

Do π – π Stacking Interactions Really Play a Role in the Magnetic Coupling Mechanisms of $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2\text{L}_2(\text{H}_2\text{O})_2]^{n+}$ (L = heterocyclic base, $n = 0, 2$) Complexes? An *ab initio* Inspection

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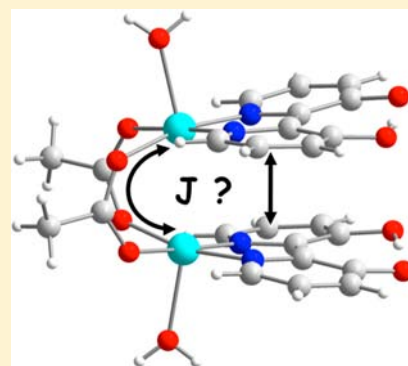
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ABSTRACT: The magnetic properties of two bis-acetate binuclear copper(II) complexes, namely $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2(\text{bpydiol-H})_2(\text{H}_2\text{O})_2]$ (bpydiol-H = mono deprotonated 2,2'-bipyridine-3,3'-diol) and $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ (phen = 1,10-phenanthroline), is revisited using *ab initio* wave function-based calculations (CASSCF, DDCl). Thanks to an analysis of the magnetic exchange coupling based on localized orbitals, it is shown that, unlike stated in the original work [C. Hou et al. *Dalton Trans.* **2008**, 5970], π – π interactions do not contribute to the overall antiferromagnetism character of these complexes.



INTRODUCTION

Weak bonds, namely hydrogen bonds or π – π stacking interactions, are known to be of tremendous importance in various fields of research such as supramolecular chemistry,¹ crystal engineering,² DNA structuration,³ or spin-crossover (SCO) materials.⁴ For instance, over the past decades, the latter phenomenon concentrated impressive efforts both experimentally and theoretically since information storage devices can be anticipated with such bistable architectures.^{4,5} The need for cooperativity led to numerous attempts to control the weak interactions through supramolecular and crystal engineering strategies.⁶ Concomitantly, the need for interpretation has stimulated intense theoretical developments.⁷ In particular, the synergy between weak bonds and electrostatic interactions in the generation of the hysteretic behavior of various SCO materials was recently established on the basis of wave function *ab initio* calculations.⁸

In molecular magnetism, weak bonds also play a central role since they act both as organizers of the crystal architecture and, in some cases, as mediators of the magnetic exchange coupling. In this respect, several experimental studies have highlighted the importance of hydrogen bonds in magnetic systems of various dimensionalities.^{9,10} Quantum chemical calculations, either based on density functional theory (DFT) or wave function methods, were also successfully applied to provide insights into such through-weak-bonds magnetic exchange

coupling mechanisms.^{10,11} To date, much less attention has been devoted to systems that exhibit magnetic coupling via nonbonded interactions such as π – π stacking.¹²

In this context, Hou et al. recently synthesized and characterized a binuclear Cu(II) complex, $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2(\text{bpydiol-H})_2(\text{H}_2\text{O})_2]$ (**1**, bpydiol-H = mono deprotonated 2,2'-bipyridine-3,3'-diol) where the Cu(II) ions are bridged by two acetate anions (Figure 1).¹³ The

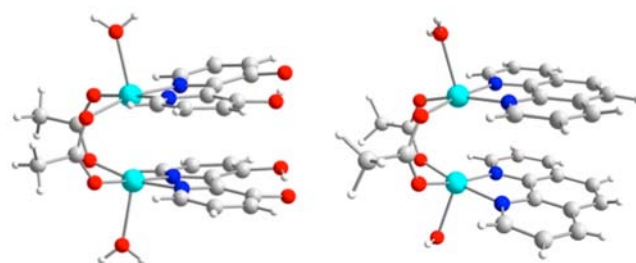


Figure 1. Molecular structures of $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2(\text{bpydiol-H})_2(\text{H}_2\text{O})_2]$ (**1**, left) and $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_2(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ (**2**, right). Cu, N, O, C, and H atoms are depicted in green, blue, red, gray, and white, respectively.

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coordination sphere of each metal ion is completed by a water molecule and a 2,2'-bipyridine-3,3'-diol ligand. The latter ring faces that on the adjacent copper center generating π - π stacking interactions. This complex exhibits moderate antiferromagnetism ($J = -59.6 \text{ cm}^{-1}$), which was attributed, based on DFT calculations (see the magnetic description of the complex that is given below), to a competition between antiferromagnetic mechanisms brought by the acetate bridges and ferromagnetic interactions through π - π overlap.¹³ A molecule with similar structural features was synthesized earlier by Tokii et al. using 1,10-phenanthroline instead of bpydiol-H as a π adduct (**2**, Figure 1).¹⁴ The magnetic exchange coupling of this parent complex was found experimentally to be $J = -86 \text{ cm}^{-1}$, i.e. slightly more antiferromagnetic than in **1**, despite similar Cu...Cu distances (3.01 and 3.06 Å in **1** and **2**, respectively). Moreover, the J values in these complexes are significantly weaker than the one observed for $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$ (**3**, Figure 2, $J = -294 \text{ cm}^{-1}$).¹⁵ DFT

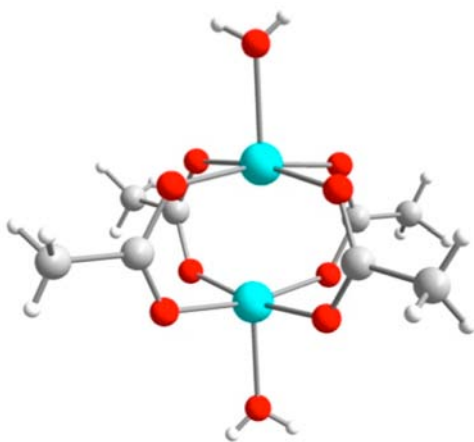


Figure 2. Molecular structure of $[\text{Cu}_2(\mu_2\text{-CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$ (**3**). Cu, O, C, and H atoms are depicted in green, red, gray, and white, respectively.

calculations, with the broken symmetry approach,¹⁶ on complex **3** and other binuclear Cu(II) models with acetate bridging ligands confirmed the expected correlation between (i) the number of bridging carboxylate ions and (ii) the Cu...Cu distance with the intensity of the magnetic coupling, i.e. the larger the Cu...Cu distance or the lesser the number of bridging ligands, the weaker the magnetic coupling intensity.¹⁷ Clearly, many electronic or geometric factors, including π - π stacking interactions, influence the nature and intensity of the magnetic exchange coupling in this family of complexes. Unfortunately, the theoretical analysis of the magnetic properties of complex **1**,

previously proposed in the literature,¹³ appears to be questionable. In the present contribution, we thus propose another inspection based on ab initio wave function calculations to clarify the magnetic properties of complexes **1** and **2**.

This paper is organized as follows: after a brief description of the computational methodology, the two complexes **1** and **2** are presented with an emphasis given to their magnetic properties. In the following section, results and interpretation of our multireference wave function calculations of the magnetic exchange couplings in both complexes **1** and **2** as well as the tetra-acetate binuclear complex **3** are discussed shedding light on the respective role of the acetate bridges and the π - π stacking interactions.

■ COMPUTATIONAL DETAILS

Complete active space self-consistent field (CASSCF)¹⁸ calculations, including two electrons in two molecular orbitals (MOs), were performed on complexes **1**–**3** using the MOLCAS 7.6 package¹⁹ to generate a reference space (CAS[2,2]), which consists of the configurations that qualitatively describe the problem. The dynamical correlation effects were then incorporated by using the dedicated difference configuration interaction (DDCI)²⁰ method implemented in the CASDI code.²¹ With this approach, one concentrates on the differential effects rather than on the evaluation of the absolute energies. DDCI1 involves one hole and one particle (1h, 1p, 1h–1p) single excitations on the full active space. DDCI2 also accounts for the two holes or two particles diexcitations (2h, 2p). Finally, the two holes/one particle (2h–1p) and one hole/two particles (1h–2p) excitations are taken into account in DDCI3. The DDCI approach has proved to give good agreement with experiment in many applications on biradicals,²² inorganic molecules,²³ and a wide family of ionic insulators.²⁴ Since the DDCI philosophy relies on the simultaneous characterization of different spin states which share similar spatial descriptions, one has to initially determine a set of common MOs to build up the CI space. In this work, the CASSCF triplet orbitals were used. On the other hand, natural orbitals (NOs) were obtained from the average of the singlet and triplet states one-electron density matrices at various DDCI levels through an iterative procedure (I-DDCI)²⁵ using the NATURALS code,²⁶ until the singlet–triplet energy difference is converged, i.e. the relative change is less than 2%. All atoms were depicted with Atomic Natural Orbital basis sets²⁷ of either ANO-RCC²⁸ or ANO-S²⁹ types. The ANO-RCC basis set calculations involved a default atomic mean field integral (AMFI)³⁰ computation with a second-order Douglas–Kroll Hamiltonian.³¹ The following contraction schemes were used: for Cu $21s15p10d6f4g2h \rightarrow 5s4p3d$ and $17s12p9d4f \rightarrow 5s4p3d$; for O, N, and C $14s9p4d3f2g \rightarrow 3s2p$ and $10s6p3d \rightarrow 3s2p$; for H $8s4p3d1f \rightarrow 1s$ and $7s3p \rightarrow 1s$. Orthogonal localized orbitals (LOs) were finally constructed based on the canonical CASSCF orbitals using a previously published approach.^{32,33} These LOs are constrained to be symmetry adapted, to maintain point group symmetry. The use of such LOs allows for a chemically intuitive analysis of the relevant mechanisms accompanying

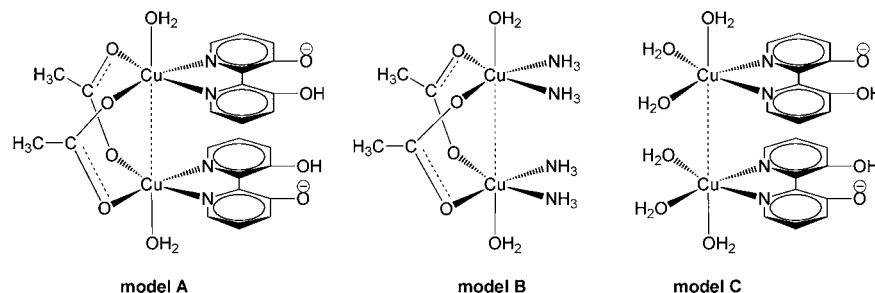


Figure 3. Schematic representation of the binuclear models used in ref 13.

the singlet–triplet splitting. It permits a differential evaluation of the presence of each ligand in the calculation of the magnetic exchange constants by freezing (deleting) selective occupied (virtual) LOs in the DDCI step. Representation of the orbitals (isocontour = 0.05 au) and difference density maps (isocontour = 1.0×10^{-3} a.u.) was done using the Chemcraft package.³⁴

MAGNETIC PROPERTIES OF 1 AND 2

The experimental magnetic susceptibility data of both complexes were fitted using the Bleaney–Bowers equation, well adapted for a copper(II) binuclear model.^{35,36} A weak antiferromagnetic interaction operates between the copper(II) ions, with $J(1) = -59.6 \text{ cm}^{-1}$ and $J(2) = -86 \text{ cm}^{-1}$. No interpretation of the respective role of the direct Cu...Cu interaction, the acetate bridging ligands, and the π – π stacking via the face-to-face arrangement of the phenanthroline units in the magnetic properties of **2** was given in the original work.¹⁴ On the other hand, a tentative explanation of the mechanisms at the origin of the exchange coupling in **1** was proposed in what was considered by the authors as “the first example using theoretical calculations that evaluate the magnetic coupling intensity for a π – π stacking system”.¹³ DFT calculations were performed on three models (models A, B, and C in Figure 3) corresponding to the binuclear Cu(II) complex **1**, a binuclear Cu(II) complex with no π – π stacking (the aromatic rings were replaced by NH_3 ligands), and two mononuclear Cu(II) complexes in interaction through the π – π overlap of the bipyridyl-H moieties (the acetate bridging ligands were replaced by water molecules), respectively, so as to obtain approximate partial exchange coupling constants from the individual coupling paths. The magnetic coupling constant J was obtained for all models as the energy difference $E(\text{BS}) - E(\text{T})$ where BS and T correspond to the broken symmetry¹⁶ and the triplet states, respectively ($\hat{H} = -J\hat{S}_1\hat{S}_2$). For model A, the calculated J value was found equal to -166.7 cm^{-1} , an antiferromagnetic interaction strongly larger than the experimental fitted value ($J = -59.6 \text{ cm}^{-1}$). This large error was attributed to (i) the size of the molecule, (ii) the presence of the π – π stacking, and (iii) the nature of the exchange-correlation functional.¹³ Whereas the first two arguments are not really convincing, the question about the choice of a GGA (generalized gradient approximation) functional, such as BP86,³⁷ is pertinent. Indeed, it is well-established that pure gradient corrected functionals over-stabilize the broken symmetry state for strong antiferromagnetic complexes.^{11e,38} Despite such a discrepancy between the calculated and experimental J values, the authors went on further with this methodology applying the same computational procedure to models B ($J = -292.4 \text{ cm}^{-1}$) and C ($J = 21.0 \text{ cm}^{-1}$). They thus concluded that the strong antiferromagnetic interactions attributed to the acetate bridge pathways were counter-balanced by a weak ferromagnetic coupling from the π – π stacking pathway.¹³

RESULTS AND DISCUSSION

The present work is divided into two separate sections. First, compound **3** is used as a benchmark molecule for our multireference wave function calculations. By comparison with the calculated exchange coupling values that have been previously reported in the literature, we finally end up with a procedure that quantitatively reproduces the experimental data. This was considered as a prerequisite before, in a second step, having a closer look at the mechanisms behind the magnetic coupling in **1** and **2**.

[Cu₂(μ -CH₃COO)₄(H₂O)₂] (3) in Retrospect: A Test Case for the ab initio Procedure. The binuclear complex $[\text{Cu}_2(\mu\text{-CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$ (**3**, Figure 2), also known as copper acetate monohydrate since this complex was first assumed to be mononuclear, has been the quintessential molecule in molecular magnetism since the pioneering work of Guha,³⁹ soon followed by Bleaney and Bowers.³⁵ The structure of this compound was determined a year later confirming the presence of interacting pairs of copper ions.⁴⁰ In the ensuing decades, numerous discussions concerned the existence and nature of a potential metal–metal bond,^{41,42} as well as the investigation of the isotropic exchange^{42,43} and the anisotropic parameters.^{44,45} The value of the experimental magnetic exchange constant was finally settled from neutron inelastic scattering spectroscopy ($J = -298 \pm 4 \text{ cm}^{-1}$).¹⁵

Moreover, complex **3** (CCDC ref code CUAQAC04)⁵¹ served as a perfect benchmark molecule in the calculation of the exchange coupling constant using either ab initio CI or DFT approaches, with particular emphasis given to the analysis of the nature of the magnetic orbitals. A selection of previously published quantitative estimates of J with respect to the applied methodology is given in Table 1. In one of the pioneering

Table 1. Selected Values Found in the Literature for the Exchange Coupling (J , cm^{-1}) in **3** Calculated with Various Methodologies

| methodology | J | ref |
|------------------------------------|------|-----|
| QDMPT ^a | –244 | 46 |
| CASPT2 | –117 | 48 |
| NEVPT2 | –40 | 45 |
| DDCI3 | –224 | 48 |
| DDCI3 | –238 | 47 |
| DDCI3 | –271 | 45 |
| DFT (B3LYP) | –308 | 17 |
| DFT (B3LYP) | –299 | 48 |
| DFT (M06) | –264 | 49 |
| DFT (ω -B97X) ^b | –316 | 50 |

^aQuasi-degenerate many body perturbation theory.⁴⁶ ^bSpin projected calculation.

works in the field of theoretical molecular magnetism, de Loth et al. performed a perturbative second-order analysis which allowed not only a quantitative computation of J when including higher order corrections ($J = -244 \text{ cm}^{-1}$) but also an analysis of various contributions to the singlet–triplet splitting.⁴⁶ Separate second-order perturbation theory (CASPT2) calculations severely underestimate the coupling constant ($J = -117 \text{ cm}^{-1}$) highlighting the limit of this perturbative approach.⁴⁸ In this case, the more recently developed n -electron valence second-order perturbation theory (NEVPT2)⁵² method did not succeed either (see Table 1).⁴⁵ As stated recently,^{23f} an efficient way to correct this apparent failure of MRPT2 methods consists in building up a weighted set of more delocalized MOs from the neutral and ionic CASSCF singlets. The variational DDCI3 magnetic coupling constants compare much better with experiment (see Table 1) even if the nature of the magnetic orbitals as well as a certain basis set dependence may strongly affect the computed value.^{45,47,48} The success of DDCI3 has been attributed to the dominant role of the $2h$ – $1p$ excitations in the kinetic exchange contributions.⁵³

For completeness, we shall mention that, in the meantime, DFT calculations, using the broken symmetry approach,¹⁶ with the B3LYP functional achieved almost quantitative results compared to experiment (within 10 cm⁻¹, see Table 1).^{17,48} Unfortunately, discussion on which formulation is more valid for extracting J couplings from DFT energies is still ongoing,⁵⁴ and the choice of a pertinent exchange-correlation functional for a specific question or molecule may still be considered somewhat arbitrary. For instance, the recent M06 and the long-range corrected ω -B97X-D do not systematically improve the results (Table 1).^{49,50}

As mentioned above, among wave function-based methodologies, the more convincing results, i.e. the closest exchange coupling constant to experiment, were obtained with the DDCI procedure. We thus performed similar CI calculations using both ANO-S and ANO-RCC basis functions (see Computational Details). The results are reported in Table 2, and the CAS[2,2] active orbitals are depicted in Figure 4.

Table 2. Calculated Exchange Coupling Constants (J , cm⁻¹) for 1–3 at Various CI Levels, with ANO-S (ANO-RCC in Parentheses) Basis Functions

| | 1 | 2 | 3 |
|--------------------|-----------|-----------|-------------|
| CAS[2,2]SCF | -6 (-4) | -7 (-5) | -27 (-23) |
| DDCI1 ^a | -20 (-18) | -23 (-20) | -87 (-78) |
| DDCI2 ^a | -21 (-19) | -24 (-21) | -91 (-82) |
| DDCI3 ^a | -45 (-35) | -62 (-48) | -239 (-201) |
| I-DDCI1 | -23 (-20) | -26 (-23) | -98 (-88) |
| DDCI3 ^b | -49 (-39) | -65 (-53) | -259 (-218) |
| I-DDCI3 | -57 (-45) | -81 (-66) | -324 (-271) |
| exp ^c | -60 | -86 | -298 |

^aBased on triplet CAS[2,2]SCF wave function. ^bFrom I-DDCI1 NOs. ^cSee refs 13–15.

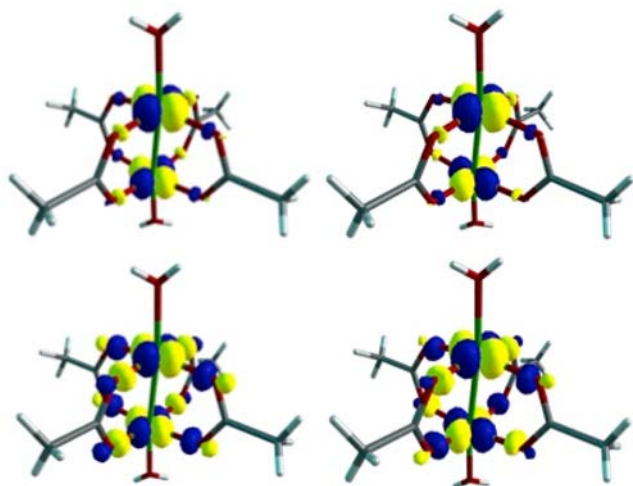


Figure 4. Active orbitals of complex 3 from CAS[2,2]SCF calculation of the triplet state (top) and average natural orbitals at the I-DDCI1 level (bottom).

One first notes that the type of basis function has non-negligible influence on the calculated J values. Regardless of the level of calculation, ANO-S functions always stabilize the singlet state with respect to ANO-RCC functions, with a difference around 17% (19%) at the CAS[2,2]SCF (DDCI3) level for 3. At the best level of calculation, i.e. DDCI3, the calculated

coupling value ($J = -239$ cm⁻¹) perfectly matches the result reported by Calzado et al. on the basis of NOs obtained from DDCI1 wave function⁴⁷ but still remains off by approximately 20% from the experimental data.¹⁵ We therefore decided to further explore the potentialities of NOs, since such a procedure has already proven its applicability in various types of complexes.^{47,55} As already rationalized,⁴⁷ the delocalization tails of the magnetic orbitals between the ligands and the metallic centers become substantially larger in the NOs than in the CASSCF ones (Figure 4). This induces important modifications in effective parameters with an increase of the direct exchange K_{ab} (a and b referring to the magnetic orbitals), a reduction of the on-site Coulomb repulsion U , and an increase in the value of the hopping integral $|t_{ab}|$.⁴⁷ Since the exchange coupling may be written as a sum of a ferromagnetic part (J_F) and an antiferromagnetic one (J_{AF}), $J = J_F + J_{AF} = 2K_{ab} - 4t_{ab}^2/U$, the resulting effect on J depends on the respective weight of these terms. In 3, using NOs unambiguously favors antiferromagnetism (see Table 2). For instance, the I-DDCI3 value agrees with less than 10% deviation with experiment.

Complexes 1 and 2: Their Magnetic Properties Revisited. This excellent agreement obtained for complex 3 gives us confidence in applying an identical approach to the calculation of the exchange coupling in compounds 1 and 2. The results are gathered in Table 2. Similarly to what was observed for 3, the DDCI3 coupling constants are off by approximately 25% compared to the experimental values, which may be considered as an untypically poor performance for DDCI3, at least with these average sized basis sets (results are even worse with ANO-RCC basis sets).⁵⁶ Using NOs corrects the missing antiferromagnetism in both complexes yielding I-DDCI3 values that are almost identical to the experimental ones: -57 vs -60 cm⁻¹ and -81 vs -86 cm⁻¹ for 1 and 2, respectively (see Table 2). The delocalization of the NOs comparatively to the triplet CASSCF orbitals is again significant (see Figure 5).

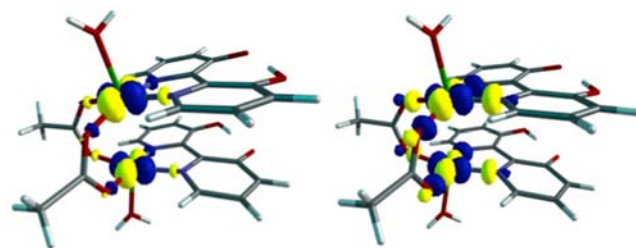


Figure 5. Active orbitals of complex 1 from CAS[2,2]SCF calculations of the triplet state (left) and average natural orbitals at the I-DDCI1 level (right). Only the in-phase contribution is presented.

With this quantitative agreement between I-DDCI3 and experiment, one may now concentrate on the evaluation of the various exchange pathways in 1 and 2. Similar description was also applied to 3 for comparison. To this purpose, we took advantage of localized molecular orbitals (LOs) that are a valuable tool of interpretation since DDCI is invariant to orbital rotations and a heuristically more “chemical” representation can be obtained from these results. Such LOs are mainly made up of two-center bonding and antibonding contributions, except for the copper orbitals that remain mostly atomic, and each of them can be classified as belonging to a particular part of the molecule. Using LOs makes it possible to treat separately all

parts of the molecule (all different ligands and the copper atoms). One must note that each two-center LO belongs to one ligand only. In such a way, it becomes possible to quantify the contributions of the different moieties of the complexes.

In a first step, this approach has been tested on compound **3**, for which three kinds of geographical parts are considered, namely the copper atoms, the acetate, and water ligands. To evaluate the role of the acetate ligands, they are “frozen” in the calculation, i.e. the corresponding occupied and virtual LOs are frozen and deleted, respectively. The difference between the results obtained for the whole molecule and for the complex with the frozen ligand is interpreted as the contribution of this ligand that will be called J_{acetate} . In the same way, J_{water} describes the contribution of the water molecules that should in principle be negligible. To evaluate the contribution of the copper atoms, an inverse approach is necessary, since one Cu LO is the open shell active orbital and cannot be frozen. Therefore, all ligands were frozen, and the exchange coupling constant J_{Cu} is limited to mechanisms involving mostly 3d-type MOs, disposing of all mechanisms that can be attributed to dynamical responses of the metal ion environments. Results of this decomposition are listed in Table 3. The sum of all contributions (-315 cm^{-1})

Table 3. Chemical-type Contributions to J (cm^{-1}) for **1–3** at the I-DDCI3 Level of Calculation^a

| | 1 | 2 | 3 |
|-----------------------|-----|-----|-------------|
| J_{Cu} | –33 | –44 | –200 (–50) |
| J_{acetate} | –27 | –38 | –117 (–183) |
| $J_{\pi\text{-ring}}$ | +1 | –1 | |
| J_{water} | –1 | –1 | +2 (–11) |
| sum of J_x | –60 | –84 | –315 (–244) |
| J_{calc} | –57 | –81 | –324 (–239) |
| exp ^b | –60 | –86 | –298 |

^aThe DDCI3 contributions are given in parentheses for **3**. ^bSee refs 13–15.

reasonably matches the global calculated value of -324 cm^{-1} which strengthens their potential additivity. As expected, the main channel corresponds to the copper–copper J_{Cu} contribution with important superexchange mechanisms through the acetate ligands pathway. J_{water} is found residual. A comparison with similar chemical-type decomposition at the DDCI3 level shows a large enhancement of the antiferromagnetic J_{Cu} quantity at the expense of the acetate channel. This clearly reflects the effect of the iterative procedure that tends to extend the acetate delocalization tails in the magnetic orbitals. A plot of the difference density map between CASSCF and I-DDCI3 orbitals is given in Figure 6. Bringing these

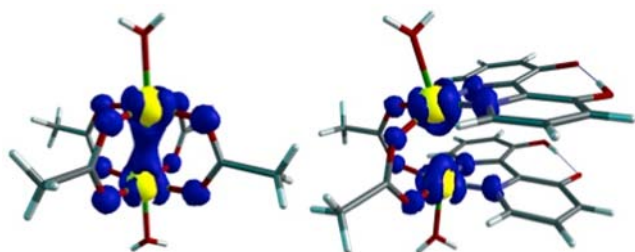


Figure 6. Difference density map $\rho_{\text{CASSCF}} - \rho_{\text{I-DDCI3}}$ for complexes **3** and **1**. Negative and positive signs are given in blue and yellow, respectively.

delocalization tails into the active space directly improves the description of the coupling and is essential for the accurate description using the DDCI approach since it takes into account explicitly the superexchange mechanism via the acetate ligands.

If we now address the magnetic properties of the title complexes **1** and **2** with the same methodology, we may determine if the π -stacking ($J_{\pi\text{-ring}}$) plays indeed a non-negligible role in the magnetic pathway as previously stated.¹³ The results are listed in Table 3. First, one notes that, not surprisingly, **1** and **2** behave similarly. J_{Cu} and J_{acetate} are roughly of the same magnitude and together they take up the whole antiferromagnetism, thereby revealing no sign of direct interaction through π – π stacking. Consequently, if one trusts the I-DDCI results, the prediction of a substantial ferromagnetism brought by the π -type ligands in **1**¹³ should certainly be considered as erroneous. This misleading description based on the DFT broken symmetry calculations¹³ can be understood by a wrong modeling of the various magnetic effects (see Figure 3) and the use of a nonadapted functional, i.e. a functional without exact exchange.

CONCLUSIONS

Multireference wave function calculations were used to revisit the description of the magnetic properties of two binuclear Cu(II) complexes **1** and **2** both based on acetate bridges and aromatic π ligands. An efficient ab initio strategy for the calculation and interpretation of the magnetic exchange coupling constant was first established for the quintessential copper acetate monohydrate (**3**). For a correct agreement with experiment, it becomes necessary to go beyond conventional DDCI calculations, whereby the triplet CAS[2,2]SCF orbitals are utilized, and instead undergo an iterative procedure (I-DDCI) that allows for a better description of the necessary delocalization tails on the ligands of the magnetic orbitals. This same approach was then applied successfully to reproduce the coupling constants in the aromatic derivatives **1** and **2**.

Then, the role of the ligands in the magnetic coupling channels was quantitatively established by an orbital localization procedure of the I-DDCI density. In copper acetate monohydrate **3**, the indirect role of the acetate ligand orbitals is around -29 cm^{-1} per acetate whereas the direct involvement of the magnetic orbitals centered on the metal ions yields the overwhelming source of antiferromagnetism. The π -ring currents do not seem to bring any ferromagnetism to the two species **1** and **2** contrary to what was previously suggested in the literature.¹³ We believe that the proposed description is based on a more rigorous approach that may allow studying the magnetic properties through nonbonded channels in other families of complexes.

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Notes

The authors declare no competing financial interest.

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