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Evaluation of magnetic terms in Cu$_4$O$_4$ cubane-like systems from selected configuration interaction calculations: A case study of polynuclear transition-metal systems

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We present the evaluation of magnetic terms in a Cu$_4$O$_4$ cubane-like system from truncated CI calculations, as a case study of polynuclear transition-metal complexes. We employ a new excitation selected configuration interaction (EXSCI) method based on the use of local orbitals. Taking advantage of the locality and then of the fact that the interactions vanish when the distance is large, the dimension of the CI is largely reduced. To the best of our knowledge these CI calculations are the largest one performed for polynuclear transition metal systems so far. The results show the presence of two leading ferromagnetic interactions between bridged Cu ions. Also the interactions between the unbridged Cu ions are ferromagnetic, but very weak, in contrast to the experimental data. The nature and amplitude of all the computed interactions are consistent with the relative orientation of the magnetic orbitals in the molecule, and correctly reproduce the susceptibility versus temperature curve. Our results indicate that it is possible to obtain similar fittings with sets of parameters representing different physical effects and put in evidence the drawbacks of the fitting based on oversimplified magnetic models. In this context, the presented computational strategy can be considered as a useful tool to help in the interpretation of the magnetic data and the validation of the magnetic interaction model in the polynuclear magnetic systems. © *2011 American Institute of Physics.* [doi:10.1063/1.3659141]

I. INTRODUCTION

Polynuclear transition-metal complexes have been receiving much attention over the years due to their role in the field of molecular devices.[1–4] Their properties result from the presence of unpaired electrons in the system and the interactions established among them. In fact these systems are involved in processes such as the molecular conductivity, rectification, switching, molecular wires, single-molecule transistors, and molecular magnetic memories, with a special emphasis on single-molecule magnets. Since the macroscopic properties observed in these systems come from a high number of local interactions among all the active centers (magnetic and electronic couplings, hole repulsions, *d–d* repulsions, ...), a big effort has been dedicated to the evaluation, rationalization, and understanding of the factors governing the amplitude and nature of these local interactions. However, the determination of the leading magnetic interactions in polynuclear systems is not an easy task, it faces some problems both from experimental and theoretical points of view. The experimental evaluation of the coupling constants first needs to establish a magnetic model Hamiltonian which takes into account the interactions among unpaired electrons. The number of local interactions increases with the number of active centers, in such a way

that a direct evaluation of all the local terms is impossible, even when the spin Hamiltonian is reduced to the isotropic interactions. In general, the experimental evaluation of the coupling constants in these systems requires to assume some leading interactions and to neglect the rest. This fixes a model of magnetic interactions, which can only be validated from the numerical fitting of thermodynamic and/or spectral properties. Since the model contains several parameters, larger uncertainty than in common binuclear systems is expected.

In this context, independent and as accurate as possible evaluations of the coupling constants would be welcome, in order to clarify the mechanisms governing the local coupling and the collective properties. But dealing with these systems is not only difficult from an experimental point of view, in fact, transition metal-based polynuclear molecular systems constitute a real challenge for quantum chemistry methods for several reasons. These compounds, even when molecular, present several transition metal centers, with several *d* active electrons. Furthermore, they are composed of extended and polytopic ligands, which complete the coordination sphere of the metal atom and allow a significant amount of control over the formation of clusters with a desired geometry. Most of these ligands impose a low symmetry. Together with restrictions due to the size and symmetry, there is an additional constraint related to the necessity to explicitly deal with electron-correlations effects due to the quasi-degenerate *d* electrons. Moreover, most of the technological applications are related to spin-orbit coupling effects.

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Nowadays, *ab initio* multireference configuration interaction (CI) techniques can be considered as the best tools for obtaining correct descriptions of the electronic configurations of the states involved in the coupling, as well as for determining with numerical accuracy the amplitude of the magnetic coupling constants.[5–7] Among them, the difference dedicated CI (DDCI) approach by Miralles *et al.*[8,9] has been particularly successful in evaluating magnetic coupling constants in molecular and solid state magnetic materials, with a remarkable good agreement with experiment.[10–19] In this variational method, a truncation of the CI space is performed, based on the perturbative arguments in such a way that the CI expansion only contains the determinants that play a role in the energy difference of the states involved in the coupling. Even when the DDCI approach makes possible a considerable computational time saving with respect to conventional single and double excitation configuration interaction (SDCI) calculations, it is still too demanding for a system containing several metallic centers and extended ligands (most of its applications have been restrained to binuclear complexes), and additional truncation schemes need to be considered. One possibility is to take profit of the locality of the dynamical electron correlation effects to introduce important truncations of the CI space. In this context, Maynau and co-workers[20,21] have recently proposed a new method of selection of the configurations to be included in a CI calculation: the EXSCI method, based on the use of localized orbitals. They proposed to retain only those excitations which were among the "interacting local orbitals," using as threshold the value of the corresponding exchange integral. This criteria makes possible a considerable reduction of the size of the matrix to be diagonalized, and consequently to deal with larger and more complex systems.

The procedure is completely general, and can be applied to any type of system and/or any type of CI space. Here we have employed this procedure to evaluate all the magnetic terms in a cubane-like Cu(II) Cu_4O_4 system, described in Sec. II, to check the consistency of the reported experimental fitting. The theoretical approaches used to evaluate the magnetic terms are presented in Sec. III, and the computational details in Sec. IV. The resultant estimates of the magnetic terms are employed to simulate the susceptibility $\chi T(T)$ curves as shown in Sec. V. Finally, the main conclusions are summarized in Sec. VI. Our results put in evidence the drawbacks of the fitting based on the oversimplified magnetic models and the importance of the theoretical evaluations to reveal the physics of the large systems, as a helpful and complementary tool to the experimental fittings.

II. DESCRIPTION OF THE SYSTEM

Among polynuclear transition-metal complexes, much of the attention has been dedicated to high-nuclearity copper(II) complexes which are not only relevant in the field of molecular magnetism, but also to the active-site properties of multinuclear copper oxidases.[22–25] The flexibility of the coordination sphere around Cu(II) combined with the use of multidentate ligands have produced a rich variety of Cu(II) complexes of different nuclearity with a large structural diversity, intimately related to their magnetic properties.[26] Copper(II) cubanes (Cu_4O_4) constitute one of the simplest and most common cases of such multinuclear Cu(II) complexes, of interest
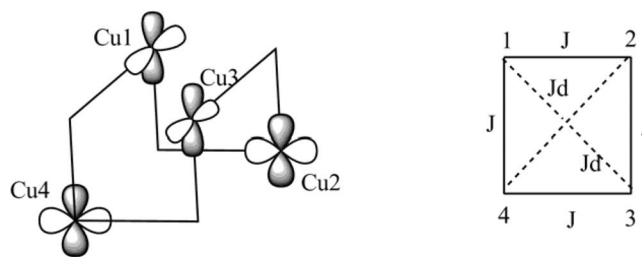
SCHEME 1. (Left) Open cubane structure, only showing the short Cu–O distances. The relative orientation of the Cu $3dx^2$-y^2 orbitals is also shown. (Right) The imposed S_4 symmetry of the cubane is projected onto a square.

for their magnetic properties, which are tunable by making small variations in the structural parameters.[27–33] Copper(II) cubanes can show dominant ferromagnetic as well as antiferromagnetic exchange interactions depending on the specific geometry in the Cu_4O_4 core. They have been classified in literature according to the number of short and long Cu–Cu distances[34–37] as 2+4 class (or type I), 4+2 class (or type II), and 6+0 class (or type III).

Our study focuses on a tetranuclear Cu(II) complex $[Cu_4(hpda)_4][ClO_4]$ H_2O with Hhpda = N-(2-hydroxyethyl)-1,3-propane-diamine synthesized by Shi Tan *et al.*[38] and characterized as having a magnetic ground state. The complex can be classified as a 4+2 or type II cubane, with four short and two long Cu-Cu distances resulting in an open cubane-like Cu_4O_4 core structure, where each Cu(II) atom presents a slightly distorted square-planar coordination with the two nearest O and N atoms. Each hpda acts as a tridentate ligand to one Cu atom (see Figure 1) in such a way that the dihedral angle between the square planes of two Cu atoms bridged with a single oxygen atom is nearly 90° (Cu_1-Cu_2, Cu_1-Cu_4, Cu_2-Cu_3, and Cu_3-Cu_4 in Scheme 1). Unbridged Cu atoms are placed on parallel planes, with the Cu atoms shifted along the x (or y) axis (Cu_1–Cu_3 and Cu_2–Cu_4 in Scheme 1).

There are six two-body exchange interactions between the four magnetic ions: four interactions between bridged Cu atoms (nearest neighbours: J_{12}, J_{14}, J_{23}, and J_{34}) and two interactions between unbridged Cu atoms (next-nearest neighbours: J_{13} and J_{24}). The magnetic susceptibility χ vs T curve has been fitted[38–40] to a Heisenberg model of the form
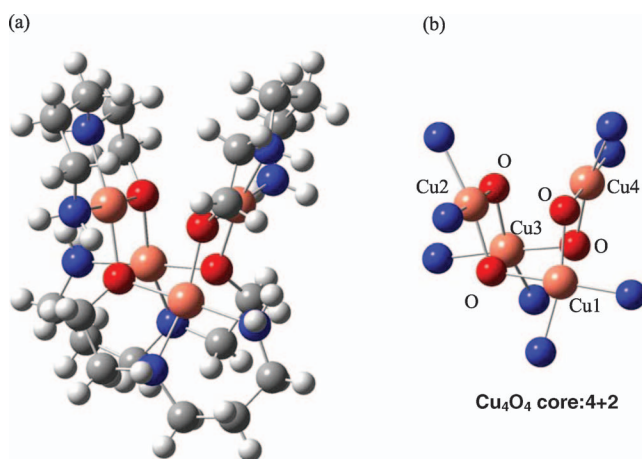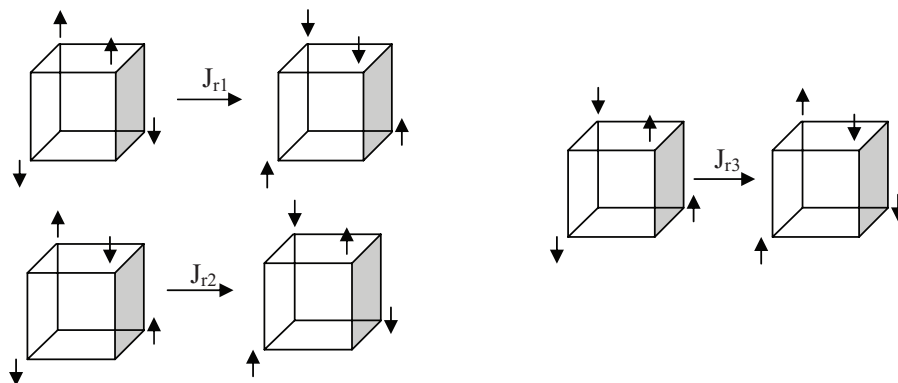

FIG. 1. (a) X-ray structure of the $[Cu_4(hpda)_4][ClO_4]$ H_2O cubane. (b) Open cubane-like Cu_4O_4 core structure. White, grey, and blue atoms are hydrogen, carbon, and nitrogen, respectively.

SCHEME 2. Four body operators in the cubane.

H $= -\Sigma\, J_{ij}\, S_i\, S_j$, with only two coupling constants J ($J = J_{12}$ $= J_{23} = J_{34} = J_{14}$) and J_d ($J_d = J_{24} = J_{13}$) (see Scheme 1). That is, the magnetic model employed by these authors neglects the distortions around each magnetic center. The best least-squares fit parameters proposed by these authors were $J = 89.8$ cm^{-1}, $J_d = -32.6$ cm^{-1}, $g = 2.06$, $\rho = 5.1$ $\times 10^{-4}$, and $N_\alpha = 240 \times 10^{-6}$ emu mol^{-1}. The two last terms correspond, respectively, to the molar fraction of mononuclear Cu(II) ions and the temperature independent magnetic contribution.

The ferromagnetic J interaction is consistent with the relative orientation of the Cu $3dx^2$-y^2 orbitals in two bridged Cu atoms (Scheme 1). However, the non-negligible antiferromagnetic nature of the coupling between unbridged Cu atoms J_d is quite surprising at first glance, and it will be contrasted by our calculations.

III. THE PROCEDURE

A. Theoretical evaluation of *J*

The theoretical analysis of the magnetic properties of these systems requires the determination of the energy of the low-lying states and their mapping onto the eigenvalues of the model spin Hamiltonian. For the cubane the model spin, Hamiltonian contains three different types of magnetic interactions: the nearest and next-nearest neighbours J and J_d interactions, which are two-body terms, and the four-body terms, J_r, which produce the simultaneous permutation of the four spin on the cubane (Scheme 2). This term is important in high-Tc and spin ladders cuprates since it originates from the electron cyclic circulation in Cu$_4$O$_4$ plaquettes, and it has been claimed to be necessary to fully understand the magnetic excitations, and the infrared and neutron scattering spectra of these systems.[41–44] For Cu$_4$O$_4$ cubane these terms are

expected to be small, but they can be evaluated without any additional cost once the effective Hamiltonian is built as discussed below. The so-resulting spin model Hamiltonian takes the form

$$H = -J \sum_{\langle ij \rangle}^{NN} \left(S_i S_j - \frac{1}{4}\right) - J_d \sum_{\langle ij \rangle}^{NNN} \left(S_i S_j - \frac{1}{4}\right)$$
$$- J_r \sum_{\langle ijkl \rangle} \left[(S_i S_j)(S_k S_l) + (S_i S_l)(S_j S_k) - (S_i S_k)(S_j S_l) - \frac{1}{16}\right].$$
(1)

The real system belongs to the C$_1$ symmetry point group, but a slight modification allows us to impose the C$_2$ symmetry. This symmetrised structure is employed in our calculations, and the discussion hereafter takes this aspect into account.

The unpaired electrons are essentially located on Cu $3dx^2$-y^2 orbitals, although with delocalization tails on the neighbour atoms. Such Cu centered orbitals are labelled {a, b, c, and d}, localized on Cu$_1$, Cu$_2$, Cu$_3$, and Cu$_4$, respectively. They constitute the active space CAS. The six S_z $= 0$ determinants can be written on the basis of these four orbitals: $|a\bar{b}c\bar{d}|$, $|\bar{a}b\bar{c}d|$, $|ab\bar{c}\bar{d}|$, $|\bar{a}\bar{b}cd|$, $|a\bar{b}\bar{c}d|$, $|\bar{a}b c\bar{d}|$, and constitute the model space. For C$_2$ symmetry, there are two different first-neighbour interactions J_1 ($J_1 = J_{12} = J_{34}$) and J_2 ($J_2 = J_{23} = J_{14}$) and two next-nearest neighbour interactions J_{d1} ($J_{d1} = J_{13}$) and J_{d2} ($J_{d2} = J_{24}$).

Regarding the four-spin operators, three different terms can be distinguished: J_{r1}, J_{r2}, and J_{r3}, where the former concerns the circulation of the electrons between only first-neighbour sites, while J_{r2} and J_{r3} arise from the circulation of electrons involving hopping between second-neighbour sites (Scheme 2). The spin Hamiltonian on the basis of these determinants has the following form, where $A = (J_{r1} + J_{r2} - J_{r3})/8$, $B = (J_{r1} - J_{r2} + J_{r3})/8$, and $C = (-J_{r1} + J_{r2} + J_{r3})/8$,

$\lvert a\bar{b}c\bar{d}\rvert$	$\lvert\bar{a}b\bar{c}d\rvert$	$\lvert ab\bar{c}\bar{d}\rvert$	$\lvert\bar{a}\bar{b}cd\rvert$	$\lvert a\bar{b}\bar{c}d\rvert$	$\lvert\bar{a}bc\bar{d}\rvert$	
$J_1 + J_2$	$-J_{r1}/2$	$-J_2/2 + A$	$-J_2/2 + A$	$-J_1/2 + B$	$-J_1/2 + B$	
	$J_1 + J_2$	$-J_2/2 + A$	$-J_2/2 + A$	$-J_1/2 + B$	$-J_1/2 + B$	
		$J_2 + (J_{d1} + J_{d2})/2$	$-J_{r2}/2$	$-J_{d2}/2 + C$	$-J_{d1}/2 + C$	
			$J_2 + (J_{d1} + J_{d2})/2$	$-J_{d1}/2 + C$	$-J_{d2}/2 + C$	(2)
				$J_1 + (J_{d1} + J_{d2})/2$	$-J_{r3}/2$	
					$J_1 + (J_{d1} + J_{d2})/2$	

The six eigenvalues of this Hamiltonian can be expressed on the basis of the seven magnetic parameters. Then, it is not possible to fix the amplitude of the magnetic parameters just from the energy of the magnetic states if *a priori* any parameter is assumed to be negligible. Instead we can build an *ab initio* effective Hamiltonian which is in one-to-one correspondence with the model Hamiltonian. We need the six eigenstates having the largest projections on the model space and their eigenvalues. A detailed description of the procedure can be found in Refs. 45–48. The comparison between the *ab initio* effective Hamiltonian and the model Hamiltonian elements fixes the amplitudes of the integrals appearing in the latter and allows one to verify whether non-negligible additional interactions are present.

The magnetic states can be evaluated with different accuracy depending on the methodology employed. In the case of DDCI calculations, the CI space for this system contains several hundred millions of determinants. Therefore, additional truncation schemes need to be considered as those discussed in Sec. III B.

B. EXSCI calculations

The EXSCI method has been initially proposed by Bories *et al.*[20] and recently improved by Ben Amor *et al.*[21] The goal of this method is to hugely reduce the size of CI matrices and consequently of the computational time, in order to make possible the use of CI calculations to deal with larger and more complex systems. It can be applied to any set of excitations, but here it will be used to truncate the DDCI space. The procedure requires the use of localized orbitals. Indeed, taking advantage from the fact that electron correlation is a local phenomenon, their use allows one to neglect long range interactions. Moreover, a quasi linear dependence between the computational time and the number of basis function (N-scaling) is obtained. A brief description of the localization method and of the CI program is given hereafter.

1. A priori localization method

The localization method is described in detail in Ref. 49. It differs from the various methods that can be found in the literature such as Boys,[50] or Pipek and Mezey.[51] In these approaches, canonical self-consistent field (SCF) or complete active space self-consistent field (CASSCF) orbitals are localized according to a given criterion, i.e. the orbitals are optimised in the first step and then localized, so that one can speak of *a posteriori* methods. In the *a priori* approach, guess local orbitals are built in the first step, and then optimised to reach a SCF or CASSCF quality in the second step. The guess local orbitals are not uniquely defined and can be chosen according to the physical problem under consideration. They can be bond orbitals, lone pairs, and atomic or fragment orbitals. The optimisation step consists of a super-CI-like method. In this approach, a contracted CI matrix of the single excitations on the CAS eigenvector is constructed and then block diagonalised. Thanks to the block diagonalisation the pseudo-natural orbitals resulting from this operation remain as local as the guess orbitals and can be used as guess orbitals for a next iteration. At convergence, the iterative process gives a set of local CASSCF orbitals (one obtains the CASSCF energy). Some applications are presented in Ref. 52.

Another possibility is to perform a CASSCF calculation using a standard program and to project each occupied (active and virtual, respectively) guess orbital onto the space of occupied (active and virtual, respectively) canonical delocalized orbitals.

The method yields a set of well localized occupied, active, and virtual orbitals (see in Refs. 20 and 21 illustrations of the method). The *a priori* approach presents some drawbacks and some advantages. The main defect is that the final set of localized orbitals is not unique and depends on how the guess orbitals are built. Furthermore, this construction may be sometimes complicated. The main advantage is that one can easily get well localized virtual orbitals, which is not the case in many other approaches. In many situations, the drawbacks quoted above may be advantageous, since one can build the local orbitals according to the physical problem under consideration.

2. Reducing the CI size and the list of bielectronic repulsion integrals

Once a set of localized occupied, active, and virtual orbitals are obtained, only excitations among "interacting local orbitals" are retained, using as threshold the value of the corresponding exchange integral. Two orbitals a and b are interacting when the corresponding exchange integral: $K_{ab} = \langle ab|ba \rangle$ is larger than a certain threshold sl. Let us consider some examples of how this criterion works on a double excitation $j \rightarrow a, i \rightarrow r$, the corresponding operator being $a_a^\dagger a_r^\dagger a_i a_j$, where i, j are occupied, a is an active and r is a virtual orbital. Figure 2 represents three different situations, where the active orbital space is represented by a box and the occupied and virtual orbitals placed on the same region are represented by parallel lines. In this figure, a line close to the box represents an orbital localized in regions near the active centers.

(a) The first example is shown in Figure 2(a). For excitation $i \rightarrow r$, the orbitals i and r are close in space and then the integral K_{ir} is larger than the threshold sl. The excitation $j \rightarrow a$ moves one electron from one occupied orbital j to an active orbital. If one active orbital b (not necessarily a) is in interaction with j ($K_{jb} > sl$), one considers that j interacts with the CAS as a whole. Then, the corresponding determinant is kept on the CI space.

(b) In Figure 2(b) the orbital j interacts with the CAS (for instance, with the active orbital b), but the orbital i does not interact with r. Then, the integral $K_{bj} > sl$, but $K_{ir} < sl$. The corresponding determinant is eliminated.

(c) For Figure 2(c) the situation is similar to those described in (a), but here the couples {CAS,j} and {i,r} occupy distant regions on the molecule. All the integrals K_{bi} and K_{br} are small for all active orbitals b. An additional threshold, $sl2$, can be defined which takes into account this type of situations. When all the integrals K_{bi} and K_{br} are smaller
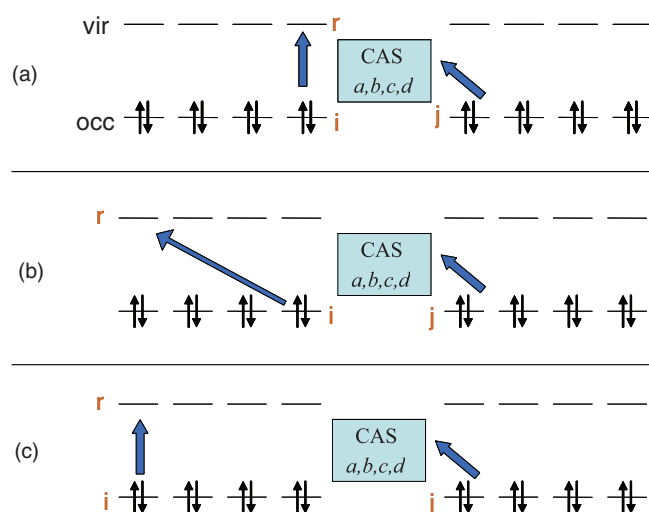
FIG. 2. Three examples of a double excitation $j \rightarrow a$, $i \rightarrow r$ in a set of localized MOs to illustrate how the EXSCI method works (see text). The box represents the CAS, and the horizontal lines the occupied and virtual MOs. The blue arrows represent the excitations. A line closest to the box represents an orbital located near the active centers.

than $sl2$, the corresponding determinant is eliminated. For $sl2 = 0$, this determinant is kept.

Additional saving cost can be obtained by eliminating small molecular integrals, following a procedure similar to that used to shorten the list of determinants. This option does not affect the size of the CI matrix, but the computational time of each iteration on Davidson procedure.

The whole process employed to obtain theoretical estimates of the magnetic parameters is summarized in Figure 3.

IV. COMPUTATIONAL DETAILS

All the calculations have used the geometry from x-ray crystal structure, slightly modified to impose a C_2 symmetry point group (Figure 1). The main geometrical parameters have been collected in Table I.

Core electrons of Cu atoms (up to $3s$) were replaced with effective core potentials, and the $(9s6p6d)/[3s3p4d]$ basis set
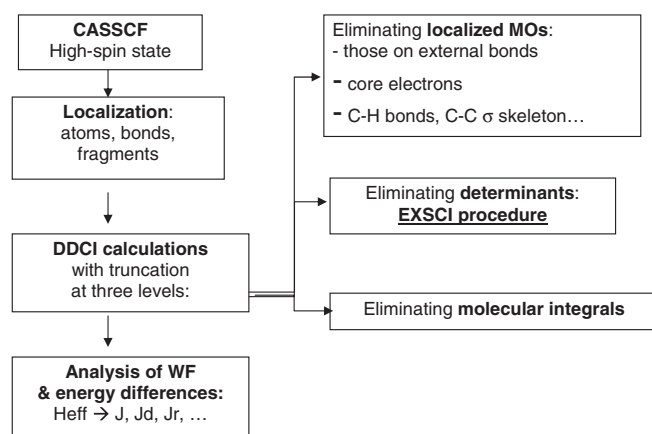

FIG. 3. Schematic representation of the complete strategy employed to simultaneously extract all the magnetic parameters in the Cu$_4$O$_4$ cubane.

TABLE I. Geometrical parameters of the molecule. In parenthesis, the corresponding first and second neighbour interactions are included. Notice that Cu$_1$(Cu$_2$) and Cu$_3$(Cu$_4$) are related by the C_2 axis.

Distance (Å)		Bond angles (°)	
Cu$_1$–Cu$_2$ = Cu$_3$–Cu$_4$ (J_1)	3.204	Cu$_1$–O–Cu$_2$ = Cu$_3$–O–Cu$_4$	111.5
Cu$_1$–Cu$_4$ = Cu$_2$–Cu$_3$ (J_2)	3.149	Cu$_2$–O–Cu$_3$ = Cu$_1$–O–Cu$_4$	107.9
Cu$_1$–Cu$_3$ (J_{d1})	3.403	Cu$_1$–O–Cu$_3$	98.3
Cu$_2$–Cu$_4$ (J_{d2})	3.407	Cu$_2$–O–Cu$_4$	97.3
		Dihedral angles (°)	
Cu$_1$–O–Cu$_2$–O	−9.7	O–Cu$_2$–O–Cu$_3$	−90.7
Cu$_2$–O–Cu$_3$–O	11.9	O–Cu$_3$–O–Cu$_4$	89.9

was used for the valence electrons of Cu.[53] ANO-type basis functions are used for the ligands of different quality depending on the specific position. Contractions $[4s3p1d]$ are employed for N and O in bridging positions, $[3s2p1d]$ for C placed between N and O atoms, $[3s2p]$ for external C atoms, and $[1s]$ for all H atoms.[54–56] The system contains 88 atoms with 616 basis functions.

DDCI calculations have been performed by means of CASDI code[57] on its EXSCI version. MOLCAS 7.2 code[58] is used to obtain the CASSCF (4/4) quintet MOs set, which is used as common MOs set in all the CI calculations. The active space contains four orbitals resulting from the symmetry-adapted combinations of the Cu $3dx^2$-y^2 orbitals with tails on the bridging O and N atoms. Figure 4 shows two views of one of the four symmetry-adapted MOs, with large coefficients on the $3dx^2$-y^2 orbitals of Cu$_1$ and Cu$_3$, which are in parallel planes but not face-to-face, and small contributions coming from Cu$_2$ and Cu$_4$, which are in planes orthogonal to those containing Cu$_1$ and Cu$_3$ atoms. It is worth recalling that the interaction between Cu$_1$ and Cu$_3$ (similarly between Cu$_2$ and Cu$_4$) has been proposed to be antiferromagnetic by Shi Tan et al.[38]

Next, the MOs are localized as core, bond, and diffuse orbitals. To reduce the cost of DDCI calculations, after localization all the occupied and virtual σ C–H and N–H orbitals have been eliminated, as well as the 1s core orbitals of all C, N, and O atoms. Also the diffuse orbitals on external C atoms have been frozen. Notice that although N atoms are linked to the magnetic centers, the N–H bonds are out of the exchange pathway between Cu atoms, and they do not participate on the
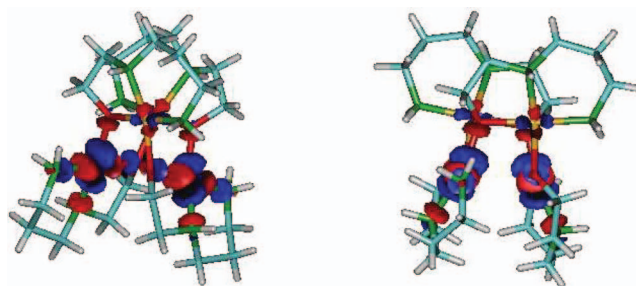

FIG. 4. Two views of one of the symmetry-adapted magnetic MOs, with large coefficients on the $3dx^2$-y^2 orbitals of Cu$_1$ and Cu$_3$, and small on Cu$_2$ and Cu$_4$.

magnetic coupling. Test calculations on binuclear fragments have been carried out and confirm that this choice does not affect the magnetic coupling amplitudes.

V. RESULTS

A. Ground state and low-lying spectrum and magnetic parameters from EXSCI calculations

The six low-lying states of the cubane have been evaluated by means of the EXSCI calculations. They correspond to a quintet state (Q), three triplet states (T_1, T_2, and T_3), and two singlet states (S_1 and S_2), all of them with large projections on the eigenvectors of the model Hamiltonian (Eq. (2)). This means that all the computed states correspond to the magnetic states, resulting from the distribution of the four unpaired electrons on the four active orbitals, and that non-magnetic states such as those resulting from metal to ligand or ligand to metal excitations are higher in energy.

The ground state of the system is the spin quintet, in agreement with the amplitude of the effective magnetic moment of about 5 μ_B at 5 K. The lowest excited state is a triplet state, with a singlet state lying above the triplet. Next, there are two triplet and one singlet states.

The whole DDCI space contains more than 870×10^6 determinants prior to applying any truncation. Several tests have been performed to analyze the impact of the selection criteria on the values of the magnetic terms, the results of two of the most significant have been collected in Table II. This table shows the different selection thresholds (sl, $sl2$, and sli), the computational time per iteration and root of the Davidson diagonalization, the number of determinants included in the CI matrix and the resulting two-body magnetic coupling terms. In all the considered tests, the three four-body operators, J_{r1}, J_{r2}, and J_{r3} are null.

For test A we have dealt with around 100×10^6 determinants once that, the excitations that do not match the selection criteria ($sl = 10^{-3}$, $sl2 = 10^{-4}$, and $sli = 10^{-4}$) have been eliminated of the DDCI space. The gaps between the quintet ground state and the five excited states are: 24.3 (T_1), 27.2 (S_1), 29.6 (T_2), 52.7 (T_3), and 79.5 (S_2) cm^{-1}. The first-neighbour interactions J_1 and J_2 are both ferromagnetic with close values of 24 and 29 cm^{-1}, respectively, which agree with the relative Cu–Cu distance (larger for J_1 than J_2). The second-neighbour J_{d1} and J_{d2} interactions are also ferromagnetic although with a negligible absolute value.

Regarding the four-body operators, the three J_{r1}, J_{r2}, and J_{r3} terms vanish. Notice that J_{r1} scales as $t_1^2 t_2^2/U^3$ (Refs. 47 and 48) where U is the on-site Coulomb repulsion and t_1 and t_2 correspond to the hopping integrals between

first-neighbour Cu atoms. Both integrals are expected to be quite small due to the quasi-orthogonal relative position of the $3dx^2$-y^2 orbitals on first-neighbour Cu atoms, while U is a rather large quantity (around 5-7 eV for molecular Cu(II) systems[59]). J_{r2} and J_{r3} scale as $t_{d1}t_{d2}t_2^2/U^3$ and $t_{d1}t_{d2}t_1^2/U^3$, respectively,[47] with t_{d1} and t_{d2} being the hopping integral between second-neighbour centers. t_{d1} and t_{d2} result from the δ overlap of the $3dx^2$-y^2 orbitals on second-neighbour Cu atoms, which are separated by 3.4 Å of distance, and they are not face to face as can be seen in Scheme 1 and Figure 1. Then, their absolute values are expected to be quite small, and consequently, also the amplitudes of J_{r2} and J_{r3}.

Increasing the number of determinants in the CI space by diminishing the sl threshold as in test B, practically does not affect the amplitude of any of these terms. Consequently, the spectrum is not affected either: the gaps between the quintet ground state and the five excited states are now: 25.5 (T_1), 28.6 (S_1), 32.0 (T_2), 56.7 (T_3), and 85.6 (S_2) cm^{-1}. Notice that, although the size of the CI space has augmented by a factor 2, the computational time per root and iteration has only increased by a factor 1.3, thanks to the molecular integral threshold, here one order larger than in test A.

It is possible to enlarge the size of the CI space by reducing the sl and $sl2$ values. However, this results in prohibitive computational times. On the other hand, the thresholds employed are in good agreement with those assuring the convergence on systems where a complete calculation is possible.[21] Since neither the amplitudes nor the nature of the interactions have changed when going from test A to B and the DDCI calculations on the complete space are unfeasible, we can consider test B as the best one available and the resulting effective magnetic parameters as converged. It is also important to notice that these CI calculations are probably the largest (and most expensive) performed on systems of this nature, which constitute by itself a milestone in the field.

Then our best estimates of the magnetic parameters are: $J_1 = 25.1$ cm^{-1}, $J_2 = 31.6$ cm^{-1}, $J_{d1} = 0.2$ cm^{-1}, $J_{d2} = 0.6$ cm^{-1}, and $J_{r1} = J_{r2} = J_{r3} = 0.0$ cm^{-1}. These results are in good agreement with the estimates obtained by Ruiz et al.[34,35] from density functional theory (DFT) based calculations. In these calculations, a S_4 symmetry is imposed which results in only two different couplings, $J = 44.1$ cm^{-1} and $J_d = 6.2$ cm^{-1}.

An additional point to be considered is the impact of the size-consistency errors in the evaluation of magnetic terms from these truncated CI calculations. Traditionally, this error is not quantified when DDCI method is used to evaluate magnetic coupling terms, assuming that the error, if any, is not important. Only recently some tests have been published[60–64]

TABLE II. Magnetic coupling terms (in cm^{-1}) for the molecule obtained from EXSCI calculations, computational time in minutes per iteration and root, and number of determinants in the CI space. In parenthesis, the corresponding percentage of the DDCI space included in the calculations is shown. The full DDCI space contains 874.3×10^6 determinants.

Test	sl	$sl2$	sli	CI size	Time (min)	J_1	J_2	J_{d1}	J_{d2}
A	10^{-3}	10^{-4}	10^{-4}	99.9×10^6 (11%)	417	23.7	29.1	0.6	0.6
B	$5 \cdot 10^{-4}$	0	10^{-3}	204.1×10^6 (23%)	536	25.1	31.6	0.2	0.6

where the Davidson equation[65] was employed to correct the DDCI energies as follows:

$$E^m_{\text{DDCI-SC}} = E^m_{\text{CAS}} + \frac{E^m_{\text{DDCI}} - E^m_{\text{CAS}}}{\left(C^m_0\right)^2}, \qquad (3)$$

where E^m_{CAS} and E^m_{DDCI} correspond to the zeroth-order CASCI and DDCI energies of the m state, respectively, and $(C^m_0)^2$ is the norm of the projection of the wavefunction of m on the CAS. A recent work on magnetic C-Be model systems, where we have analyzed the effect of size-consistency errors by comparing the DDCI and FCI estimates, indicates that the Davidson formula overestimates the size-consistency errors in the case of the DDCI approach,[61] since this formula takes into account the inactive double excitations which are not contained in the DDCI wavefunction. Monari et al.[60] have formulated a modified Davidson equation to take into account the particularities of DDCI with respect to standard SDCI calculations. These authors proposed that the correction for DDCI energies has to be multiplied by a factor $(N_A-1)/N_A$, where N_A is the number of active orbitals. The corrected DDCI energy becomes

$$E^m_{\text{DDCI-SC}} = E^m_{\text{DDCI}} + \frac{N_A - 1}{N_A}\left(E^m_{\text{DDCI}} - E^m_{\text{CAS}}\right)\left(1 - \left(C^m_0\right)^2\right). \qquad (4)$$

When this modified Davidson equation is employed, the impact of the size-consistency errors on the DDCI values is attenuated.[61] In the case of EXSCI calculations (with additional truncation with respect to DDCI ones), there has not been any study on this issue. We have employed both equations to correct the energies of the cubane obtained from test B in the EXSCI calculations. The J values obtained once the SC errors are corrected with Davidson (SC) or modified Davidson (SCm) equations for test B are shown in Table III. The same behaviour observed in the C-Be model systems is found for the cubane: (i) the absolute values of the magnetic parameters are enhanced when size-consistency errors are corrected and (ii) the impact is larger for the original Davidson equation than for the modified one. Additionally, the correction improves the comparison with the DFT values. But it is important to keep in mind that the corrections of the size-consistency errors in DDCI calculations and in particular in EXSCI ones is still an open question, which requires in-depth study.

As shown in Tables II and III, for each type of interaction our two calculated values (J_1 and J_2; J_{d1} and J_{d2}) are quite close. Then, it is reasonable to assume that $J = J_2 \approx J_1$ and

TABLE III. Impact of the size-consistency errors on the amplitudes of the magnetic coupling constants (in cm^{-1}) obtained from EXSCI calculations (test B). SC and SCm refers to size consistency corrected parameters, the former using the original expression by Davidson, and the last one using the modified expression proposed for DDCI truncation.

	J_1	J_2	J_{d1}	J_{d2}
DDCI	25.1	31.6	0.2	0.6
+SC	38.5	48.3	0.4	1.2
+SCm	33.3	41.9	0.3	1.0

$J_d = J_{d2} \approx J_{d1}$, as done in the experimental work[38] and by Ruiz et al.[34,35] But, notice that in the case of the experimental data, it is an assumption made prior to the fitting, whose adequacy cannot be checked, while our procedure does not need to make any assumption, and this information is only recovered once the calculations are analyzed.

B. Verifying the nature and extension of the interactions

Comparing with the experimental values, there are two points in disagreement: (i) the absolute value of both first- and second-neighbour interactions are smaller than those resulting from the experimental fitting and (ii) the calculated second-neighbour interactions are not antiferromagnetic. The former point can be related to the selection procedure. Since it is not technically possible to perform a DDCI calculation involving the complete set of determinants, it could happen that the extracted values are underestimated. However, regarding the second point we are confident on the sign of the respective interactions. As it is well known,[59] the magnetic coupling constant J results from two opposite contributions $J = 2K\text{-}4t^2/U$: the direct exchange, $2K$ which is ferromagnetic, and the kinetic exchange, $-4t^2/U$, resulting from the delocalization of the electrons on the active centers and it is antiferromagnetic. Since the interaction between Cu$_1$ and Cu$_3$ (respectively Cu$_2$ and Cu$_4$) is mainly through space, it is expected that the superexchange mechanism ($-4t_1^2/U$ or $-4t_2^2/U$, with $t_1 \to 0$ and $t_2 \to 0$) has a negligible role, then the interaction should be controlled by the direct exchange $2K$, being ferromagnetic and small in absolute value due to the δ-type overlap between Cu$_1$–Cu$_3$ (Cu$_2$–Cu$_4$) $3dx^2$-y^2 orbitals.

To verify both points we have carried out a computational experiment. We have built three binuclear models from the cubane representative of the nearest- and next-nearest neighbour interactions: dimer NN which contains Cu$_1$ and Cu$_4$ atoms and is used to evaluate J_2, dimer NN2 which contains Cu$_1$ and Cu$_2$ atoms, used to evaluate J_1, and dimer NNN which contains Cu$_2$ and Cu$_4$ atoms and is used to evaluate J_{d2}. Each Cu atom maintains the coordination with one hpda ligand. The broken C–C bonds have been saturated with H atoms (C–H distance of 1.07 Å). Despite the approximations, the models retain the closest environment to each magnetic center. Then the so-resulting J values are expected to be close to the amplitude of these interactions in the whole cubane.

Each dimer contains two active electrons on two orbitals, and J can be directly obtained from the energy difference between the lowest singlet and triplet states, evaluated by means of full DDCI calculations. The so-obtained J values are +48.2 cm^{-1} for dimer NN, +37.8 cm^{-1} for dimer NN2, and +3.8 cm^{-1} for dimer NNN, all in agreement with the amplitude and signs of the estimations obtained from the complete Cu$_4$O$_4$ cubane (Tables II and III). If instead of full DDCI calculations, we perform EXSCI calculations with the same selection criteria than in the whole cubane (test B), the J values obtained for dimer NN and NNN are, respectively, +41.0 and +2.4 cm^{-1}. This indicates that the truncation introduced by the EXSCI method could slightly underestimate the amplitude

of the magnetic terms. Furthermore, the ferromagnetic nature of the interaction between unbridged Cu atoms predicted by the EXSCI calculations on the whole cubane is confirmed, i.e., the truncation does not affect the sign of the interactions, and only slightly their amplitudes.

C. Susceptibility curves

A way to check the reliability of the calculated magnetic constants consists of simulating the susceptibility versus temperature curve. Although it is well known that the χ vs T curve is normally insensitive to the J values for ferromagnetic compounds as the one studied here, this seems to be the procedure employed to obtain the fitting parameters in the experimental work.[38] Then we start by comparing the χ vs T curves obtained with the fitted parameters and that resulting with the calculated magnetic constants.

Figure 5(a) represents the χ vs T plot for five sets of values. Black line corresponds to the experimental values, while the *ab initio* values are employed in the rest: red, green, violet, and maroon symbols correspond, respectively, to the fitting obtained with the calculated values for the cubane, values obtained from the dimers, values for the cubane corrected by the Davidson equation or by the modified Davidson equation. The values of g, N_α, and ρ provided by Shi Tan *et al.*[38] have been employed. The mononuclear Cu(II) ions and TIP contributions are negligible in all the range of temperature, and similar behaviour has been obtained when these two extra contributions are not taken into account. The five sets of parameters give similar plots. The deviation between the curve fitted with the experimental values and those obtained with the calculated ones is measured through the reliability factor $R = \Sigma_i[(\chi_{exp}(T_i) - \chi_{calc}(T_i)]^2/\Sigma[\chi_{exp}(T_i)]^2$. R is very small for all sets of calculated values: 1.3×10^{-5} for the values calculated for the cubane and 3.6×10^{-6} for the values obtained from the dimers or from the SC corrected cubane values. Then, similar fittings are obtained with sets of parameters representing different physics effects. The fitting seems to be sensitive neither to the absolute value of the two leading interactions nor to the nature of them, at least for the range of values analyzed.

Additional insight is obtained with the χT vs T plot. Figure 5(b) contains this plot for the four sets of parameters, with the same colour code as for the χ vs T plot. The curve for the *ab initio* values of the cubane deviates from the experimental one, although the reliability factor is still very small ($R = 2.9 \times 10^{-3}$). A better agreement is observed for the *ab initio* values once the size-consistency errors are corrected (+SCm values in Table III), with $R = 8.0 \times 10^{-4}$ and also for the values of the dimers ($R = 2.7 \times 10^{-4}$). This confirms that the parameters obtained directly from the cubane are slightly underestimated, as mentioned above, and a better agreement is obtained with larger J and J_d values, as those obtained once the size-consistency errors are corrected. But notice that in all sets of calculated parameters the unbridged Cu atoms present a ferromagnetic interaction.

In summary, it is possible to fit the susceptibility magnetic data with sets of parameters with different absolute val-
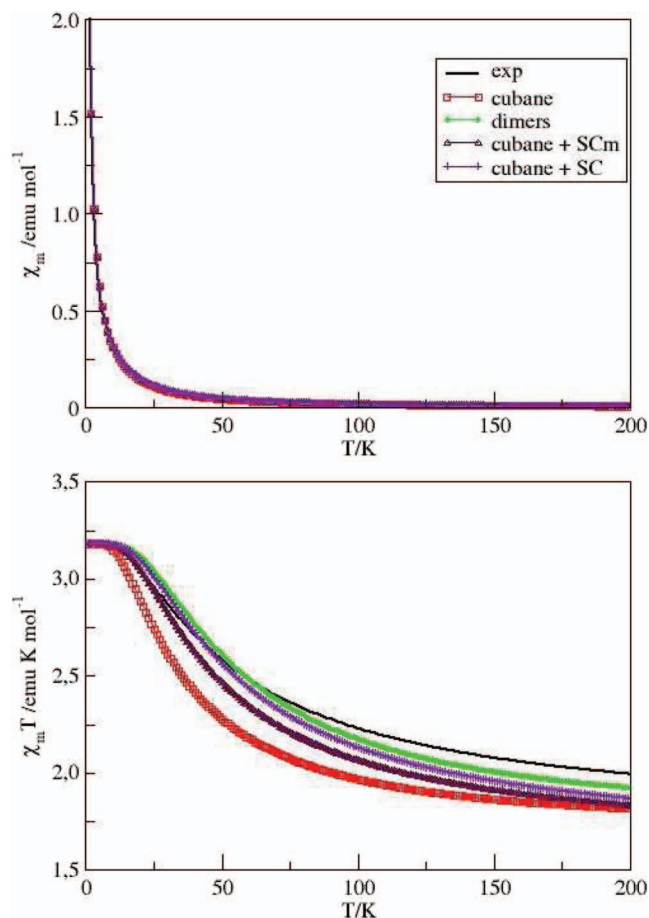

FIG. 5. (Top) χ vs T plot and (bottom) χT vs T plot obtained by using different values of J and J_d : experimental values (black line, $J = 89.8$ cm^{-1}, $J_d = -32.6$ cm^{-1}), those resulting from the *ab initio* calculations on the cubane (red square, $J = 31.6$ cm^{-1}, $J_d = 0.6$ cm^{-1}), those from the calculations on the dimers (green circle, $J = 48.2$ cm^{-1}, $J_d = 3.8$ cm^{-1}), the cubane values corrected by the Davidson equation (violet plus, $J = 48.3$ cm^{-1}, $J_d = 1.2$ cm^{-1}) or by the modified Davidson equation (maroon triangle, $J = 41.9$ cm^{-1}, $J_d = 1.0$ cm^{-1}).

ues and with different physics. We observe that not only the ratio between the magnetic coupling values determines the shape of the χT vs T plot, as expected, but there also exists a certain compensation between the parameters, as mentioned by Tercero *et al.*,[34] in such a way that a moderate antiferromagnetic exchange J_d (–32.6 cm^{-1}) compensates the large ferromagnetic exchange J between bridged Cu atoms (89.8 cm^{-1}) found in the fitting, and it gives a similar plot than a neglible J_d and a moderate ferromagnetic J value. In this context, the fitting could take benefit of the predictions provided by theoretical calculations, at least to establish the ferromagnetic/antiferromagnetic nature of the leading interactions.

VI. CONCLUSIONS

In this paper we have evaluated the magnetic coupling constants in a Cu_4O_4 cubane isolated by Shi Tan *et al.*,[38] as a case study of magnetic polynuclear transition metal systems. DDCI calculations have been performed and the resulting

wavefunctions have been analyzed by means of the effective Hamiltonian theory to simultaneously extract the amplitude of the first-neighbour, second-neighbour, and four-body terms. In order to make plausible the CI calculations the EXSCI procedure has been employed, which allows us to reduce considerably the number of DDCI determinants to be included in the Davidson diagonalization in a rational way. To the best of our knowledge these calculations are the largest never performed with the CI approach on polynuclear transition metal systems.

Seven magnetic parameters have been explicitly determined, without introducing any previous assumption about their relative amplitude. This is an important difference with respect to the experimental fitting where a magnetic model is fixed beforehand, only the relevant parameters are introduced in the model, the remaining presumably small parameters are neglected. The results show the presence of two leading ferromagnetic interactions between bridged Cu ions, with which magnetic constants J_1 and J_2 are close in absolute value. Also the interactions between the unbridged Cu ions (J_{d1} and J_{d2}) are ferromagnetic, but very weak. The four-body terms are negligible. The nature of the interactions agrees with the relative orientation of the magnetic orbitals in the molecule, imposed by the coordination of the hpda ligands. Both the amplitude and the nature of the two-body interactions have been validated by means of DDCI calculations on binuclear clusters extracted from the cubane structure. Finally, the susceptibility versus temperature curve has been simulated by using the calculated magnetic coupling constant values. Although the calculated J values appreciably differ from the experimental ones, the corresponding χ vs T and the always more sensitive χT vs T plots are similar. Then, it is possible to obtain fittings of similar quality with sets of very different parameters. This indicates that the fittings are not univocal for these polynuclear systems, which moreover show larger uncertainty than in common binuclear systems. This explains why it has been reported J values which are not consistent with the system geometry as in the system under study. It is important to mention that the system considered here is not an isolate case but many other examples involving Cu$_4$O$_4$ cubane compounds can be found in literature. For instance, Tercero and co-workers have collected in Table IV of Ref. 34 a set of open 4+2 Cu(II) cubanes, similar to the system considered in this work, presenting antiferromagnetic exchange coupling constants between the unbridged Cu centers, which are in contradiction with the relative orientation of the Cu active orbitals.

This scenario is not comfortable since many of the efforts done by experimental groups in synthesizing and characterizing new molecular systems are driven by the aim of understanding the main factors controlling the magnetic properties. In this context, an efficient computational strategy, combining the performance of the DDCI procedure in determining the magnetic coupling constants, and the ability of dealing with large systems containing several magnetic centers and extended ligands such as EXSCI does, can be considered as a useful tool to help in the interpretation of the magnetic data and the validation of the magnetic interaction model.

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