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Addressing Through-H Magnetic Interactions: A Comprehensive *ab Initio* Analysis of This Efficient Coupler

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Abstract: The exchange coupling in a structurally characterized Cu^{II}_2 complex is analyzed to highlight the role of H bonds in the generation of efficient magnetic interactions. The interest for complementary insights which are not accessible through DFT calculations (Desplanches, C. et al. *J. Am. Chem. Soc.* **2002**, 124, 5197) has driven this state-of-the-art *ab initio* inspection. The wave function expansion based upon localized orbitals allows us to selectively turn on specific mechanisms and quantitatively evaluate their roles in the exchange interactions. Our singlet–triplet splitting calculations demonstrate the enhancement of the magnetic coupling through a concerted oxygen-to-metal charge transfer and electronic redistribution within the OH bond of the $\text{OH}\cdots\text{O}$ magnetic linker. This mechanism accounts for $\sim 35\%$ of the total experimentally measured singlet–triplet energy difference. This analysis strongly suggests that H bonds might be particularly useful not only in the establishment of intermolecular contacts but also within the basic units of magnetic materials.

Introduction

The importance of hydrogen bonds¹ in biology, physics, and chemistry has been much debated since these weak bonds might be at the origin of fundamental phenomena such as DNA structuration, biochemical reactions, and spin transition. While the former phenomena have been evidenced and much studied for several decades, it is more recently that magnetic systems involving H bonds have been the subject of intense research due to the tremendously promising spin-crossover behavior.² The possibility to generate bistability using various nuclearities building blocks interacting through weak bonds contacts has been suggested as an original synthetic route.³ Cooperativity is known to be of particular importance, and

its origin might be found in π -stacking or H-bond networks formation. The quantification of such weak bonds using quantum chemical calculations has thus become a challenging issue.

Traditionally, the analysis of magnetically coupled systems relies on the Heisenberg Hamiltonian H assuming that the spatial parts of the spin-states wave functions are very similar. Thus, one introduces a so-called exchange coupling constant J which is expected to depict the low-energy spectroscopy writing $H = -JS_1S_2$. For a dinuclear species with one unpaired electron on each metal ion, the resulting singlet–triplet energy separation $E_{\text{T}} - E_{\text{S}}$ simply reads J . The corresponding value extracted from magnetic susceptibility measurements can be compared to quantum chemical calculations.

Even though density functional theory (DFT) based methods have often reached good agreement in the determination of such constants,⁴ they may not give access to

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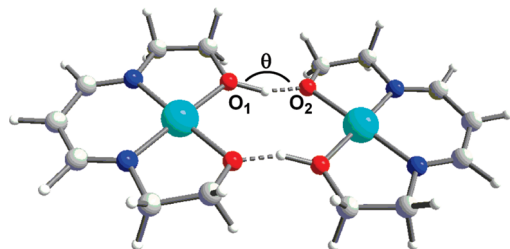


Figure 1. Cu₂ centrosymmetric model complex **1**. The experimental O₁H...O₂ angle θ is 159°.

the underlying mechanisms which govern the spin-states ordering. Besides, it is known that the evaluation of weak interactions relies on explicitly correlated ab initio calculations which are flexible enough to account, for instance, for the dynamical charge fluctuations (i.e., dipole–dipole interactions). Nevertheless, their accurate evaluation remains a challenging issue of constant interest since the system sizes preclude the use of such quantum theory methods. This kind of wave-function-based calculation has proved to reach spectroscopic accuracy for magnetically coupled extended materials.⁵

We report herein a detailed investigation of the exchange interactions in the Cu₂ model complex **1** (see Figure 1), extracted from the reported [Cu(DiimH)]₂,⁶ where four methyl groups were replaced by H atoms. The theoretical strategy we suggest allows us to (i) perform ab initio wave function calculations (i.e., configurations interaction, CI) on these rather extended architectures and (ii) quantify the contributions arising from the hydrogen-bond backbone. One may wonder how much the O₁H...O₂ (see Figure 1) structural and electronic characteristics influence the nature and amplitude of the magnetic interactions between the two paramagnetic centers. Part of the answer is to be found in quantum chemistry calculations in which specific mechanisms can be turned on at will. In that sense, this work complements the quantitative evaluations which are accessible by means of DFT-based approaches. In fact, the reading of the multideterminantal wave functions based upon localized orbitals (i.e., valence-bond-like picture) offers a step-by-step analysis of the relevant mechanisms accounting for the spin-states hierarchization. By selecting the valence orbitals, one can grasp their role in the establishment of efficient magnetic channels. Particular attention is paid to the O₁H...O₂ bridge geometry and the valence orbitals involved in the exchange mechanism. A detailed analysis of the correlated wave function suggests that the charge fluctuation within the OH bond facilitates the ligand-to-metal charge transfer (LMCT). This superexchange-like mechanism is very sensitive to the O₁H...O₂ angle θ since colinearity along the H bond greatly enhances (~20%) the antiferromagnetic behavior.

Computational Details

The coupling between the magnetic moments localized on the Cu^{II} metal ions was investigated using wave-function-based calculations. This framework is particularly appealing in the microscopic analysis of the exchange interactions. With

this goal in mind, the difference dedicated configurations interaction (DDCI) method⁷ has been designed and successfully applied⁸ to evaluate vertical energy differences. First, complete active space self-consistent field (CASSCF) calculations were performed to generate a reference space including the leading electronic configurations in the desired spin multiplicities, singlet ($S = 0$, S) and triplet ($S = 1$, T). The minimal active space includes two electrons localized upon the two mainly d-type molecular orbitals (CAS[2,2]). In order to grasp the importance of the hydrogen bonds in the exchange coupling, this minimal active space was enlarged to include the O₁H...O₂ bridge molecular orbitals (MOs) in the reference wave function. Thus, a CAS[10,8] (10 electrons in 8 MOs) was considered to account for the contributions arising from the oxygen atoms lone pairs (n_{O_2}) and bonding and antibonding O₁H groups MOs (σ_{O_1H} and $\sigma^*_{O_1H}$). This particular CAS is flexible enough to incorporate all the contributions arising from the charge fluctuations within the O₁H...O₂ bridges. All CASSCF calculations were performed using the Molcas 6.0 package⁹ and available ANO-RCC-type functions. The Cu atoms were described with a (21s15p10d6f4g2h)/[5s4p3d] contraction.¹⁰ Particular attention was paid to the bridge parts and first nearest neighbors of the metal ions. Thus, a (14s9p4d3f2g)/[3s2p1d] contraction was used for the N and C atoms, whereas the O atoms were described by a (14s9p4d3f2g)/[3s3p1d] contraction.¹¹ A (8s4p3d1f)/[2s1p] contraction was used for the H atoms involved in the hydrogen bonds.¹² The other H atoms were depicted with a smaller basis set (8s4p3d1f)/[2s]. In a valence-bond (VB) type framework, orthogonal localized orbitals (LOs) were finally constructed using the canonical CASSCF orbitals. These LOs allow for a chemically intuitive analysis of the relevant mechanisms accompanying the singlet–triplet hierarchization.

The dynamical polarization and correlation effects were then incorporated using the DDCI method as implemented in the CASDI code.¹³ A detailed analysis of the underlying mechanisms was given in the pioneer work of de Loth et al.¹⁴ It has been clearly demonstrated that a bare valence-only description (i.e., CASCI energy difference) is not reliable to accurately grasp energy differences as small as a few tens of wavenumbers.¹⁵ Thus, one should include selected configurations reached by excitations on top of the CASSCF wave function. As the number of degrees of freedom (i.e., holes in doubly occupied (inactive) MOs or particles generated in empty (virtual) MOs) grows, the successive CAS+S (also referred to as DDCI-1), CAS+DDCI-2, and CAS+DDCI-3 levels are reached by expanding the CI space. Since the DDCI philosophy relies on the simultaneous characterization of different states which share similar spatial descriptions, a common set of MOs must be initially determined to build up the CI space. The CASSCF triplet LOs were used. Nevertheless, we checked that these J values are almost unaffected by the use of the singlet state LOs, whatever the level of calculations.

Following the minimal active space CAS[2,2] inspection, we were able to reach a DDCI-3 level of calculations. This is to be contrasted with the use of the enlarged CAS[10,8] which disposes any calculation beyond CAS+S. Neverthe-

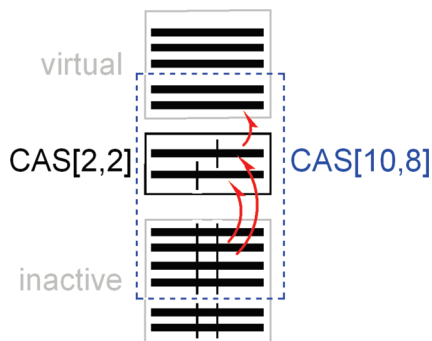


Figure 2. Most important CAS[2,2]+DDCI-3 mechanisms included within the CAS[10,8] strategy.

less, it has been shown that inclusion of the bridge MOs allows one to reach spectroscopic accuracy at a CAS+S level.¹⁶ Indeed, this enlarged CAS[10,8] incorporates all the electronic configurations which are likely to qualitatively discriminate the singlet from the triplet states. In particular, it contains all the leading CAS[2,2]+DDCI-3 mechanisms, i.e., the ones which involve the bridges MOs (see Figure 2). At a CAS[10,8]+S level, the important instantaneous charge relocation upon the external part of the ligands are taken into account.¹⁴ Besides, some particular mechanisms involving the charge redistributions within the O₁H bonds are explicitly turned on ($\sigma_{\text{O}_1\text{H}}^2 \sigma_{\text{O}_1\text{H}}^{*0} \rightarrow \sigma_{\text{O}_1\text{H}}^0 \sigma_{\text{O}_1\text{H}}^{*2}$ double excitation process), and their coupling to LMCT can be evaluated. This concerted scenario, which allows for the electron transfer from one Cu^{II} center to the other, is absent in the CAS[2,2]-based DDCI-3 calculations.

Complementary DFT calculations were performed to clarify the preference for linearity in the O₁H...O₂ fragment. We used the B3LYP exchange-correlation functional with triple- ζ basis sets as implemented in the Gaussian03 code.¹⁷ Starting from the triplet DFT MOs, the broken-symmetry (BS) state¹⁸ was converged to extract the exchange coupling constant $J = E_{\text{BS}} - E_{\text{T}}$. Even though the J extraction based upon unrestricted DFT calculations is still controversial,^{4a,19} we used the same strategy as suggested in ref 20.

Results and Discussion

On the basis of quantitative DFT calculations,²⁰ it has been previously stated that the H bridges play essentially an indirect structural role. Nevertheless, the single-reference character of the DFT wave function does not provide a microscopic picture for the underlying mechanisms. In particular, how much a H bond gets involved in the establishment of efficient magnetic interaction is of particular importance in the preparation of magnetic materials. To complement the DFT data and offer a detailed analysis of the magnetic exchange mechanism, we first performed multireference CASSCF calculations on **1**. Considering the d⁹ electronic configuration of the Cu^{II} ion, the minimal active space consists of two electrons in two molecular orbitals (MOs). As expected, the active MOs of both *S* and *T* states are essentially the in-phase and out-of-phase linear combinations of the Cu d_{yz} atomic orbitals (see Figure 3).

The CAS[2,2]SCF energy difference $\Delta E = E_{\text{S}} - E_{\text{T}}$ leads to a poor estimation of $J \approx -9 \text{ cm}^{-1}$. Nevertheless,

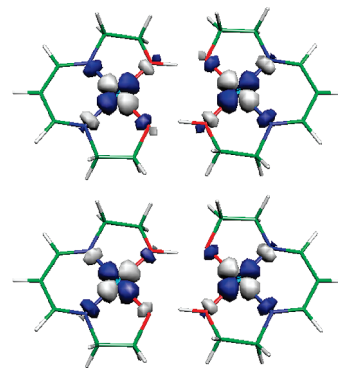


Figure 3. Magnetic MOs a_g (left) and a_u (right) extracted from a CAS[2,2] calculation over the *T* state.

Table 1. Calculated Exchange-Coupling Constant J (cm⁻¹) in Complexes **1** and **2**^a

	minimal valence space, CAS[2,2]+DDCI-3	extended valence space, CAS[10,8]+S	DFT
1	-62	-106	-100
2	-81	-128	-119

^a $J_{\text{exp}} = -94 \text{ cm}^{-1}$.

subsequent CI calculations significantly changed this state of affairs. Along the reported DDCI scheme,⁷ one includes a selection of determinants constructed on the triplet MOs. Since these calculations might be out of reach due to the large CI space, a strategy consists of building LOs to take advantage of the local character of the correlation effects. This valence-bond-type (VB) description allows one to concentrate on the most relevant determinants.²¹

From our DDCI-3 calculations, the *S*–*T* energy difference J is found to be -62 cm^{-1} (Table 1), reflecting a $\sim 35\%$ deviation from the reported experimental value -94 cm^{-1} .⁶ This numerical discrepancy is rather puzzling since the DDCI framework offers spectroscopic accuracy in the investigation of magnetically coupled systems.⁸ Therefore, this non-negligible deviation from both experimental⁶ and previous DFT estimation (-87 cm^{-1})²⁰ suggests that either (i) the H atomic positions are ill defined since an intuitive chemical picture would anticipate quasi-linearity of the O₁H...O₂ bridge or (ii) some important mechanisms contributing to the exchange coupling scheme are missing in the minimal valence space approach.

Thus, DFT/UB3LYP and similar CAS[2,2]+DDCI-3 calculations were performed upon a hypothetical structure **2** constructed from **1** by setting $\theta = 180^\circ$. Along this deformation, we maintained the O–H bond distances ratio constant, imposing a simultaneous shortening ($\sim 0.02 \text{ \AA}$) of these particular distances. As seen in Table 1, $|J|$ is significantly enhanced as the O₁H...O₂ angle θ reaches 180° , in agreement with previous calculations.²⁰ A similar conclusion holds in light of the DDCI-3 calculations which exhibit a -81 cm^{-1} exchange constant in **2**. These results demonstrate the apparent role of the H bonds in the establishment of efficient exchange coupling channels. At this stage, let us mention that the ground state *S* is lowered by $\sim 10\,000 \text{ cm}^{-1}$ as the geometry is modified from **1** to **2**. This energy stabilization was confirmed by full geometry DFT/UB3LYP optimization which highlights a quasi-linearity of the

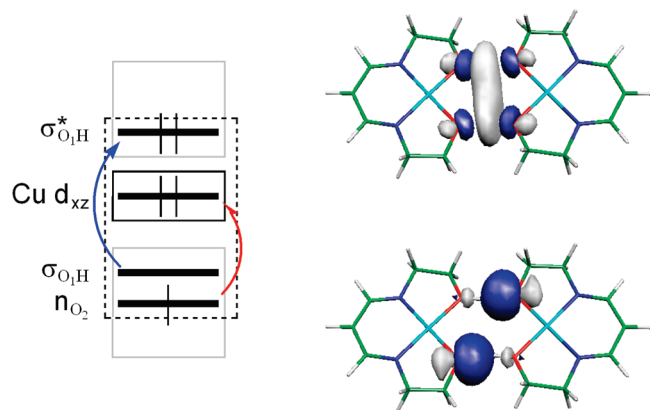


Figure 4. Selected active spaces (a_g symmetry): minimal valence space (CAS[2,2], full-line box) and extended valence space (CAS[10,8], dashed-line box). The blue arrow stands for a double excitation, whereas the red harpoon corresponds to a single excitation. The n_{O_2} (bottom) and $\sigma^*_{O_1H}$ (top) orbitals are sketched on the right-hand side.

$O_1H \cdots O_2$ bridge ($\theta = 178^\circ$) while the rest of the structure is negligibly modified. Even though the crystallization conditions are likely to control the molecular units structuration, our “magneto-structural” inspection suggests that the role of the hydrogen bonds may not be limited to a structural one.²⁰ The oxygen atom lone pairs n_{O_2} might be directly involved in a superexchange-like mechanism with the adjacent O_1H group σ_{O_1H} and $\sigma^*_{O_1H}$ orbitals, making the $O_1H \cdots O_2$ fragment an efficient coupler.

Thus, the active space was enlarged to CAS[10,8] to incorporate the valence orbitals and electrons of the $O_1H \cdots O_2$ linkers (see Figure 4). In a CAS[2,2] approach, the kinetic exchange²² is explicitly introduced. At a DDCI-3 level, this contribution is not only revisited but the mechanisms involving the bridging ligand orbitals are turned on.¹⁴ However, a mechanism involving the simultaneous charge reorganization within the OH bond and oxygen-to-metal charge transfer is absent and might play a determinant role. Thus, the CAS[10,8] strategy allows one to evaluate the contributions of superexchange mechanisms which were not accessible within the minimal CAS[2,2] approach. While the CAS[10,8]SCF S and T energies are easily obtained, the required CI treatment is much more demanding. Nevertheless, the VB-type description based on the LOs considerably reduces the CI space. Besides, the use of this particular active space including the valence LOs of the bridge (i.e., n_{O_2} , σ_{O_1H} , $\sigma^*_{O_1H}$) affords a limited expansion of the wave function to single excitations (so-called CAS+S space).¹⁶ As seen in Table 1, our CAS[10,8]+S result displays quantitative agreement (deviation smaller than 12%) with the experimental data since J is calculated to be -106 cm^{-1} . Besides, the reading of the wave function based on the bond LOs sheds the light on the importance of some specific electronic configurations (i.e., charge transfer forms) which may participate in the exchange coupling interaction. Any mechanism which enhances the effective hopping integral between the two Cu^{II} ions is likely to favor the antiferromagnetic behavior.²³ Since the antibonding orbital $\sigma^*_{O_1H}$ is mostly localized upon the H atom, the $\sigma_{O_1H}^2 \sigma^*_{O_1H} \rightarrow \sigma_{O_1H} \sigma^*_{O_1H}^2$ double-excitation process (see Figure 4) tends to accumulate

electronic density upon the H atom and deplete the O_1 one. Interestingly, this instantaneous charge reorganization within the O_1H bonds turned out to be concerted with the ligand-to-metal $n_{O_2} \rightarrow d_{xz}$ excitations (see Figure 4). Finally, the corresponding electronic configuration amplitude, though small, is increased by an order of magnitude when the $O_1H \cdots O_2$ fragment becomes linear. The comparison with the previous minimal valence space calculations is rather instructive. In fact, the here-evidenced electronic circulation was not included in the CAS[2,2] calculations and led to an underestimation of the effective hopping parameter. This is to be contrasted with the improved $S-T$ energy difference as soon as the intrinsically through-H bond superexchange mechanism is turned on. Finally, the corresponding electronic density fluctuations bring a complementary stabilization (47 cm^{-1} as compared to the minimal CAS description) of the S state over the T state in complex **2**. In light of the $\sim 36\%$ deviation with the reported experimental value, one can conclude that a much better agreement with experiment is reached for structure **1** and structure **2** might not be a satisfactory candidate. Besides, the need for an enlarged CAS[10,8] demonstrates the importance of charge fluctuations within the $O_1H \cdots O_2$ motif.

Conclusion

Our study sheds new light on to the prime role of hydrogen bonds in magnetically coupled systems and the strength of wave function methods to convey interpretative pictures. DFT-based calculations have demonstrated satisfactory accuracy in magnetic coupling evaluation, even if they remain biased due to the arbitrariness of the exchange-correlation functional. Moreover, they may not be well adapted to provide such pictures since they rely on single-determinant expansions of the wave functions. From our inspection using wave-function-based calculations, the deviation between experimental and a minimal valence space approach can be ascribed to a non-negligible electronic circulation within the $O_1H \cdots O_2$ bridge. This contribution, possibly among others, accounts for a supplementary 44 cm^{-1} stabilization of the singlet state over the triplet state. As expected, the coupling constant is very sensitive to the $O_1H \cdots O_2$ angle, and it is demonstrated that the hydrogen bond is directly involved in a superexchange-like mechanism. Using localized orbitals, we demonstrate that the H bond should not be a priori disposed when exchange coupling constants are considered in any magnetic systems. Our initial hypothesis regarding the crystallographic positions of the bridging hydrogen atoms can be discarded in light of comparative experimental and theoretical exchange constant values. The rational design of magnetic materials incorporating cooperativity effects through weak bond contacts should benefit from this theoretical inspection.

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