approximately linearly with n_b. The expected overall trend for J is therefore the linear increase with n_b found in Figure 3, with J^{AF} representing the effective antiferromagnetic contribution to J for each type of bridge.

An interesting compound with three benzoato bridges and a relatively weak coupling ($J = -81.4$ cm^{-1}) has been reported recently by Geetha and Chakravarty.[107] As these authors noted, one of the benzoato ligands should be "magnetically inactive" since one of its oxygen atoms is coordinated to the axial position of one of the copper atoms (**6**). To test the validity of this hypothesis we have computed the coupling constant for a model structure of this compound in which the bulky benzoato groups have been replaced by acetato ligands. The calculated value (-111 cm^{-1}) is in good agreement with the experimental value, and much closer to that found for compounds with two acetato bridges than for other structures with three bridges.



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The additive contribution to J for each bridge found in Figure 3 should also be valid for hypothetical compounds with mixed bridges. The coupling constant for a compound with a total of n_b bridges would then be given by Equation (8), where

$$J = \sum_i \left(\frac{n_i}{n_b} J^F{}_i + n_i J^{AF}{}_i \right) \tag{8}$$

n_i is the number of bridges of type i. To check the validity of this relation we have calculated the coupling constants for various model compounds with mixed bridges and water as axial ligand. The results (Table 3) are in good agreement with the estimated coupling constants obtained by applying Equation (8). These findings indicate that the contribution to the overall coupling constant of each bridging carboxylato group is practically independent of the rest of the bridges in the complex.

Table 3. Calculated and estimated coupling constants [cm^{-1}] for model compounds $[(H_2O)_{5-m-n}Cu(\mu\text{-}HCOO)_m(\mu\text{-}CCl_3COO)_nCu(H_2O)_{5-m-n}]^{(4-m-n)+}$. The estimated values have been obtained by applying Equation (8) using the J^{AF} and J^F values collected in Table 2.

n_b	m	n	J_{calcd}	J from Equation (8)
4	3	1	– 365	– 365
	2	2	– 300 (*cis*), – 293 (*trans*)	– 301
	1	3	– 235	– 237
3	2	1	– 204	– 227
	1	2	– 129	– 164
2	1	1	– 98	– 90

Magnetostructural correlations: Experimental structures for carboxylato-bridged dinuclear copper(II) compounds often deviate from the idealized geometry adopted in our model compounds. In this section we will analyze the effect of the most common distortions on the coupling constant.

In complexes with four bridges, there is a varying degree of out-of-plane displacement of the copper atoms from the basal plane of the square pyramid. To analyze the effect of this parameter on the coupling constant we have changed the distance between the two copper atoms while maintaining all other structural parameters (Cu–O and Cu–L distances and the geometries of the axial and bridging ligands) fixed. The absolute value of the coupling constant (Table 4) increases as the copper atoms are separated, regardless of the axial and bridging ligands. The calculated variation of J with the Cu $\cdots$ Cu distance is practically linear, as can be seen for the case with acetato bridges (Figure 4a). The energy of the antiferromagnetic ground state in the four-bridged case (Figure 4b) varies little around $d_{Cu-Cu} = 2.8$ Å, and only about 5 kcal mol^{-1}

Table 4. Calculated coupling constants [cm^{-1}] for model compounds $[L_2Cu_2(\mu\text{-}RCOO)_4]$ as a function of the Cu $\cdots$ Cu distance.

d_{Cu-Cu} [Å]	R = SiH_3 H_2O	NH_3	R = H H_2O	NH_3	R = CH_3 H_2O	NH_3	R = CF_3 H_2O	NH_3	R = CCl_3 H_2O	NH_3
2.22	– 780	– 727	– 388	– 369	– 265	– 254	– 222	– 214	– 127	– 125
2.42	– 795	– 740	– 404	– 383	– 283	– 270	– 240	– 229	– 142	– 139
2.62	– 806	– 749	– 417	– 393	– 299	– 284	– 254	– 241	– 158	– 152
2.82	– 821	– 768	– 435	– 408	– 321	– 302	– 272	– 256	– 178	– 169

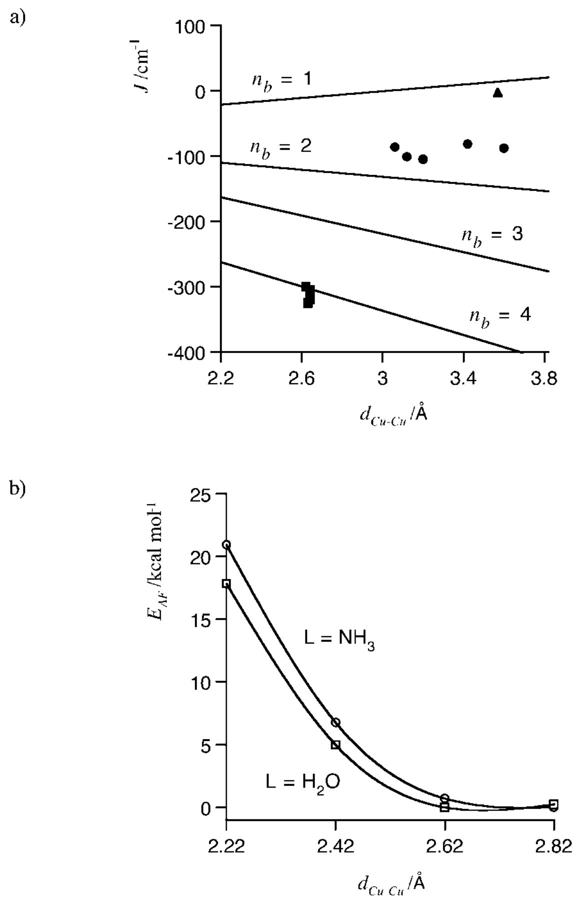


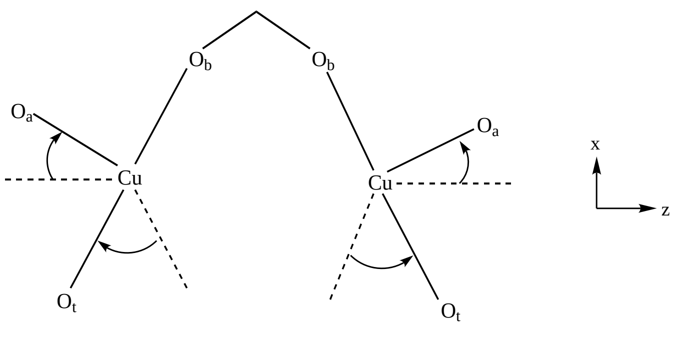
Figure 4. a) Exchange coupling constant calculated for $[(H_2O)_{2(5-n_b)}Cu_2(\mu\text{-}CH_3COO)_{n_b}]^{(4-n_b)+}$, varying n_b from 1 to 4, as a function of the distance between the two copper atoms, d_{Cu-Cu}. Experimentally determined data are indicated by squares ($n_b = 4$), circles ($n_b = 2$), and triangles ($n_b = 1$). b) Relative energy of the antiferromagnetic ground state calculated for $[(H_2O)_2Cu_2(\mu\text{-}CH_3COO)_4]$ as a function of the distance between the two copper atoms, d_{Cu-Cu}.

are necessary to shorten the distance between the metal atoms to 2.5 Å, in agreement with the experimental variability found for this structural parameter, with distances ranging from 2.6 to 2.8 Å. Similar trends are found for compounds with the other bridging ligands considered in this work.

It is interesting that the enhancement of the antiferromagnetic coupling found upon increasing the Cu ⋯ Cu distance can only be explained in terms of a superexchange mechanism. If direct through-space interaction between the two unpaired electrons were at the origin of the magnetic behavior in these compounds, one would expect a decrease in the strength of the coupling as the atoms bearing the unpaired spins are separated.

The same behavior, although less pronounced, is found for complexes with three or two bridges (Figure 4a). Removal of bridging ligands results in a loss of structural rigidity that is expressed in the longer average Cu ⋯ Cu distances found in compounds with fewer than four bridges. This finding is confirmed by the small energies (less than 3 kcal mol^{-1}) required for stretching the Cu ⋯ Cu distance from its equilibrium value (around 2.8 Å) to 3 Å. The behavior of compounds with a single carboxylato bridge is different, however: the coupling constant of −5 cm^{-1} found for the acetato-bridged structure with d_{Cu-Cu} = 2.82 Å vanishes at distances over 3 Å (see Figure 4a). In this case the direct interaction predominates over the superexchange mechanism, as can be deduced from the inverted order of the two SOMOs found for compounds with a single carboxylato bridge, with the Cu ⋯ Cu bonding combination found below the antibonding one.

In compounds with two carboxylato bridges the basal planes of the square pyramids around the copper atoms are often not parallel as assumed in the models used so far.[15, 102, 104] To consider the effect of this structural feature on the coupling constant we have displaced the four water molecules that replace two carboxylato bridges (**7**) by increasing the O$_b$-Cu-O$_t$ angle to 180° and moving the axial ligand in such a way that the oxygen atoms form O$_a$-Cu-O$_b$ and O$_a$-Cu-O$_t$ angles of 90° with the four oxygen atoms in the basal plane of the pyramid. The Cu ⋯ Cu distance considered in this case is 3.08 Å, the average found experimentally for compounds with this distortion. When increasing the O$_b$-Cu-O$_t$ angle from 155° to 180° the coupling constant for the compound with two acetato bridges decreases from −134 to −179 cm^{-1}. The geometry with an O$_b$-Cu-O$_t$ angle of 180° is considerably lower in energy (by 33 kcal mol^{-1}), in good agreement with the structural data found for experimental structures which normally present this type of geometry.



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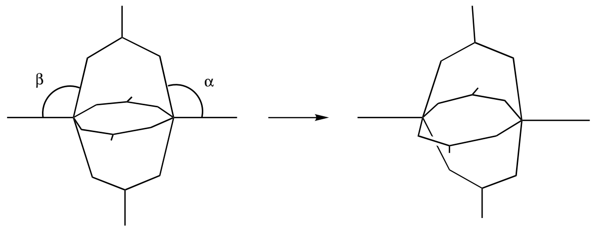
In compounds with two carboxylato bridges, the two terminal coordination positions in the basal plane are in most cases occupied by nitrogen, and not by oxygen atoms as considered in our model.[15, 102, 104] Replacement of the four water molecules by ammonia decreases the strength of the antiferromagnetic coupling. For acetato-bridged compounds the coupling constant is reduced by 20 cm^{-1}, from −179 to −159 cm^{-1}. The effect is somewhat greater for carboxylato bridges with stronger antiferromagnetic coupling: the coupling constant is reduced from −213 to −183 cm^{-1} in the model structure with two formiato bridges.

A distortion from the ideal structure that is often found in complexes with four trichloroacetato bridges is one that changes the coordination environment of the copper atoms from square-pyramidal to trigonal-bipyramidal (**8**).[13, 94, 95, 108, 109] To study the effect of this distortion on the coupling constant we have considered a model structure with ammonia molecules in the axial position and a Cu ⋯ Cu distance of 3.22 Å, the average value found for compounds with this distorted geometry. The only parameters that have



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been changed from the ideal to the distorted structure are the two N-Cu-O angles (α and β in **8**), while all other structural parameters, including the Cu···Cu distance, are kept fixed. This distortion can be expressed as a function of a unique angular parameter,[110] defined for pentacoordinated structures as $\tau = |\gamma - \delta|/60°$, where γ and δ are the two largest L-M-L angles. This parameter varies continuously, indicating the degree of distortion between a square pyramid ($\tau = 0$) and a trigonal bipyramid ($\tau = 1$). The effect of this distortion on J has been analyzed for the trichloroacetato and the formiato bridges: it results in a decrease in the antiferromagnetic coupling (Figure 5). The most stable structure is found for a distorted structure with $\alpha = 97.3°$ and $\beta = 112.3°$ ($\tau = 0.5$), although the starting geometry, with a square pyramid in which $\alpha = \beta = 104.7°$ ($\tau = 0$) is only about 3 kcal mol^{-1} higher in energy, indicating a high flexibility of the structure with four carboxylato bridges toward this mode of distortion.

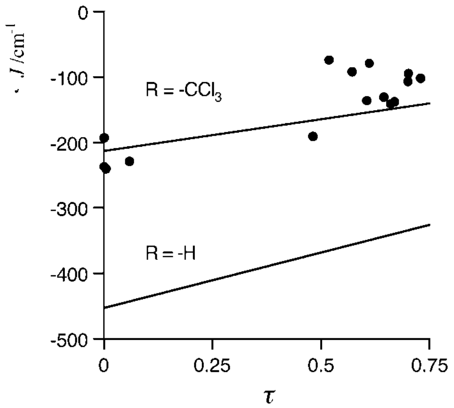
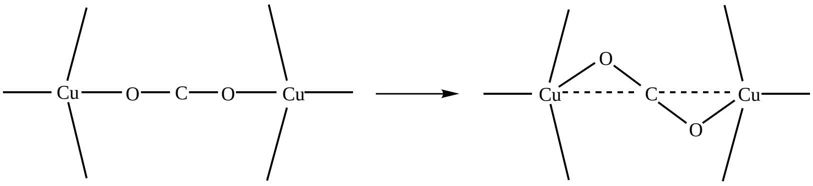


Figure 5. Exchange coupling constant for $[(NH_3)_2Cu_2(\mu\text{-}RCOO)_4]$ as a function of the parameter τ ($\tau = 0$ corresponds to a square pyramid, and $\tau = 1$ to a trigonal bipyramid). Solid circles correspond to experimentally determined data for compounds with trichloroacetato bridges.

The last structural distortion that we have analyzed is the variation of the Cu-O-O-Cu dihedral angle found in complexes with a single carboxylato bridge (**9**). The effect of increasing this dihedral angle from 0° in the ideal structure to 10° is a reduction in the antiferromagnetic coupling. For the model with a single acetato bridge the coupling constant changes from -5.0 to -1.7 cm^{-1} when the Cu···Cu distance is 2.82 Å. If the Cu···Cu distance is somewhat longer (3.02 Å), the coupling becomes weakly ferromagnetic, with J changing from 0.0 to $+1.4$ cm^{-1} when the dihedral angle increases from 0° to 10°. Our calculations indicate that this structural distortion is not energetically very demanding (about 3 kcal mol^{-1}), in good agreement with the experimental distorted structures.[111]

Effect of the coordination mode of bridging carboxylato ligands on the exchange coupling: Although in a great majority of binuclear copper(II) complexes with carboxylato bridges the bridging groups are coordinated in a *syn–syn* fashion (**1**), some compounds with other possible bridging modes have been described and their magnetic properties measured.[16–18, 20, 111–116] In this section we will compare the exchange coupling between two copper(II) ions mediated by a single formiato bridge in *syn–syn*, *syn–anti* (**2**), and *anti–anti* (**3**) coordination modes. To compare the coupling constants for these bridging geometries we have studied model structures in which the geometry of the formiato bridge and the coordination geometry around the copper atoms are preserved. In all three cases, the Cu–O distance and the Cu-O-C angle have been fixed at 1.98 Å and 126.15°, respectively. The resulting Cu···Cu distances in these model structures are 2.82, 5.15, and 5.77 Å for the *syn–syn*, *syn–anti*, and *anti–anti* compounds, respectively. In these models water has been used as the axial ligand. The calculated coupling constants range from weakly ferromagnetic ($+10.2$ cm^{-1}) in the *syn–anti* case to moderately antiferromagnetic (-61.3 cm^{-1}) in the *anti–anti* case, in good agreement with the available experimental data: the only known compound with *syn–anti* coordination presents a coupling constant of $+14$ cm^{-1}, whereas those with an *anti–anti* coordination mode have an average coupling constant of -50 cm^{-1}.[111] The model with a *syn–syn* coordination at the bridge shows an intermediate behavior, that is, a weak antiferromagnetic coupling with a coupling constant of -11.3 cm^{-1}.

The different magnetic behaviors found for the three bridge geometries can easily be rationalized by using the HTH model. If the coupling constant is given by Equation (6), in a compound with *syn–anti* coordination the second term will probably be much smaller than in the other two cases, because of the poor overlap between the orbitals on the bridge with those bearing the unpaired electrons on each copper ion (**10**). In this situation we would expect the first term, $2K_{ab}$, to dominate, giving an overall positive value for the coupling constant. In the opposite case, when we consider an *anti–anti* coordination mode for the bridging ligand, the first term is expected to be much smaller than in the other cases. This behavior can be understood by taking into account the physical nature of this term: since K_{ab} is



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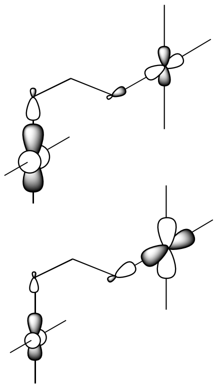

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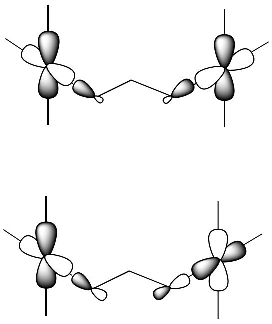
an exchange integral relating two molecular orbitals each localized on one of the copper atoms, its value is expected to decrease with an increase in the Cu⋯Cu distance. For a similar energy separation between the two SOMOs, the compound with an *anti–anti* coordination mode (**11**) should present, according to this reasoning, a stronger antiferromagnetic coupling than the compound with a *syn–syn* bridge (**5**).



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Calculation of exchange coupling constants for complete structures: The accuracy of the computational model employed in this work has been demonstrated previously by calculating the coupling constant for complete structures of dinuclear transition metal compounds with different bridging ligands and/or different transition metals.[26–33] The use of these unmodeled systems allows a straightforward comparison of the calculated coupling constants with the available experimental data and can be used to assess the accuracy of the predictions obtained with the simplified models applied above to the analysis of magnetostructural correlations. To increase further the number of complete structures for which the coupling constant has been evaluated, we have included here the calculation of J for copper acetate, to represent compounds with four bridges, and for two other compounds with two and one carboxylato bridges, respectively. The results obtained for the unmodeled structure of copper acetate have already been discussed above and will be only briefly mentioned here: the calculated value for J in this case ($-308\,\mathrm{cm^{-1}}$) is in excellent agreement with the experimental one ($-296\,\mathrm{cm^{-1}}$).

As far as the complexes with two bridges are concerned we have calculated the coupling constant for $[Cu_2(\mu\text{-}CH_3COO)_2(phen)_2(H_2O)_2](NO_3)_2\cdot 4H_2O$ (Figure 6). In this compound, the two aromatic ligands are facing each other, with important $\pi-\pi$ stacking interactions stabilizing the whole structure. The solvation water molecules not directly bonded to the copper atoms have not been included in the calculation since they are not expected to influence significantly the exchange coupling, as they are so far from the bridging region. The calculated coupling constant for this compound ($-89\,\mathrm{cm^{-1}}$) is in excellent agreement with the experimental value[104] ($-86\,\mathrm{cm^{-1}}$), confirming the great accuracy of our computational procedure, even for compounds with a considerable number of atoms.

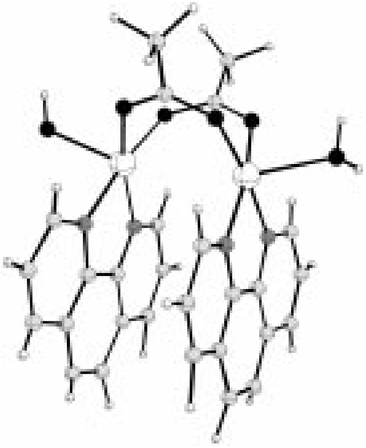

Figure 6. Crystal structure of $[Cu_2(\mu\text{-}CH_3COO)_2(phen)_2(H_2O)_2](NO_3)_2\cdot 4H_2O$ (phen = 1,10-phenanthroline). Structural parameters were taken from reference [104]. NO_3^- ions have been omitted for clarity.

The second complete structure that has been studied, $[(^{Me}TACN)_2Cu_2Cl_2(\mu\text{-benzoato})](ClO_4)$, where $^{Me}TACN$ = 1,4,7-trimethyl-1,4,7-triazacyclononane, (Figure 7) is a typical

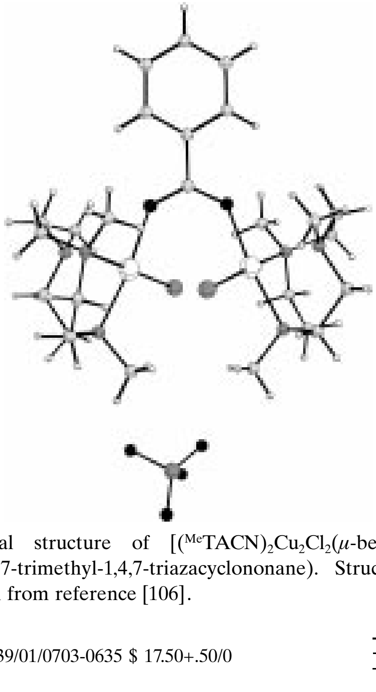

Figure 7. Crystal structure of $[(^{Me}TACN)_2Cu_2Cl_2(\mu\text{-benzoato})](ClO_4)$ ($^{Me}TACN$ = 1,4,7-trimethyl-1,4,7-triazacyclononane). Structural parameters were taken from reference [106].

representative of compounds with a single carboxylato bridge. For this structure, we have included the perchlorato counterion in our calculation. The benzoato bridge in this compound is slightly distorted with respect to its ideal geometry, presenting a dihedral Cu-O-O-Cu angle of 2.4°. Another important feature of this compound that makes it different from the models considered above is that in this case the chlorine atoms directly coordinated to the copper ions are occupying positions not far from bridging between the two metal centers (which would have a [5+1] distorted octahedral coordination sphere) and could provide an additional superexchange pathway for spin coupling.[106] The calculated coupling constant for this compound ($-3.5\,\text{cm}^{-1}$) is again in excellent agreement with the experimental data ($J = -2.4\,\text{cm}^{-1}$) in both its magnitude and sign.

Conclusion

We have applied a recently developed computational strategy to investigate exchange interactions in carboxylato-bridged copper(II) dinuclear complexes. The influence on the coupling constant of several factors related to the nature of the bridging and axial ligands has been analyzed using various model structures. Our results indicate that for almost all carboxylato-bridged compounds a moderate to strong antiferromagnetic coupling is expected. An exception to this general rule occurs in compounds with a single carboxylato bridge, where weak ferromagnetic coupling can be found, especially in complexes bridged in *syn–anti* mode. The accuracy of the method used in this work, together with its moderate demand for computer time, has allowed us to investigate separately the effect on the coupling constant of the nature of the axial and bridging ligands as well as that of the most usual structural distortions for this family of compounds. Especially interesting is the additive character found for the contribution to the coupling constant from each bridging group, which allows, in principle, the design of new molecules with a desired value of J by combining different bridges in a single compound.

Computational Details

Calculations for model compounds $[Cu_2(\mu\text{-}RCOO)_4L_2]$ were carried out using the following bond lengths [Å] and angles [°]: for the common molecular framework: Cu–O 1.98, C–O 1.25, Cu–L 2.15; Cu-O-C 123.3, O-C-O 125.0; for the axial ligands: C–H 1.08 (R = H), C–F 1.37 (R = F), C–Cl 1.75 (R = Cl), C–Br 1.88 (R = Br), C–C 1.52, C–H 1.06; H-C-C 109.0 (R = CH_3, $CClH_2$, CCl_2H); C–Cl 1.73, Cl-C-C 109.0 (R = CCl_3, CCl_2H, $CClH_2$); C–F 1.34, F-C-C = 109.0 (R = CF_3); C–Si 1.92, Si–H 1.45, H-Si-C 109.0 (R = SiH_3); O–H 0.96, H-O-H 104.5; N–H 1.02, H-N-H 109.0.

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