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Abstract

The antisymmetric exchange, also known as the Dzyaloshinskii-Moriya interaction (DMI), is an effective interaction that may be at play in isolated complexes (with transition metals or lanthanides for instance), nanoparticles and highly correlated materials with adequate symmetry properties. While many theoretical works have been devoted to the analysis of single-ion zero-field splitting and to a lesser extent to symmetric exchange, only a few *ab initio* studies concern the DMI. Actually, it originates from a subtle interplay between weak electronic interactions and spin-orbit couplings. This article aims to highlight the origin of this interaction from theoretical grounds in a real tri-copper(II) complex, capitalizing on previous methodological studies on bi-copper(II) model complexes. By tackling this three-magnetic-center system, we will first show that the multi-spin model Hamiltonian is appropriate for trinuclear (and likely for higher nuclearity) complexes, then that the correct application of the permutation relationship is necessary to explain the outcomes of the *ab initio* calculations, and finally that the model parameters extracted from a binuclear model transfer well to the trinuclear complex. For a more theory-oriented purpose, we will show that the use of a simplified structural model allows one to perform more demanding electronic structure calculations. On this simpler system, we will first check that the previous transferability is still valid, prior to perform more advanced calculations on the derived two-magnetic-center model system. To this end, we will explain in details the physics of the DMI in the copper triangle of interest, before advocating further theory/experiment efforts.

1 Introduction

The interpretation of low-temperature magnetic properties of transition metal complexes for long relies on the use of simple model Hamiltonians, in particular spin Hamiltonians[1]. Implicitly, this means that the orbital parts of the wave functions of the states of interest are very similar and can be factorized. Both the low energy spectrum and the corresponding wave functions can be well reproduced by a simple spin Hamiltonian. This appealing simplification is in fact very powerful and can be used to explain most of the molecular magnetism observations. This description may fail, however, if at least one magnetic site exhibits first-order spin-orbit coupling (SOC), which requires local orbital degeneracy (the converse is not necessarily true, *i.e.* one can have orbital degeneracy without exhibiting first-order SOC[2]). Putting aside the first-order SOC case and focusing exclusively on standard magnetic systems whose low-temperature magnetic behaviors can be consistently described by a spin Hamiltonian, a key issue in molecular magnetism is the theory behind the use of a spin Hamiltonian, whether based on (old-fashion) analytical derivations[3,4] and/or on sophisticated quantum mechanical calculations,[5] and also of course on the interplay between theory and experiment. Establishing a fruitful dialogue between theorists and experimentalists first requires the ability to reproduce experimental data reasonably well. In the field of anisotropic spin Hamiltonians, one may quote the pioneering DFT work of Pederson and Khanna on giant spin (GS) Hamiltonians of polynuclear TM complexes[6] and further applications,[7–9] many DFT and wave function theory (WFT) works related to mononuclear complexes,[10–30] and a few WFT works on dinuclear complexes[31–34] and beyond.[35] In short, theoretical chemists have clearly shown many times that the computation of symmetric anisotropic tensors belonging to GS or multi-spin (MS) models, is generally possible with satisfactory accuracy.

The case of the antisymmetric exchange, known as the Dzyaloshinskii-Moriya interaction (DMI),[36–38] is much less straightforward from both experimental and theoretical points of view. Indeed, it is difficult to have reliable experimental values of the DMI, because on the one hand the experimental fitting procedures are essentially based on the reproduction of energy differences, and on the other hand when DMI is at play, many other parameters (isotropic exchange, symmetrical exchange, local splitting of the energy levels in the absence of the magnetic field, *i.e.* local zero-field splitting –ZFS–, etc.) also affect these energies. Two recent papers [39,40] were dedicated to the identification of the main chemical ingredients that govern both the magnitude and orientation of the DMI through analytical derivations and *ab initio* calculations. An analytical formula was proposed that reproduces very well the magnitude of the DMI components far from the first-order SOC regime. One important conclusion of reference[39] was that an efficient way to increase the DMI is to approach the first-order SOC regime, *i.e.* to design complexes where some on-site d orbitals are almost degenerate. The description of the underlying physics governing the DMI close to the first-order SOC regime was then described in a follow-up article.[40] To this end, we have developed a simple electronic and spin-orbit model, used *ab initio* calculations to conduct a thorough methodological study and show the importance of the use of the effective Hamiltonian theory to accurately extract DMI. One can also mention some other theoretical chemistry studies that have been devoted to DMI.[41–46] However, in all these works either model coordination complexes unrelated to real complexes or fragments of solids were studied. Thus, although methodological conclusions could be drawn, comparisons with reliable experimental data were impossible in practice.

In order to achieve a decent comparison between theoretical and experimental data, several issues need to be addressed, severely limiting the choice of molecular systems. From a theoretical point of view, we want the calculations to be as simple as possible, since *ab initio*

calculations of DMI are still in their infancy. For this, it is necessary to have a minimal number of magnetic centers and to stick to local S = ½ spins, such as copper(II) centers. Indeed, larger local spins quickly give rise to a multitude of energy levels (or microstates) in the d^n manifold, and generate higher order interactions such as rank 4 tensors, biquadratic interactions, local anisotropies, *etc.*[32,47,48] From an experimental point of view, it would be quite simple to describe the coupling of two local spins S = ½ using the multispin Hamiltonian. However, the interpretation of the experimental data is problematic since the parameters of the multispin Hamiltonian cannot be extracted independently from the energy spectrum using fitting procedures. Therefore, the system should be at least trinuclear. Note however that the same problem of extraction from experiment occurs in a non-equilateral triangular complex (*vide infra*). In contrast, in our calculations, the DMI is extracted from the off-diagonal elements of the spin-orbit configuration interaction matrix and is not ambiguous. Nevertheless, as shown previously[40] these off-diagonal elements are very sensitive to the quality of the *ab initio* wave functions. Therefore, a system exhibiting a large DMI is necessary to validate at least semi-quantitatively a computational approach and also to reach robust conclusions, without critical problems of numerical accuracy.[49–52]

In this work, we will focus on a trinuclear systems, the tris(μ-hydroxy)tri-copper(II) complex[53] that involves N,N'-di-tert-butyl-ethylenediamine (DBED) ligands (see Figure 1, left), here after denoted **1**(3Cu) for which the appearance of a very large DMI has been clearly shown experimentally. In this complex, a strict D_3 symmetry was reported in the crystal structure.[53] Actually, experimental fits were performed by including (i) one isotropic coupling constant (J), one antisymmetric exchange constant (G) and one intermolecular isotropic coupling term (J')[53] or (ii) considering two different magnetic couplings J and $J-\frac{\delta}{2}$ and a single antisymmetric exchange constant (G), with actually a large G term in both cases (values ranging from 35 to 37 cm^{-1} depending on the technique and model Hamiltonian used).[54] In other words, despite confirmation for a symmetry lowering ($\delta \neq 0$), the introduction of a symmetry lowering parameter δ hardly reduces the extracted value of the G constant. Therefore, notwithstanding potential structural issues that will be discussed at the end of the article, we can be confident in the fact that a large DMI occurs in this real system, which we recall matters for our computational purposes. We chose to use the experimental geometry (of D_3 symmetry point group) for two main reasons: i) experience has shown us that the *ab initio* values of the magnetic parameters are very sensitive to the geometric structures[55,56] and we usually achieve good accuracy for experimental geometries; ii) a geometry optimization would necessarily have been performed using a broken symmetry DFT approach for which the optimized solution would not correspond to a pure doublet spin state.

In this paper, we will calculate the DMI in the tri-copper(II) complex and in a simplified di-copper(II) model system where one Cu(II) ion is substituted by a diamagnetic Zn(II) one. In order to apply more correlated methods, we will study a structurally simplified model system also involving either three or two Cu(II) where NH_3 groups replace the DBED ligands (see Figure 1, right). After a section on theory and methods, we will divide the discussion of the results into two main items: i) validity of the model Hamiltonian, permutation relationship and transferability of the parameters from two Cu(II) systems to three Cu(II) ones ii) impact of electron correlation on DMI values (content of the active space and use of "decontracted" wave functions), prior to conclude on the necessity for further theoretical and experimental efforts.

2 Theory and Methods of Calculation

2.1 Extraction of Model Hamiltonians Parameters

The use of the effective Hamiltonian theory[57,58] for the extraction of model parameters has proved to be particularly useful in the study of magnetic systems.[2,16,33–35,59] As this approach has already been presented several times,[5,55,60] we will only recall its main features. The objective of the method is to determine an effective Hamiltonian spanned on a small model space, typically the space of the model spin Hamiltonian for which we want to extract the interactions (here the MS Hamiltonian). The method imposes that the model energies are exactly the same as those calculated *ab initio* with the all-electron Hamiltonian and that the model wave functions are the *ab initio* wave functions projected onto the model space. To satisfy these requirements, we compute the numerical matrix of the effective Hamiltonian defined as follows:

$$\widehat{H}^{des\ Cloizeaux} = \sum_{k=1}^{N} |\widetilde{\Psi}_k\rangle E_k \langle\widetilde{\Psi}_k| \quad (1)$$

where E_k are the *ab initio* energies, $\widetilde{\Psi}_k$ are the orthonormalized projections[58] of the *ab initio* wave functions onto the model space and N is the both the size of the model space and the total number of target states. The comparison between the matrix of the model Hamiltonian expressed in terms of the analytical interactions and the numerical matrix of the effective Hamiltonian allows in general to assign values to all interactions. It should be remembered that beyond its numerical utility, this method allows us to check the appropriateness of the model and to propose new models when necessary.[32,33,43,47,48,61–67] Indeed, the norm of the projections informs us about the relevance of the model space and the comparison of the analytical and numerical matrices allows us to check the coherence of the interactions and thus of the model operators. As we will extract the model interactions for both two-magnetic-site and three-magnetic-site Hamiltonians, let us detail the procedure in both cases.

2.1.1 Complexes With Two S = ½ Magnetic Sites

For two active S = ½ magnetic sites, the MS model Hamiltonian, which includes operators acting on both local spins $\widehat{\boldsymbol{S}}_A$ and $\widehat{\boldsymbol{S}}_B$, is:

$$\widehat{H}^{MS} = J_{ab}\widehat{\boldsymbol{S}}_a.\widehat{\boldsymbol{S}}_b + \widehat{\boldsymbol{S}}_a.\boldsymbol{D}_{ab}.\widehat{\boldsymbol{S}}_b + \boldsymbol{d}_{ab}.\widehat{\boldsymbol{S}}_a \times \widehat{\boldsymbol{S}}_b \quad (2)$$

where J_{ab} is the isotropic coupling constant between the two a and b sites,[68–71] $\boldsymbol{D}_{ab}$ is the symmetric exchange tensor[72] and $\boldsymbol{d}_{ab}$ is the DM vector[37,38] (resulting from the reduction of the antisymmetric component of the second-rank exchange tensor, obtained after separation of its symmetric and antisymmetric components).
By definition, this model Hamiltonian works on the basis[73] of the $|S_a, M_{Sa}, S_b, M_{Sb}\rangle$ uncoupled functions, which may be denoted as $|M_{Sa}, M_{Sb}\rangle$ for the sake of simplicity. This model Hamiltonian may then be transformed in the coupled $|S, M_S\rangle$ basis as follows:

$$\widehat{H}^{\mathrm{MS}}(coupled) = \boldsymbol{U}^{-1}\widehat{H}^{\mathrm{MS}}(uncoupled)\boldsymbol{U} \quad (3)$$

where the basis is indicated in brackets, and the $\boldsymbol{U}$ matrix is given by the Clebsch-Gordan coefficients.[73]

The general expression of $\widehat{H}^{MS}(coupled)$ is available elsewhere.[39,43] In this 4×4 matrix, J_{ab} discriminates the diagonal elements of the triplet components from that of the singlet. The axial parameter *D* potentially affects differently the diagonal elements of all components (singlet and triplet) in the magnetic axes frame while the rhombic *E* parameter couples the $M_S = \pm 1$ components) and $\boldsymbol{d}_{ab}$ couples the components of the triplet with the singlet, *e.g.*, the z-component of the DM vector couples the $M_S = 0$ component of the triplet with the singlet. Actually, the three components (x, y and z) are obtained in the coordinate frame that is used for the calculations, even if we put special emphasis on the z-component for the sake of understanding the properties of the native tricopper(II) complex and simplicity. This is an asset of our theoretical approach: we do not need to assume any symmetry properties to perform extractions of effective parameters.

Symmetry rules for the occurrence of the DMI were initially proposed by Moriya.[38] Note that a complete picture for symmetry rules is available in the context of the nuclear spin-spin coupling tensor.[74] Typically, this term vanishes with the occurrence of a symmetry center, as in the famous copper acetate monohydrate complex.[34,75,76]

The extraction of both GS and MS Hamiltonians parameters from the effective Hamiltonian theory has been practiced many times and has proven to be particularly efficient for binuclear complexes. The validity of the MS model for two *S* = ½ spins has already been demonstrated by comparing the analytical and numerical matrices and all parameters, *J*, *D* and $|d_z|$ could easily be extracted.[39,40] We will therefore not further detail the procedure here.

2.1.2 Complexes with Three *S* = ½ Magnetic Sites

For three *S* = ½ magnetic sites, the MS model can be built in a similar way by considering the three (independent) pairs of magnetic centers (*ab*, *bc* and *ac*):

$$\widehat{H}^{MS} = J_{ab}\widehat{\boldsymbol{S}}_a.\widehat{\boldsymbol{S}}_b + \widehat{\boldsymbol{S}}_a.\boldsymbol{D}_{ab}.\widehat{\boldsymbol{S}}_b + \boldsymbol{d}_{ab}.\widehat{\boldsymbol{S}}_a \times \widehat{\boldsymbol{S}}_b + J_{bc}\widehat{\boldsymbol{S}}_b.\widehat{\boldsymbol{S}}_c + \widehat{\boldsymbol{S}}_b.\boldsymbol{D}_{bc}.\widehat{\boldsymbol{S}}_c + \boldsymbol{d}_{bc}.\widehat{\boldsymbol{S}}_b \times \widehat{\boldsymbol{S}}_c + J_{ac}\widehat{\boldsymbol{S}}_a.\widehat{\boldsymbol{S}}_c + \widehat{\boldsymbol{S}}_a.\boldsymbol{D}_{ac}.\widehat{\boldsymbol{S}}_c - \boldsymbol{d}_{ac}.\widehat{\boldsymbol{S}}_a \times \widehat{\boldsymbol{S}}_c \quad (4)$$

where a minus sign applies to the last term because of the permutation relationship that is specific to the DMI[77] ($\boldsymbol{d}_{ac} = -\boldsymbol{d}_{ca}$), while obviously $J_{ac} = J_{ca}$ and $\boldsymbol{D}_{ac} = \boldsymbol{D}_{ca}$. As noted by Boča and Herchel, missing this permutation relationship (*i.e.* by affecting a plus sign to the last term of Eq. 3) may lead to severe errors.

Symmetry rules apply at two different levels, (i) the local symmetry of each pair of magnetic sites rules the occurrence and orientation of the DM vector and (ii) the global (molecular) symmetry imposes relationships between the effective parameters of the different pairs (from trivial to complex, depending on the situation). For instance, if one considers a strict D_3 symmetry for the trinuclear complex (as in the reported experimental structure), the molecular C_3 symmetry axis imposes the three isotropic coupling constants to be equal ($J_{ab} = J_{bc} = J_{ac} = J$) and symmetry-related DM vectors between the three pairs of magnetic centers (these have equal norms and symmetry-related directions when expressed in the molecular frame).

One may introduce further simplifications which will be justified later on the basis of the outcomes of our calculations (see Section 3.1). We assume that:

- the main anisotropy axis (z by convention) of the three symmetric exchange tensors are parallel to the C_3 symmetry axis. This plus the occurrence of a C_3 axis leads to equal axial parameters for the symmetric exchange tensors: $D_{ab} = D_{bc} = D_{ac} = D$. Note that although we use the notation D for the sake of simplicity, it is truly a MS Hamiltonian parameter that must not be confused with the GS Hamiltonian $D_{S=3/2}$ parameter for the quartet state (in fact, here $D=2D_{S=3/2}$).
- the rhombic terms for the symmetric exchange tensors which are usually very small ($E_{ab} = E_{bc} = E_{ac} = E$) can be neglected.
- the x and y components of the DM vectors are much smaller than the z ones, as was assumed in the experimental extraction.[54] In fact, the local C_2 symmetry axis for a given pair of magnetic sites imposes that the component of the DM vector is strictly zero along this C_2 axis (it corresponds to the case for which the C_2 axis exchanges the two nuclei in the Buckingham *et al.* paper[74]). Then, out of the two remaining components, the largest one is along the molecular C_3 axis (here denoted *z*), and the small one is orthogonal to both the C_2 and C_3 axes (depending on the pair of magnetic sites that is considered, it may correspond to the *x* or *y* orientation or to a combination of both). In fact, one may even assume that the *x* and y components of the DM vectors are negligible (or, to be more precise, that their impact on the model spectrum is negligible). Lastly, if one further considers the C_3 symmetry, the *z* components of the DM vectors must also be equal, *i.e.* $d_{ab;z} = d_{bc;z} = -d_{ac;z} = d_z$ (using the correct permutation relationship).

The simplified model Hamiltonian matrix expressed in the uncoupled basis only involves three unknown parameters (J, D and d_z) and is given in Table S1 while that expressed in the coupled basis is provided in Table 1 (the transformation matrix is given in Supporting Information). In fact, with this simplified model, the quartet and doublet components are not coupled, *i.e.* the matrix is block-diagonal, with a diagonal block for the quartet and a block of doublets components which are coupled through the DMI. Finally, it is worth mentioning that this Hamiltonian has simple analytical eigenvalues, actually four doubly degenerate (Kramers' doublets) ones:

$$E_{\underset{3}{1}} = E_{\underset{4}{2}} = -\frac{3J}{4} \mp \frac{\sqrt{3}d_z}{2};\ E_{\underset{7}{5}} = E_{\underset{8}{6}} = \frac{3J}{4} \mp \frac{D}{2} \qquad (5)$$

where the upper indices for the energies correspond to the upper signs in the expressions.

H^{MS}	$\lvert\frac{3}{2},-\frac{3}{2}\rangle$	$\lvert\frac{3}{2},-\frac{1}{2}\rangle$	$\lvert\frac{3}{2},\frac{1}{2}\rangle$	$\lvert\frac{3}{2},\frac{3}{2}\rangle$	$\lvert\frac{1}{2},-\frac{1}{2}\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle$	$\lvert\frac{1}{2},-\frac{1}{2}\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle$
$<\frac{3}{2},-\frac{3}{2}\rvert$	$\frac{3}{4}J+\frac{1}{2}D$	0	0	0	0	0	0	0
$<\frac{3}{2},-\frac{1}{2}\rvert$	0	$\frac{3}{4}J-\frac{1}{2}D$	0	0	0	0	0	0
$<\frac{3}{2},\frac{1}{2}\rvert$	0	0	$\frac{3}{4}J-\frac{1}{2}D$	0	0	0	0	0
$<\frac{3}{2},\frac{3}{2}\rvert$	0	0	0	$\frac{3}{4}J+\frac{1}{2}D$	0	0	0	0
$<\frac{1}{2},-\frac{1}{2}\rvert$	0	0	0	0	$-\frac{1}{4}J$	0	$i\frac{\sqrt{3}}{2}d_z$	0
$<\frac{1}{2},\frac{1}{2}\rvert$	0	0	0	0	0	$-\frac{1}{4}J$	0	$-i\frac{\sqrt{3}}{2}d_z$
$<\frac{1}{2},-\frac{1}{2}\rvert$	0	0	0	0	$-i\frac{\sqrt{3}}{2}d_z$	0	$-\frac{1}{4}J$	0

$<\frac{1}{2},\frac{1}{2}\|$	0	0	0	0	0	$i\frac{\sqrt{3}}{2}d_z$	0	$-\frac{1}{4}J$

Table 1: Simplified Model Interaction Matrix obtained in the coupled Basis for tri-copper(II) Complexes of High Symmetry (Equilateral Triangles, *i.e.* C_3 Symmetry or Higher)

It is therefore possible to directly extract the $|d_z|$ value from the energy difference ΔE between the two spin-orbit states essentially spanned on the doublet spin-orbit free states:

$$|d_z| = \frac{\Delta E}{\sqrt{3}} \quad (6)$$

Note that $|d_z|$ directly corresponds to the *G* antisymmetric exchange constant in reference 54. One may note that one can also extract a value of $|d_z|$ (which can be different from the previous one) from the *ab initio* SOSI matrix elements between the two spin-orbit free doublet states:

$$|d_z| = \frac{2}{\sqrt{3}}\left|Im\left(\left\langle\frac{1}{2},\pm\frac{1}{2}\middle|H_{SO}\middle|\frac{1}{2},\pm\frac{1}{2}\right\rangle\right)\right| \quad (7)$$

The value of the axial parameter of the symmetric exchange tensor can be extracted as follows:

$$D = \mathrm{E}[3/2,\pm3/2]-\mathrm{E}[3/2,\pm1/2] \quad (8)$$

where E[3/2,±3/2] and E[1/2,±1/2] are the energy of the spin-orbit states with a large projection on the M_S = ±3/2 and M_S = ±1/2 components of the quartet, respectively.

Finally, the isotropic magnetic coupling *J* value can be extracted from the energy difference between the mean energies of the quartet block and those of the doublet ones:

$$J = \frac{2}{3}\left(\overline{\mathrm{E}[3/2,\mathrm{Ms}]} - \overline{\mathrm{E}[1/2,\mathrm{Ms}]}\right) \quad (9)$$

It is also possible to extract the pure electronic magnetic coupling from the energy difference between the quartet and degenerate doublets spin-orbit free states.

2.2 Strategy of calculation and computational information

The tris(μ- hydroxy)tri-copper(II) complex is represented on Figure 1. Its reported experimental structure displays a D_3 molecular symmetry point group.[53] The copper ions and the hydroxo groups are coplanar and the C_2 axes are directed along the O-H bonds of the hydroxo groups. The Cu-Cu distances are 3.64 Å and the $\widehat{CuOCu}$ angles are 144°. The full complex is not planar and the deviation to this planarity is introduced by the BDED (N,N'-di-tert-butyl-ethylenediamine) bidentate ligands. The corresponding coordinates are given in Table S2.

As this complex is of relatively large size, we had to choose a computational strategy allowing to introduce both non-dynamic and dynamic correlation effects which are known to be crucial for the study of magnetic anisotropy. The strategy includes three kinds of calculations:

- We first performed the less computationally demanding calculations (see below for details) on the complete molecule denoted **1**(3Cu) as it contains three Cu(II)magnetic centers.
- Since the model Hamiltonian involves only bicentric interactions and in order to verify that there are no interactions involving more than two magnetic centers, we replaced one of the Cu(II) with a Zn(II), thus introducing a diamagnetic center. This system is called **1**(2Cu,1Zn). Beyond the interest of this substitution for the validation of the model, this also allowed us to perform more sophisticated calculations on the simplified system and to check the transferability of the extracted parameters from **1**(2Cu,1Zn) to **1**(3Cu).
- Finally, we studied a model complex in which the BDED ligands were replaced by NH_3 groups. The corresponding XYZ coordinates are given in Table S3. This smaller model system allowed us to perform calculations accounting for more correlation effects, on both the tri-magnetic-site system **2**(3Cu) and on the bi-magnetic-site system **2**(2Cu,1Zn).

As we will see in the section dedicated to the results, the comparison of the extracted parameters at all levels of calculations and for all systems demonstrates the relevance of this strategy.

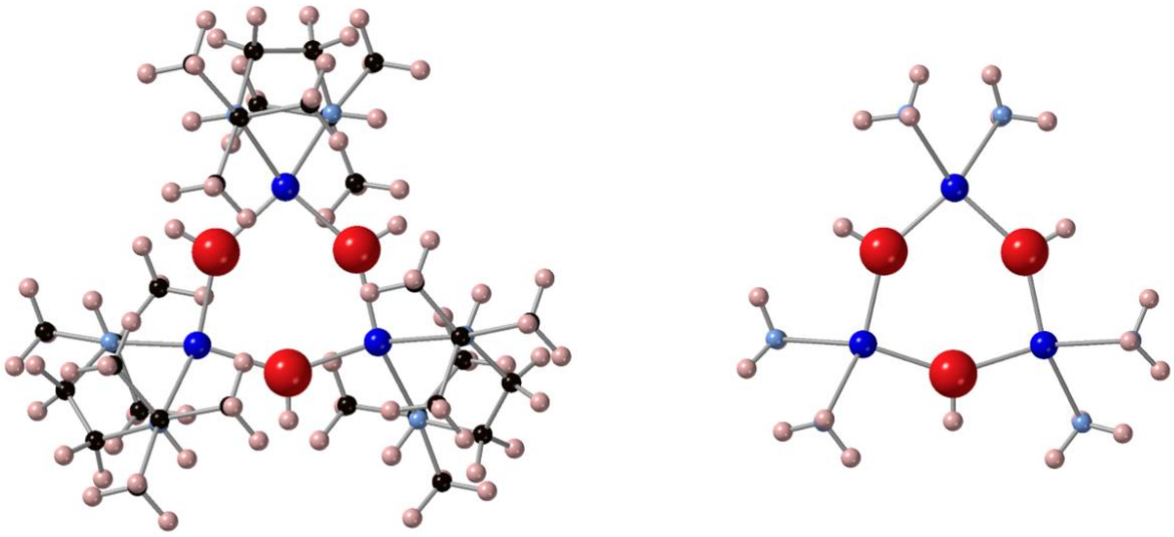

Figure 1: Ball and stick representations of the two parent structural modecules, namely **1**(3Cu) and **2**(3Cu) (see text). Color code: dark blue stands for Cu, red for O, light blue for N and light pink for H.

As the magnetic anisotropy has a relativistic origin, the spin-orbit coupling (SOC) must be computed. A two-step procedure of calculations that has successfully been used for the study of many similar transition metal complexes[16] has been used. In a first step, a set of non-relativistic or scalar-relativistic states, *i.e.* spin-orbit free states, is computed. For the DMI calculation, the minimal set consists of the states that best matches the spin eigenstates of the Heisenberg-Dirac-van Vleck Hamiltonian. For instance, for a system involving two Cu(II) sites,

this set consists of one triplet and one singlet,[35] while in the case of three Cu(II) sites it consists of one quartet and two doublets. Computing the symmetric exchange tensors requires to calculate additional electronic states still generated by the d^9-d^9-d^9 configuration, *i.e.* d orbitally-excited states.[34] In the second step, the SOC[78] between all *Ms* components of these electronic states is computed and the so-obtained Spin-Orbit State-Interaction (SOSI)[79,80] matrix is diagonalized to get the spin-orbit states and their energies. The diagonal elements of the SOSI matrix will be obtained at two different levels: i) the Complete-Active-Space Self-Consistent Field (CASSCF) level which simultaneously optimizes the coefficients of the various determinants of the spin-orbit free states and the molecular orbitals for all these states in an average manner (SA-CASSCF),[81] ii) the n-electron valence state perturbation theory (NEVPT2)[82–84] level which adds the energetic effects of dynamic correlation up to the 2nd order of perturbations. Usually the spin-orbit free states in which the SOSI matrix is spanned are the CASSCF ones. However, and as it will be shown here, quasi-degenerate NEVPT2 (QD-NEVPT2)[85] states can be used to account for effects of dynamic correlations on the wave functions. Unless specified otherwise by a "QD" flag in the tables, the standard strongly-contracted version of NEVPT2 has been employed to compute the correlated electronic energies. Also, note that when QD-NEVPT2 is explicitly mentioned ("QD" flag), both the QD-NEVPT2 correlated electronic energies and decontracted wave functions are used to compute the SOCI matrix. Depending on the studied systems, several active spaces have been considered. For the two-magnetic-site systems, either **1**(2Cu,1Zn) or **2**(2Cu,1Zn), we have defined three different active spaces: i) the minimal active space contains 2 electrons in 2 orbitals *i.e.* CAS(2,2) generating one singlet and one triplet magnetic states, ii) the intermediate active space distributes 6 electrons in 4 orbitals *i.e.* CAS(6,4) generating 4 singlet and 4 triplet magnetic states (which can be reduced to 3 and 3, respectively, if only the ground and singly-excited configurations are considered), iii) the extended active space spreads all d electrons in all d orbitals *i.e.* CAS(18,10) generating 25 triplet and 25 singlet magnetic states. Note that here the magnetic states denote the open-shell states belonging to the d^9–d^9 configuration (*i.e.* the open-shell "neutral" states). For the three-magnetic-site systems, either **1**(3Cu) or **2**(3Cu), we have considered two active spaces: i) the minimal active space contains 3 electrons in 3 orbitals CAS(3,3) generating one quartet and two doublet magnetic states, ii) the extended active space distributes 27 electrons in 15 orbitals *i.e.* CAS(27,15) generating 125 quartet and 250 doublet magnetic states.

All the calculations reported in this article have been performed with ORCA v. 4.2.1.[86] The Douglas-Kroll-Hess Hamiltonian[87–90] has been applied to account for scalar relativistic effects. Consequently, specific basis sets, have been used, namely of the DKH-def2 type (these are actually recontracted versions of the non-relativistic def2 basis sets[91]): DKH-def2-TZVP for Cu and Zn atoms, DKH-def2-SVP for O, N and C atoms and DKH-def2-SV for H atoms. The def-TZVP/C auxiliary basis sets[92] have been used for all the atoms. Note that the corresponding SOC Hamiltonian has been used (in other words, the ORCA picture change keyword[93] has been used).

3 Results and Discussion

3.1 Validity of the Model Hamiltonian and Transferability of the Extracted Parameters

It is interesting to check both the validity of the model Hamiltonian and the transferability of the extracted parameters in the **1**(3Cu) and **1**(2Cu, 1Zn) models for several reasons: i) the

Hamiltonian proposed in Equations (2) and (4) has only two-center operators. The extraction of the Hamiltonian matrix from *ab initio* calculations will allow to validate this assumption, ii) the transferability of the parameters will ensure that the *ab initio* description is correct or at least well balanced and if so, more advanced calculations will be performed on the smaller system, iii) finally, and as mentioned earlier, there is an additional subtlety when extracting the DMI from calculations performed on trinuclear systems: the permutation relationship. If it is correctly applied, one may extract $|d_z|$ according to Equations (6) or (7). Otherwise, if for instance one considers that $d_{ab,z} = d_{bc;z} = d_{ac;z} = d_z$, then $|d_z| = \sqrt{3}\Delta E$, in contradiction to Eq. (6) ($|d_z| = \frac{\Delta E}{\sqrt{3}}$) . As a matter of fact, a correct application of the permutation relation is expected to coincide with a good transferability of the extracted parameters because of the locality of the underlying interactions.

The validation of the Hamiltonian will also allow us to check the relevance of the simplifications introduced in section 2.1.2 based on symmetry considerations. For this, we used the SOSI results obtained with the extended CAS(27,15)SCF (27 electrons within 15 orbitals) energies, in the **1**(3Cu) molecule to build the effective Hamiltonian matrix given in Table 2. Comparing the simplified analytical model matrix (Table 1) to the numerical effective matrix (Table 2) shows that the main features of the effective Hamiltonian can be accounted for by only three model parameters, namely *J*, *D* and $|d_z|$. The model Hamiltonian and our simplifications are therefore perfectly appropriate as well as the use of Equations (5), (6) and (8).

H^{MS}	$\|\frac{3}{2},-\frac{3}{2}\rangle$	$\|\frac{3}{2},-\frac{1}{2}\rangle$	$\|\frac{3}{2},\frac{1}{2}\rangle$	$\|\frac{3}{2},\frac{3}{2}\rangle$	$\|\frac{1}{2},-\frac{1}{2}\rangle$	$\|\frac{1}{2},\frac{1}{2}\rangle$	$\|\frac{1}{2},-\frac{1}{2}\rangle$	$\|\frac{1}{2},\frac{1}{2}\rangle$
$\langle\frac{3}{2},-\frac{3}{2}\|$	46.26	0.00	0.00	0.00	–0.09–0.15i	0.02+0.01i	–0.15+0.09i	–0.01+0.02i
$\langle\frac{3}{2},-\frac{1}{2}\|$	0.00	44.29	0.00	0.00	0.00	–0.09–0.15i	0.00	–0.15+0.09i
$\langle\frac{3}{2},\frac{1}{2}\|$	0.00	0.00	44.29	0.00	–0.09+0.15i	0.00	–0.15–0.09i	0.00
$\langle\frac{3}{2},\frac{3}{2}\|$	0.00	0.00	0.00	46.26	–0.02+0.01i	–0.09+0.15i	0.01+0.02i	–0.15–0.09i
$\langle\frac{1}{2},-\frac{1}{2}\|$	–0.09+0.15i	0.00	–0.09–0.15i	–0.02–0.01i	10.79	0.00	–10.79i	0.00
$\langle\frac{1}{2},\frac{1}{2}\|$	0.02–0.01i	–0.09+0.15i	0.00	–0.09–0.15i	0.00	10.79	0.00	10.79i
$\langle\frac{1}{2},-\frac{1}{2}\|$	–0.15–0.09i	0.00	–0.15+0.09i	0.01–0.02i	10.79i	0.00	10.79	0.00
$\langle\frac{1}{2},\frac{1}{2}\|$	–0.01–0.02i	–0.15–0.09i	0.00	–0.15+0.09i	0.00	–10.79i	0.00	10.79

Table 2: Effective interaction matrix obtained for the 1(3Cu) complex at the SOCI Level based on the CASSCF(27/15) electronic energies and states (elements are in cm^{-1}).

Let us now comment the results reported in Table 3. In the **1**(3Cu) molecule, two active spaces were considered, i) the extended active space CAS(27,15) and ii) the minimal active space CAS(3,3). In the first case, all states resulting from the d^9-d^9-d^9 configuration, *i.e.* 125 quartets and 250 doublets, have been computed. From this calculation, since orbitally-excited states are considered, the *D* parameter is accessible. With the minimal active space, only the states reproduced by the model Hamiltonian (Eq. 3), *i.e.* one quartet and two doublets, are included in the SOSI calculation; hence the *D* value that comes from the interactions with neglected excited states is not relevant and has not been reported (in fact, the value is forced to zero with this setup). In both cases, the isotropic coupling parameter *J* and the $|d_z|$ component of the DM vector can be extracted. For *J* and $|d_z|$, two values appear in Table 3: *J* is extracted both after the SOSI calculation and at the spin-orbit free level (value in brackets) and $|d_z|$ is extracted

either from the effective Hamiltonian theory[40] or directly from the SOSI matrix (Equation (7), value in brackets).[39]

With the minimal active space, the two values for both J and $|d_z|$ are strictly identical. This is expected because both the SOC polarization of the J value and the second-order SOC contribution to $|d_z|$ require the introduction of higher-energy excited states and/or the use of an extended active space. When using the extended active space and considering in the SOSI calculation 125 quartets and 250 doublets, one can observe two effects:

- SOC slightly affects the effective parameter J with a magnitude that is similar to what has been observed in dinuclear dicopper(II)[43] and dinickel(II)[35] model systems.
- Orbitally excited states moderately modify the value of $|d_z|$, which is in fact reduced in this case. In a previous study, we have shown that this effect can be much more pronounced in the case of on-site first-order SOC.[40] In the system under study, the first orbitally-excited state is about 1eV higher in energy than the doublet ground state. Hence, it is not that surprising to observe here a smaller effect on the magnitude of the axial component of the DMI, especially given the expected range of acceptable SOC constants of a copper(II) ion (a stronger effect could always occur for a much heavier ion).

As demonstrated in reference[39], the use of a minimal active space with a common set of orbitals (SA-CASSCF) for the three lowest states should lead to zero values of the DMI. Nevertheless, these values have been reported here (i) to illustrate the transferability of the extracted parameters from **1**(2Cu, 1Zn) to **1**(3Cu) and more importantly (ii) to warn the community about this issue.

A final point that deserves comments before discussing the transferability of the extracted parameters concerns the role of dynamic correlation on J. According to the experiment (beware of the –2 factor!), a value of J of about 210 cm^{-1} is expected.[53,54] It is clear that the SA-CASSCF method fails to achieve the correct order of magnitude. NEVPT2 improves the picture, but still provides significantly underestimated values (about 30% of the experimental value). This is something that is often observed,[34,35] and has been rationalized in detail by Calzado et al.[94–96] (see also the review by Malrieu et al.[55]).

Table 3 shows that the extracted parameters transfer well from **1**(2Cu, 1Zn) to **1**(3Cu), which makes us confident in the results obtained for **1**(2Cu, 1Zn). This is important for the discussion regarding the value of $|d_z|$, especially with respect to the correct application of the permutation relation. With the extended active spaces, CAS(27,15) or CAS(18,10) (depending on the studied model), transferability is indeed ensured by the correct application of the relation. Nevertheless, it is amusing to note that if we do not apply it correctly we obtain for the complex **1**(3Cu) (with the large active space) a $|d_z|$ value of 37.5 cm^{-1}, in perfect agreement with experiment:[54] $|d_z|$=36 cm^{-1} ! At this stage, however, we have unfortunately only reached one third of the experimental value. Further calculations, in particular including dynamic correlations on the extended CAS are necessary but unfortunately impossible on the compound **1**(3Cu). Note that for **1**(2Cu, 1Zn) though, additional calculations are reported in Table S4. However, the set of calculations that could be performed is not sufficient to make a complete methodological study and validate a computational strategy to compute the DMI. Therefore, we have chosen to make a structural simplification, allowing us to test more calculation setups (*vide infra*). Table S4 is thus essentially of interest for computational chemists.

1(3Cu)						**1**(2Cu, 1Zn)					
CASSCF	States[a]	$\mathbf{E}_{el}$	*J*	*D*	$\lvert d_z \rvert$	CASSCF	States	$\mathbf{E}_{el}$	*J*	*D*	$\lvert d_z \rvert$
3/3	1Q, 2D	SCF	27.7 (27.7)	NA[b]	0.8 (0.8)	2/2	1T, 1S	SCF	33.8 (33.8)	NA	0.8 (0.8)
		PT2	58.5 (58.5)	NA	0.8 (0.8)			PT2	65.6 (65.6)	NA	0.8 (0.8)
27/15	125Q, 250D	SCF	23.0 (23.7)	2.0	12.5 (13.4)	18/10	25T, 25S	SCF	24.2 (25.0)	1.8	12.3 (13.2)

[a] Q, D, T and S respectively stand for quartet, doublet, triplet and singlet.
[b] NA stands for not applicable.

Table 3: Values of J, D and |dz| (in cm-1) extracted from the effective Hamiltonian theory and SOSI calculations performed either using the CASSCF (noted SCF) or NEVPT2 (noted PT2) electronic energies ($\mathbf{E}_{el}$) for both **1**(3Cu) and **1**(2Cu,1Zn). The spin-orbit free J value and the $|d_z|$ value extracted directly from the SOSI matrix appear in brackets.

3.2 Towards more advanced calculations on a model complex and methodological study

As already mentioned, in the real complex, it is quite difficult to push the calculations much further than what has been done. Therefore, it may make sense to simplify the ligands, compare the extracted parameters to those of the real complex, and then perform more demanding calculations on the simpler structural model with NH_3 groups instead of BDED ligands by (two NH_3 per DBED unit). The results are reported in Table 4. Calculations being less demanding in this smaller system than in the real complex, NEVPT2 calculations which account for dynamic correlations could be performed on the extended active space for both the tri-copper(II) structural model and the corresponding model system with only two actual magnetic sites. The comparison of the results on **1**(3Cu) vs. **1**(2Cu, 1Zn) and **2**(3Cu) vs. **2**(2Cu, 1Zn) , shows as before a good transferability of the parameters from the bi-magnetic-center system to the tri-magnetic-center one. Moreover, the values obtained for the simpler model complex are in very good agreement with those of the real complex. One can therefore conclude that both **2**(3Cu) and **2**(2Cu, 1Zn) are good models to extract the parameters of **1**(3Cu).
The results obtained show that dynamic correlations brought by NEVPT2 have a very limited impact on the value of $|d_z|$. From a methodological point of view, the next step consists in correcting the well-known error of PT2 methods linked to the wave function contraction. We have indeed shown in the paper[39] that the use, in the SOSI step, of functions resulting from a variational calculation could dramatically affect the DMI value. Multi-Reference Configuration Interaction (MRCI) type calculations are unfortunately not feasible for the moment on the studied system. Hence, we have used an alternative method: the "decontracted" QD-NEVPT2[85] approach which revises the CASSCF wave functions by taking linear combinations of them. The results, reported in Table 5, (see in particular the last two lines that can be considered as our most accurate results), show an increase in $|d_z|$ of around 50% (by comparison which the appropriate values reported in Table 4), demonstrating again the important role of the wave functions in the calculation of DMI. Besides, one may note that the decontraction provided by QD-NEVPT2 is not of any help in the calculation of *J*'s. As discussed elsewhere, a variational treatment is indeed required.[55,94–96]

		2(3Cu)						**2**(2Cu, 1Zn)			
CASSCF	States[a]	$\mathbf{E}_{el}$	*J*	*D*	$\|d_z\|$	CASSCF	States	$\mathbf{E}_{el}$	*J*	*D*	$\|d_z\|$
3/3	1Q, 2D	SCF	26.0 (26.0)	NA[b]	0.8 (0.8)	2/2	1T, 1S	SCF	32.0 (32.0)	NA	0.8 (0.8)
		PT2	55.2 (55.2)	NA	0.8 (0.8)			PT2	62.1 (62.1)	NA	0.8 (0.8)
27/15	125Q, 250D	SCF	21.5 (22.3)	2.2	12.8 (13.7)	18/10	25T, 25S	SCF	22.7 (23.6)	2.0	12.7 (13.6)
		PT2	55.9 (56.5)	1.9	13.2 (13.7)			PT2	58.2 (59.2)	1.6	13.0 (13.6)

Table 4: Values of *J*, *D* and $|d_z|$ (in cm^{-1}) extracted from the effective Hamiltonian theory and SOSI calculations performed either using the CASSCF (noted SCF) or NEVPT2 (noted PT2) electronic energies ($\mathbf{E}_{el.}$) for both **2**(3Cu) and **2**(2Cu,1Zn). The spin-orbit free *J* value and the $|d_z|$ value extracted directly from the SOSI matrix appear in brackets.

Finally, for the theorist reader, it is interesting to note that an intermediate active space, in this case CAS(6,4) which includes in the active space only the *d* orbitals which are strongly mixed in the magnetic orbitals, allows one obtain results of comparable quality to those of the extended active space. The results obtained for compound **2**(2Cu,1Zn) with the two active spaces CAS(6,4) and CAS(18,10) are reported in Table 5 for comparison. This procedure reduces the computational cost of DMI and seems very promising for the study of large systems. Moreover, it must be noted that convergence of intermediate active spaces for systems with multiple magnetic centers can be tricky (we have not been able to converge the analogous active space correctly for the **2**(3Cu) complex). We therefore want to emphasize here that the use of model systems with fewer magnetic sites is particularly interesting for converging intermediate active spaces. A more detailed discussion is provided in Supporting Information.

	2(2Cu, 1Zn)					
CASSCF	States[a]	$\mathbf{E}_{el}$	$\mathbf{\Psi}_{el}$	*J*	*D*	$\|d_z\|$
6/4	3T, 3S	SCF	SCF	27.0 (27.8)	2.0	13.1 (13.5)
6/4	3T, 3S	PT2	SCF	58.1 (58.9)	1.7	13.3 (13.5)
6/4	3T, 3S	PT2	QD	58.1 (58.9)	1.7	20.7 (21.1)
18/10	25T, 25S	PT2	QD	58.1 (59.2)	2.0	19.4 (19.9)

Table 5: Values of *J*, *D* and $|d_z|$ (in cm^{-1}) extracted from the effective Hamiltonian theory and SOSI calculations performed either using the CASSCF (SCF) or CASPT2 (PT2) electronic energies ($\mathbf{E}_{el.}$) and the and the CASSCF or QD-NEVPT2 decontracted wavefunction for **2**(2Cu,1Zn). The spin-orbit free *J* value and the $|d_z|$ value extracted directly from the SOSI matrix appear in brackets.

Last but not least, one can represent the orientations of the DM vectors, allowing one to visualize their actual deviations with respect to the C_3 (pseudo-)symmetry axes (here chosen as the *z* Cartesian axis). In practice, the three components of the DMI can be extracted in any coordinate frame from *ab initio* calculations that are performed with two active copper(II) sites. Locally, a C_2 symmetry axis allows exchange of the two copper(II) centers. Therefore,

according to symmetry, the DMI component along this axis is zero. If this local C_2 axis corresponds to the x Cartesian axis, only the y and z components of the DMI are non-zero. Once one DMI vector is defined, the remaining two are generated by symmetry. For representation purposes, we have depicted arrows whose origins are arbitrarily set at the middle of the corresponding Cu-Cu segments. The extraction performed on the different systems or by means of different calculations (except the minimal CAS) produces vectors orientations that are not distinguishable by the naked eye. Figure 2 represents those obtained on the **2**(2Cu,1Zn) model by means of the SOSI method using CAS(18,10)NEVPT2 energies. Clearly, the z-component dominates, which justifies our special focus on this component. One should stress again that this is a strong argument in favor of theoretical studies of the DMI: we can determine its orientation and not only its magnitude.

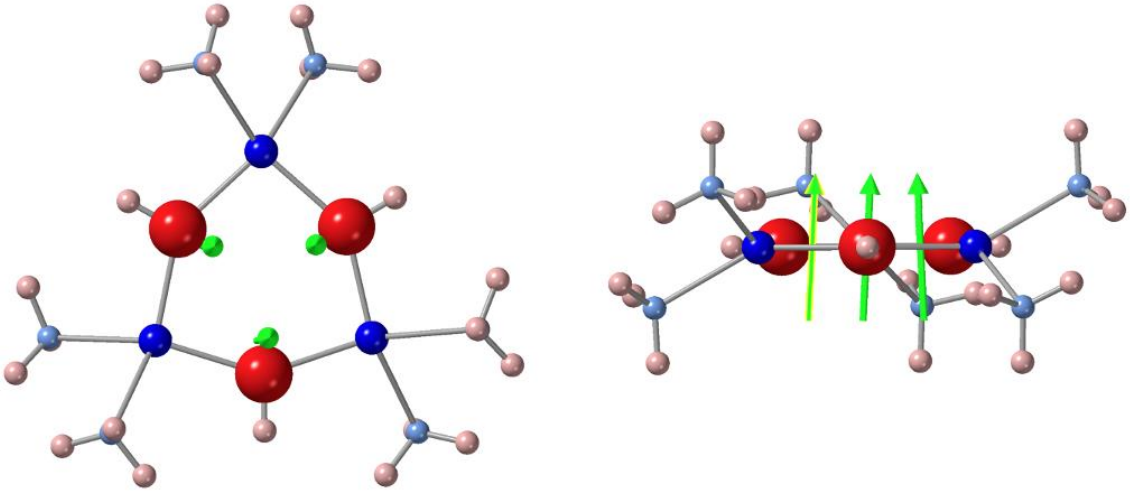

Figure 2: Representation of the orientations of the Dzyaloshinskii-Moriya vectors (green arrows) based on a SOSI calculation using the QD-NEVPT2 CAS(18/10)SCF states and energies for **2**(2Cu, 1Zn). The two other vectors are generated by symmetry. Left: the C_3 axis is perpendicular to the paper plane and the C_2 axes are in it. Right: the C_3 axis is vertical in the paper plane and one C_2 axis is perpendicular to it.

4. Summary and perspective

Capitalizing on recent studies,[39,40] we proposed a computational approach to study the DMI in a real trinuclear copper complex based on state-of-the-art *ab initio* calculations. By assessing the role of specific computational degrees of freedom (*e.g.* the active space, the use of contracted vs. uncontracted wave functions for computing the SOCI matrix), we have paved the way for future methodological studies of interest for the theoretical chemistry community. Even if we have used the idealized D_3 structure provided by X-Ray performed at 140K, we have already reached three important general conclusions for the extraction of the MS Hamiltonian parameters in molecular complexes:

- The standard MS Hamiltonian that involves only bicentric operators is perfectly suited to capture all the features of the effective Hamiltonian. In other words, the MS Hamiltonian (equation 4) has now been validated based on subtle and demanding *ab initio* calculations.

- We have demonstrated the transferability of the computed DMI parameters from clusters with only two active copper(II) sites to the ones with three active ones. This has two main implications, (i) the local nature of the DMI is confirmed and (ii) the permutation relationship has now been validated based on *ab initio* calculations. Of course, this opens the way for fragment calculations of even larger polynuclear systems. More importantly and also more generally, one should definitely apply the permutation relationship in the interpretation of experimental data, which also means that one should treat with care the contracted expressions of the MS Hamiltonian based on a summation of the DMI terms (e.g. $\sum_{ij} \boldsymbol{d}_{ij}.\widehat{\boldsymbol{S}}_i \times \widehat{\boldsymbol{S}}_j \neq \boldsymbol{d}_{ab}.\widehat{\boldsymbol{S}}_a \times \widehat{\boldsymbol{S}}_b + \boldsymbol{d}_{bc}.\widehat{\boldsymbol{S}}_b \times \widehat{\boldsymbol{S}}_c - \boldsymbol{d}_{ac}.\widehat{\boldsymbol{S}}_a \times \widehat{\boldsymbol{S}}_c$ in triangular systems)."

- The orientation and the large amplitude of the DMI in this complex have been rationalized. As shown in the analytical derivation presented in our previous articles concerning the physical origin of the DMI, it is the mixing of the d_{x2-y2} and d_{xy} orbitals that triggers i) the occurrence of the d_z component and ii) the large magnitude of the DMI. Indeed, this hybridization of the spherical harmonics d_{2+} and d_{2-} leads to the largest $l_Z s_Z$ coupling (which is proportional to the $|m_l|$ values) between the ground and first excited states that can be obtained by mixing these two orbitals. In this respect, the triangular geometry which forces this mixing is in fact responsible for the large DMI. Moreover, as the mixing with the other d orbitals is particularly small, the other components, d_x and d_y, are particularly weak.

Concerning the comparison between experimental and theoretical values of the DMI, we believe that we have reached a reasonable agreement. As this complex is likely to be non-equilateral, as pointed out in ref [54] to explain NMR spectrum, the experimental estimate is in fact an upper bound of the DMI. Indeed, the experimental value comes from the doublets energy difference which would analytically contain both the difference between the two magnetic couplings of an isosceles triangle and the DMI. On the other hand, the decontraction of the wavefunction which has shown to increase the DMI, is not complete at the QD-NEVPT2 level of calculation and it is likely that a variational method (as DDCI) would lead to a slightly enlarged value of the DMI. In other words, our best estimate is a lower bound of the DMI, meaning that both current experimental and theoretical data are actually compatible.

In fact, our approach is general and does not require any symmetry of the triangle nor any specific type of isotropic magnetic couplings for consistent and independent extraction of all the effective parameters of the MS Hamiltonian. Note that we have illustrated its power based on a D_3 symmetric structure for the sake of pedagogy. The results obtained are in reasonable agreement with the experimental value (orientation and order of magnitude). Therefore, we confirm by theory the occurrence of a large DMI in this system, even though two points still deserve to be discussed for reaching finer theoretical and experimental estimates of the DMI in this system:

- The extraction of the experimental value relies on the splitting of the doublet energies.[54] The crystal structure is considered to be of symmetry D_3, while it could be that by averaging effects, a lowering of the symmetry would not be detected.[30] Furthermore, the attempts of experimentalists to extract the DMI with a broken symmetry model only considered the breaking on *J* and not on the DMI. Test calculations based on density functional theory (DFT) have shown that in the gas phase, even the high spin state

spontaneously lowers its symmetry to form an isosceles triangle instead of an equilateral one. Then, one can strongly expect that a low spin state will do so as well (geometry optimization becoming problematic for the doublet since the DFT solution is spin symmetry broken). In any case, if such a symmetry lowering occurs, part of the splitting of the doublet energies would come from this effect leading to a lower value of the DMI in comparison to the one currently extracted from experiments, *i.e.* part of the splitting attributed to $|d_z|$ would come from the energy difference between the spin-orbit free doublets. Note that the $|d_z|$ value is expected to be less critically dependent on the symmetry lowering, unlike J, which has been confirmed by test calculations (not reported). A complete structural study would require to account for environment effects and maybe even dynamics, which is clearly out of the scope of the present paper.

- The dependence of the theoretical results on the level of computation, in particular the importance of accounting for correlation effects on wave functions, suggests that additional studies of real compounds are needed to firmly establish the level of computation required to address DMI. To date, there are very few molecular compounds for which experimental information on DMI are available, yet these values are necessary to produce benchmark calculations.

Finally, we strongly believe that further joint theoretical/experimental efforts are needed at this stage to accurately determine the DMI in real complexes, with tri-copper(II) complexes most likely being excellent showcases for this purpose. The extension of this work to Cr_3 or Fe_3 triangular systems, although theoretically possible, is not at all straightforward in practice because of the size of the model space of the MS Hamiltonian on the one hand and because of the number and ranks of the anisotropy tensors on the other hand.[32,73,97] For this reason, we consider that research on S = 1/2 spin triangles should be pursued before tackling these even more difficult cases, which we hope to be able to handle in a reasonable time.

Supporting information available. Simplified model matrix in the uncoupled basis, XYZ coordinates of the **1**(3Cu) and **2**(3Cu) systems, additional calculations on the **1**(2Cu,1Zn) model system and discussion on the intermediate active space for the bi-magnetic-center models (PDF).

The authors declare no competing interest.

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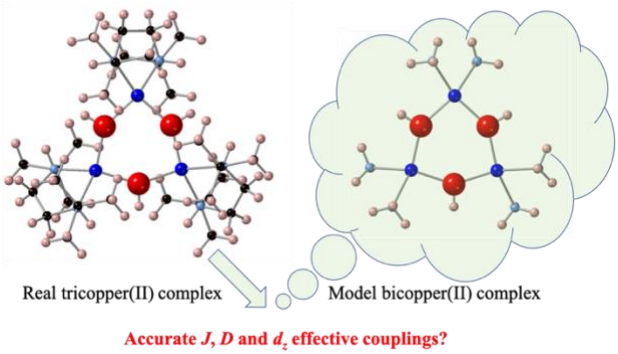

The description of the magnetic properties of copper(II) triangles is often ambiguous. In this article, we show that the combination of spin-orbit configuration interaction and the effective Hamiltonian theory leads to a non-ambiguous extraction of key terms of the multispin Hamiltonian: isotropic exchange, symmetric exchange and more importantly antisymmetric exchange. Several computational and structural biases may occur and while we actually report state-of-the-art *ab initio* calculations, we conclude by formulating current challenges for the community.