Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

Theoretical Determination of the Zero-Field Splitting in Copper Acetate Monohydrate

Rémi Maurice,[†,‡] Kanthen Sivalingam,[§] Dmitry Ganyushin,[§] Nathalie Guihéry,[*,†] Coen de Graaf,[‖,‡] and Frank Neese[§]

[†]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3, 118, route de Narbonne, 31062 Toulouse, France

[‡]Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain

[§]Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, 53115 Bonn, Germany

[‖]Institució Catalana de Recerca i Estudis Avançats, Passeig Lluis Companys 23, 08010, Barcelona, Spain

S Supporting Information

ABSTRACT: The zero-field splitting of the copper acetate monohydrate complex is studied using wave function based calculations. The anisotropy parameters extracted from highly correlated methods are in excellent agreement with the most accurate experimental results; in particular, the negative sign of the axial anisotropy parameter *D* is reproduced. During several decades, the interpretation of experimental data based on an analytical expression derived from perturbation theory led to a positive *D*-value. Although the validity of this expression is confirmed, it is explained that the incorrect attribution of a positive *D* is related to the assumption of an antiferromagnetic coupling between excited states. We have found in the present work that this coupling is actually ferromagnetic. The analysis of the various contributions to the anisotropy parameters shows that both spin−spin and spin−orbit couplings participate in the magnetic anisotropy of this complex. Although the anisotropy arising from the spin−spin coupling is essentially independent of the level of calculation, the zero-field-splitting parameters resulting from the spin−orbit coupling are strongly sensitive to the effects of dynamic correlation. This works provides important new insights into the physical origin of the zero-field-splitting parameters in copper dimers.

INTRODUCTION

Copper acetate monohydrate is a "signature molecule" in the field of molecular magnetism. Early on, the complex was assumed to be mononuclear. However, the magnetic susceptibility measured as a function of temperature published by Guha in 1951[1] shows a maximum at room temperature as well as a dramatic decrease at lower temperatures. This unexpected behavior attracted the attention of Bleaney and Bowers who performed a careful electron paramagnetic resonance (EPR) study of system. They found that an excited triplet state that exhibits a small zero-field splitting (ZFS) is populated at room temperature, whereas the ground state is nonmagnetic, i.e., a spin singlet.[2] On the basis of these observations, they proposed the presence of interacting pairs of cupric ions. This hypothesis was corroborated by the observed copper hyperfine interaction.[2] Assuming a dinuclear tetragonal structure of the complex, Bleaney and Bowers also derived an analytical expression explaining the presence of an axial ZFS. The axial ZFS parameter *D* determined using this expression was found to be positive. One year later, in 1953, the structure of the compound was determined by X-ray crystallography.[3] This confirmed the hypothesis of interacting pairs of copper ions. The Cu−Cu distance was found to be approximately 2.6 Å, and the molecular structure was close to D_{2h} symmetry (see Figure 1).

Since these pioneering works, copper acetate compounds have received much attention by the scientific community. The possible presence of a metal−metal bond in this molecule was intensely debated.[4,5] Moreover, the isotropic exchange[6] or the anisotropy parameters[7−9] were also investigated. Despite all efforts, the sign of the axial ZFS parameter of the triplet state has only been experimentally determined in 2008.[10] High-field high-frequency electron paramagnetic resonance (HF-EPR) spectroscopy was used to unambiguously extract the small ZFS parameters of the thermally accessible triplet state. *D* was finally found to be negative, at variance with all previous results extracted from experiments all of which relied on the original analytical expressions put forward by Bleaney and Bowers.

Because of the smallness of the ZFS in this system ($D = -0.335$ cm^{-1}),[10] the correct prediction of the anisotropy parameters constitutes a real theoretical challenge. In addition, it is of utmost importance to examine the validity of the analytical expression that led to the wrong sign of *D* in order to understand the previous obtained results. In the present paper, we address both issues. Although we concentrate on copper acetate monohydrate, it appears obvious to us that our conclusions have much broader implications with respect to the interpretation of the physical origin of ZFSs in transition metal dimers.

Received: March 11, 2011
Published: June 02, 2011

dx.doi.org/10.1021/ic200506q | Inorg. Chem. 2011, 50, 6229–6236

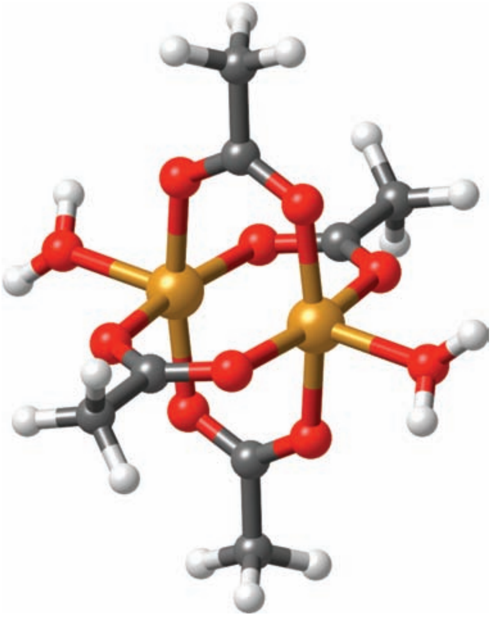

Figure 1. Ball and stick representation of $[Cu(CH_3COO)_2]_2(H_2O)_2$. The easy axis of magnetization almost coincides with the Cu−Cu direction.

Since the early ab initio calculation of anisotropic parameters in 1998,[11] in the $H_2Ti(\mu\text{-}H)_2TiH_2$ complex, different theoretical approaches have been developed to calculate the ZFS parameters. One of the first density functional theory (DFT) implementations was provided by the NRLMOL code[12,13] and uses perturbation theory for the spin−orbit coupling (SOC) to obtain the anisotropy. The method has been applied to various single molecule magnets (SMMs).[14−20] Also in 1998, the first general perturbation equations for the calculation of the spin−orbit contributions to the ZFS were derived and implemented in a semiempirical INDO/S configuration interaction program.[21] In 2002, Vahtras et al. presented the first ab initio implementation of the spin−spin coupling (SSC) interaction for the complete active space self-consistent field method.[22] In 2003, the restricted active space state interaction spin−orbit (RASSI-SO) method,[23,24] which also proposes a treatment of the SOC from a wave function theory (WFT)-based approach, was implemented in the MOLCAS code.[25] This method has frequently been used to study the ZFS of transition metal complexes for which the ZFS is often dominated by the SOC contribution.[26−35] The treatment of the SSC in the framework of highly correlated multireference configuration interaction (MRCI) wave functions has been developed by Gilka et al.[36] as well as Ganyushin and Neese.[37] In fact, the ORCA program[38] is capable of using either DFT or WFT methods (MRCI, CASSCF, and multireference perturbation theory) to calculate all parts of the ZFS perturbatively or in the framework of quasi-degenerate perturbation theory.[39−42] These methods have been applied to several mononuclear inorganic complexes and organic molecules.[43−48] Density fitting approximations for both the SOC and the SSC have been implemented to treat large molecules.[49,50]

The first section of the present paper is dedicated to the theoretical description of copper acetate. We will discuss the physical origin of the ZFS and its description using a model Hamiltonian. Analytical expressions for the SOC contributions to the ZFS parameters will be derived from the second-order perturbation theory. From these expressions, it is shown that an accurate description of the SOC requires a correlated treatment of both the ground and several excited nonrelativistic states. In the third section, the role of dynamic correlation on the extracted ZFS parameters is analyzed. The validity of the analytical expression of the SOC contribution to the axial ZFS parameter will finally be studied, and it will be investigated in detail why the established expressions led to the wrong sign of D.

■ MODEL DESCRIPTION OF THE ZERO-FIELD SPLITTING AND ITS PHYSICAL ORIGIN IN COPPER ACETATE COMPOUNDS

Model Hamiltonians. As in other binuclear systems with $S = 1/2$ magnetic centers, the low-lying spectrum of the copper acetate complex can be described using the following multispin Hamiltonian:[51,52]

$$\hat{H}^{\mathrm{MS}} = J\hat{\mathbf{S}}_a\cdot\hat{\mathbf{S}}_b + \hat{\mathbf{S}}_a\bar{\bar{\mathbf{D}}}_{ab}\hat{\mathbf{S}}_b + \vec{\mathbf{d}}\,\hat{\mathbf{S}}_a\times\hat{\mathbf{S}}_b \tag{1}$$

where J is the isotropic exchange, $\bar{\bar{\mathbf{D}}}_{ab}$ is the second-order symmetric ZFS tensor, and $\vec{\mathbf{d}}$ is the Dzyaloshinskii−Moriya pseudovector (equivalent to the antisymmetric second-order ZFS tensor). However, because of the presence of inversion symmetry (the only symmetry element of copper acetate monohydrate), the antisymmetric components will vanish,[53,54] and the low-lying spectrum can be completely described by the isotropic exchange and a symmetric ZFS tensor. The matrix representation of this Hamiltonian in the $|S, M_s\rangle$ basis is given in the Supporting Information. In the case considered here, we are only interested in the ZFS of the triplet state, which can be modeled by the giant spin Hamiltonian defined as

$$\hat{H}^{\mathrm{GS}} = \hat{\mathbf{S}}\bar{\bar{\mathbf{D}}}\hat{\mathbf{S}} \tag{2}$$

where $\hat{\mathbf{S}}$ is the spin operator associated to the triplet state and $\bar{\bar{\mathbf{D}}}$ is the associated ZFS tensor. The matrix representation of this Hamiltonian is also given in the Supporting Information. Comparing the matrix elements of the multispin spin Hamiltonian to those of the giant spin Hamiltonian expressed in the $|S, M_s\rangle$ basis and restricted to the triplet components, it is evident that

$$\bar{\bar{\mathbf{D}}} = \frac{1}{2}\bar{\bar{\mathbf{D}}}_{ab} \tag{3}$$

The $\bar{\bar{\mathbf{D}}}$ tensor is diagonal in the magnetic axis frame. The matrix representation of the GS Hamiltonian in this axis frame is again provided in the Supporting Information. The axial and rhombic ZFS parameters D and E are defined as

$$\begin{aligned} D &= D_{ZZ} - \frac{1}{2}(D_{XX} + D_{YY}) = \frac{3}{2}D_{ZZ} \\ E &= \frac{1}{2}(D_{XX} - D_{YY}) \end{aligned} \tag{4}$$

where $|D| > 3E$ and $E > 0$ in the standard conventions of molecular magnetism. The first convention fixes the attribution of the Z axis as the most different one in comparison to the two others, i.e., the Z magnetic axis is either the hard or easy axis of magnetization. The second convention fixes the sign of E and imposes X to be either the intermediate or hard axis of magnetization, respectively. In this way, the magnetic axes frame is defined univocally as well as the ZFS parameters. In the copper acetate complex, the Z axis almost coincides with the Cu−Cu direction.

The axial D and rhombic E ZFS parameters reflect the splitting and mixing of the three M_S components of the triplet induced by SSC and SOC[55] which are the main relativistic contributions to the ZFS.[56] In the general case and in absence of symmetry, the *separate* consideration of SSC and SOC interactions will generate different magnetic axes frames. The final eigenframe of the ZFS tensor will then not coincide with either axis frame. However, for a (nearly) D_{2h} symmetric molecule the two effects can be considered separately (as will be shown in the Role of Dynamic Correlation on the ZFS Parameters section) and the following approximations can be made:

$$\begin{aligned} D_{SSC+SOC} &\approx D_{SSC} + D_{SOC} \\ E_{SSC+SOC} &\approx E_{SSC} + E_{SOC} \end{aligned} \tag{5}$$

where the index SSC+SOC refers to a joint treatment of SSC and SOC, and the indices SSC and SOC refer to separate treatments.

The ab initio calculations will be performed using both joint and separate treatments, but the analytical derivation of the ZFS only concerns the SOC contribution. Although the SSC contribution is non-negligible, it is not the dominant interaction. Moreover, it is relatively straightforward to calculate the SSC in an accurate way with the here-used ab initio methodology, and hence, it does not require a profound analysis to rationalize its sign or magnitude. One should, however, notice that the ab initio value of D_{SSC} obtained in this work is different from the value obtained using the point-dipole approximation[10] due to the role of the delocalization of the magnetic orbitals as shown by Riplinger et al.[57] On the contrary, the SOC contribution is quite difficult to calculate precisely from ab initio methods, and since it is dominant, an accurate rationalization of the sign is crucial to ensure that the ZFS parameters are correctly calculated. Besides, it is quite easy to develop a good model using a simple spin−orbit operator and the quasi-degenerate perturbation theory up to the second order. Such a derivation provides analytical expressions of the D_{SOC} and E_{SOC} parameters that lead to a better understanding of the physical origin of the anisotropy in copper acetate complexes and rationalizes their strong dependence on electron correlation.

Analytical Derivation of the Spin−Orbit Coupling Contribution to the Zero-Field Splitting. Analytical expressions for D_{SOC} in copper acetate have already been presented and used in the literature.[2,9] However, they are usually expressed as functions of the *g*-matrix components (which, in general, is incorrect[21]), and to the best of our knowledge, no expression has been presented for E_{SOC}. To facilitate the discussion below, the derivation of both parameters is given below. The molecule is assumed to belong to the D_{2h} symmetry point group, and the derivation is performed in the magnetic axes frame. Second-order QDPT is used to analytically derive the expression of the SOC contribution to the ZFS tensor using the giant spin Hamiltonian formalism. The model space S_0 consists of the three M_S components of the lowest triplet Φ_0:

$$|\Phi_0, 1\rangle = |\mathrm{d}_{x^2-y^2}(a)\mathrm{d}_{x^2-y^2}(b)\rangle \tag{6}$$

$$|\Phi_0, -1\rangle = |\bar{\mathrm{d}}_{x^2-y^2}(a)\bar{\mathrm{d}}_{x^2-y^2}(b)\rangle \tag{7}$$

$$|\Phi_0, 0\rangle = \frac{1}{\sqrt{2}}(|\bar{\mathrm{d}}_{x^2-y^2}(a)\mathrm{d}_{x^2-y^2}(b)\rangle + |\mathrm{d}_{x^2-y^2}(a)\bar{\mathrm{d}}_{x^2-y^2}(b)\rangle) \tag{8}$$

where only the singly occupied orbitals are specified. The overbar is used to indicate an orbital occupied by a spin-down electron, and (a) and (b) refer to the magnetic centers A and B. The effective single-electron SOC operator is treated as a perturbation and defined by

$$\hat{H}_{SOC} = \zeta \sum_i \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \tag{9}$$

Here, ζ is the effective SOC constant, which is slightly reduced from the free-ion value due to covalency effects (a detailed discussion of central-field vs symmetry-restricted covalency has been given in ref 21). Although the total number of interacting states is quite large, it is possible to reduce the size of the outer space to only eight excited states using symmetry and energetic arguments. Since Φ_0 belongs to the A_u irreducible representation, the SOC operator only couples the M_S components of this triplet with higher-lying singlet and triplet states belonging to ungerade irreducible representations. Furthermore, these excited states only interact with Φ_0 if they arise from a single spatial excitation. Let us consider the lowest excited triplet and singlet states which interact with Φ_0. The $M_S = 1$ of the former and the $M_S = 0$ of the latter can be expressed as

$$\begin{aligned} |\Phi_n^T, 1\rangle &= \frac{1}{\sqrt{2}}[|d_n(a)d_{x^2-y^2}(b)\rangle + |d_{x^2-y^2}(a)d_n(b)\rangle] \\ |\Phi_n^S, 0\rangle &= \frac{1}{2}[|d_n(a)\bar{\mathrm{d}}_{x^2-y^2}(b)\rangle - |\bar{\mathrm{d}}_n(a)d_{x^2-y^2}(b)\rangle - |d_{x^2-y^2}(a)\bar{\mathrm{d}}_n(b)\rangle \\ &\quad + |\bar{\mathrm{d}}_{x^2-y^2}(a)d_n(b)\rangle] \end{aligned} \tag{10}$$

where Φ_n^{T} and Φ_n^{S} are triplet and singlet states in which an electron is excited from a local (on site a or b) $\mathrm{d}_n(a, b)$ orbital to the $\mathrm{d}_{x^2-y^2}(a, b)$ orbital. The matrix elements of the $\hat{H}_{SOC}$ operator between Φ_0 and these excited singlet and triplet states are given in the Supporting Information. The matrix elements of the effective anisotropic model Hamiltonian $\hat{H}^{\mathrm{eff}}$ expanded in the model space S_0 are derived from the elements of $\hat{H} = \hat{H}_e + \hat{H}_{SOC}$, involving the electronic energies of the spin-free states and the SOC interactions, using second-order QDPT:

$$\begin{aligned} \langle \Phi_0, M_S|\hat{H}^{\mathrm{eff}}|\Phi_0, M_{S'}\rangle &= \langle \Phi_0, M_S|\hat{H}|\Phi_0, M_{S'}\rangle \\ &\quad - \sum_{\Phi_k, M_{S_k}} \frac{\langle \Phi_0, M_S|\hat{H}|\Phi_k, M_{S_k}\rangle\langle \Phi_k, M_{S_k}|\hat{H}|\Phi_0, M_{S'}\rangle}{\Delta_k} \end{aligned} \tag{11}$$

with $\Delta_k = E(\Phi_k) - E_0$, the energy difference between the spin orbit free states Φ_k and Φ_0. The effective Hamiltonian matrix is given in the Supporting Information. Comparing these elements with those of the GSH leads to the relations

$$\begin{aligned} D &= \frac{\langle \Phi_0, 1|\hat{H}_{eff}|\Phi_0, 1\rangle + \langle \Phi_0, -1|\hat{H}_{eff}|\Phi_0, -1\rangle}{2} - \langle \Phi_0, 0|\hat{H}_{eff}|\Phi_0, 0\rangle \\ E &= \langle \Phi_0, 1|\hat{H}_{eff}|\Phi_0, -1\rangle \end{aligned} \tag{12}$$

The following quantities are introduced to simplify the final expressions:

$$\begin{aligned} \Delta E_{x^2-y^2,n} &= \sqrt{\Delta_{\Phi_n^T} \cdot \Delta_{\Phi_n^S}} \\ J_{x^2-y^2,n} &= E_{\Phi_n^T} - E_{\Phi_n^S} \end{aligned} \tag{13}$$

where $\Delta E_{x^2-y^2,n}$ is the geometric mean of the excitations energies $\Delta_{\Phi_n^{\mathrm{T}}}$ and $\Delta_{\Phi_n^{\mathrm{s}}}$ corresponding to the same spatial single-excitation and $J_{x^2-y^2,n}$ is the energy difference between the corresponding singlet and triplet states. The intermediate steps in the derivation of the analytical relations for D and E are given in the Supporting Information. The final expression for D is

$$D = 2\frac{\zeta^2 J_{x^2-y^2,xy}}{\Delta E^2_{x^2-y^2,xy}} - \frac{1}{4}\frac{\zeta^2 J_{x^2-y^2,xz}}{\Delta E^2_{x^2-y^2,xz}} - \frac{1}{4}\frac{\zeta^2 J_{x^2-y^2,yz}}{\Delta E^2_{x^2-y^2,yz}} \tag{14}$$

while the analytical expression for the rhombic parameter E is

$$E = \frac{1}{4}\frac{\zeta^2 J_{x^2-y^2,yz}}{\Delta E^2_{x^2-y^2,yz}} - \frac{1}{4}\frac{\zeta^2 J_{x^2-y^2,xz}}{\Delta E^2_{x^2-y^2,xz}} \quad (15)$$

One should notice that excited states involving singly occupied d_{z^2} orbitals cannot contribute to these expressions in the D_{2h} symmetry point group. Since the matrix element $\langle d(z^2)|\hat{l}\cdot\hat{s}|d(x^2-y^2)\rangle$ is zero, it is clear that the single-electron SOC operator cannot couple the $\Phi_{z^2}{}^S$ and $\Phi_{z^2}{}^T$ states with the lowest triplet state Φ_0.

These expressions provide important insight into the origin of the ZFS parameters in binuclear complexes and the computational treatment required for an accurate determination of their magnitude. Both of them are governed by the interaction $(J_{x^2-y^2,n})$ between pairs of excited singlet and triplet states with the same electronic configuration. Since in D_{2h} symmetry the orbitals $d_{x^2-y^2}(a)$ and $d_n(b)$ are orthogonal for symmetry reasons, the corresponding interactions which could be seen as isotropic exchange couplings do not contain any kinetic contribution. In absence of electron correlation they are completely determined by the sum of direct exchange integrals $K_{x^2-y^2,n}$ and bielectronic integrals of the following type:

$$\begin{aligned} J^u_{x^2-y^2,n} &= 2\langle d_{x^2-y^2}(a)d_n(b)|r_{12}{}^{-1}|d_n(b)d_{x^2-y^2}(a)\rangle \\ &\quad - 2\langle d_n(a)d_{x^2-y^2}(b)|r_{12}{}^{-1}|d_{x^2-y^2}(a)d_n(b)\rangle \\ &= 2K_{x^2-y^2,n} - 2\langle d_n(a)d_{x^2-y^2}(b)|r_{12}{}^{-1}|d_{x^2-y^2}(a)d_n(b)\rangle \quad (16) \end{aligned}$$

where the upper index u indicates the ungerade symmetry of the states for which the coupling is calculated. The second integral arises from the interaction between two *monocentric* distributions and could therefore be larger than the direct exchange integral which consists in the interaction of a *bicentric* distribution with itself. Moreover, electron correlation may deeply affect the magnitude of the excited states' magnetic couplings as is the case for the ground state. As a consequence the determination of the ZFS parameters may require a high level of theoretical treatment.

Computational Details. The experimental geometry of the complex has been considered for the present study.[58] Calculations have been performed using the two-step approach implemented in the ORCA[38] code in which the SOC and SSC relativistic effects are included a posteriori. First, several solutions of the nonrelativistic Born−Oppenheimer Hamiltonian are computed with complete active space self-consistent field (CASSCF) and post-CASSCF methods. Then, the SOC and SSC between these different solutions are treated variationally,[39] through the diagonalization of the state interaction (SI) matrix. The Breit−Pauli SSC Hamiltonian and a mean-field SOC Hamiltonian are used.[49,59]

Dynamic correlation effects can be introduced either by using correlated energies in the diagonal elements of the SOC/SSC matrix[60,61] while keeping the CASSCF wave functions, or by using both the correlated energies and wave functions. Since accurate $J_{x^2-y^2,n}$ values are imperative for the present study, various post-CASSCF methods are considered. The n-electron valence second-order peturbation theory (NEVPT2) method[62−64] is used to compute correlated energies, and the difference dedicated configuration interaction (DDCI) method[65,66] is used to calculate both correlated wave functions and energies. Configuration interactions noted DDCI1 involve one hole and one particle single excitations on the full active space; DDCI2 also accounts for the one hole/one particle single-excitations and the two holes and two particles diexcitations. The two holes/one particle and one hole/two particles excitations (2h−1p and 1h−2p) are taken into account in DDCI3. The t_{pre} and t_{sel} thresholds explained elsewhere in detail[67] were set to tight values of 10^{-5} and 10^{-8} au, respectively, in the DDCI calculations.

Table 1. Ground-State Magnetic Coupling (in cm^{-1}) Computed Using Different Methods

method	$J_{x^2-y^2,x^2-y^2}$
CASSCF	+18.9
NEVPT2	+39.8
DDCI2	+67.5
DDCI3	+271.3
experiment (ref 75)	+292.2

Two different active spaces are considered: in the CAS(2,2) only the ground-state magnetic orbitals of mainly Cu-3$d_{x^2-y^2}$ character are included in the active space. The CAS(18,10) includes all the Cu-3d valence orbitals and electrons. The SOC and SSC interactions are computed in the basis of five triplet and four singlet states of A_u symmetry, i.e., the lowest triplet and the eight excited singlet and triplet states $\Phi^{S,T}_{x^2-y^2,n}$. Since the symmetry of the complex slightly deviates from perfect D_{2h} symmetry, the $\Phi^{S,T}_{x^2-y^2,z^2}$ states, which according to eqs 14 and 15 do not contribute to the ZFS parameters, are also considered in the QDPT matrix. Whereas the orbitals have been optimized in a state average self-consistent field calculation on the lowest singlet and triplet states for the CAS(2,2), the orbitals of the CAS(18,10) are obtained from an energy minimization of the average of the five lowest triplet and the four lowest singlet states of A_u symmetry.

Def2-sv(p) basis sets are used for all atoms. Test calculations show that the spin−orbit free energies obtained with larger basis sets, e.g., Def2-tzvpp,[68] are very similar to those obtained using the Def2-sv(p) basis sets.

Final ZFS parameters are extracted using the effective Hamiltonian theory.[69,70] This method uses both the ab initio energies and wave functions in order to determine numerically the matrix representative of the best effective Hamiltonian working in a chosen model space (here the space of the giant spin Hamiltonian). The effective Hamiltonian fulfills two conditions: its eigenvalues are the ab initio energies, whereas its eigenvectors are the orthonormalized projections of the ab initio wave functions onto the model space. The one-to-one comparison of the numerical matrix elements to those of the analytical matrix of the model Hamiltonian leads to the determination of the full $\bar{\bar{\mathbf{D}}}$ tensor. The magnetic axes are those that diagonalize the $\bar{\bar{\mathbf{D}}}$ tensor, and the D and E parameters are obtained using eq 4. This method has successfully been applied to several mononuclear and binuclear compounds.[31−35]

■ RESULTS AND DISCUSSION

Role of Dynamic Correlation on the ZFS Parameters. In the first part of the study, we have computed the ground-state exchange coupling using several theoretical approaches. This antiferromagnetic interaction is given by the energy difference between the lowest A_u triplet and the ground-state singlet A_g spin orbit free states. Results are reported in Table 1. Different values of $J_{x^2-y^2,x^2-y^2}$ are obtained depending on the level of theory. As already observed in many other publications,[71−74] the DDCI3 magnetic coupling value compares well with the experimental one,[75] whereas the J-values obtained with other computational methods are considerably too small. The high accuracy of the

Table 2. Relative Energies $\Delta E_{x^2-y^2,n}$ and Excited-State Magnetic Couplings $J_{x^2-y^2,n}$ (in cm^{-1}) Computed Using Different Methods

method	$\Delta E_{x^2-y^2,xy}$	$\Delta E_{x^2-y^2,z^2}$	$\Delta E_{x^2-y^2,yz}$	$\Delta E_{x^2-y^2,xz}$
CASSCF	8659	10778	11632	11954
NEVPT2	11272	12851	14049	14447
DDCI1	8628	10253	11418	11728
DDCI2	10180	11701	13153	13521
DDCI3	12280	13313	15510	15090
method	$J_{x^2-y^2,xy}$	$J_{x^2-y^2,z^2}$	$J_{x^2-y^2,yz}$	$J_{x^2-y^2,xz}$
CASSCF	−1.8	−53.5	−30.0	−35.4
NEVPT2	−0.6	−102.0	−16.2	−21.3
DDCI1	−1.4	−233.9	−31.5	−39.9
DDCI2	−15.9	−265.4	−31.5	−38.5
DDCI3	−29.9	−359.0	−63.9	−64.0

DDCI3 approach has been attributed to the important role of the 2h−1p excitations for the kinetic exchange contribution.[74]

Since the SOC contribution to the ZFS depends on the excited-state magnetic couplings and the relative energy with respect to the lowest triplet state, we first proceed to compute these spin−orbit free quantities using different correlated methods. The magnetic coupling in excited states has a different physical origin than the magnetic coupling of the lowest singlet and triplet states. The kinetic exchange, an important factor in the antiferromagnetic character of the ground-state coupling, is almost absent in the excited-state coupling due to the symmetry of the complex. Actually, magnetic couplings in the excited states of copper acetate are ferromagnetic, whatever the computational method is: see Table 2. The variation of the coupling is weak for CASSCF and becomes much stronger when electron correlation is taken into account. Note that the trends in the different couplings are the same for all levels of calculation.

The zeroth-order description of the excited-state magnetic couplings given in eq 16 is exactly reproduced with CAS(18,10)SCF. It is interesting to note that these two integrals only bring small contributions to the magnetic couplings before the inclusion of dynamic correlation. This is particularly true for the $J_{x^2-y^2,xy}$ coupling which is the leading contribution to the D_{SOC}. Including charge and spin polarization effects by single excitations (DDCI1 entry in Table 2) does not significantly increase the strength of the couplings. The main contribution is provided by the 2h−1p and 1h−2p excitations accounted for in the DDCI3 calculation. Since these contributions usually make the magnetic orbitals more diffuse,[71] one could attribute the increase of the magnetic coupling to this physical effect.

The relative energies of the excited states with respect to the ground state ($\Delta E_{x^2-y^2,n}$) also depend considerably on the electron correlation. Although NEVPT2 is not precise enough for an accurate description of magnetic couplings as already observed in previous works,[74] it provides quite accurate values of $\Delta E_{x^2-y^2,n}$. From the experimental study[9] performed on the copper acetate pyrazine complex, which has a structure similar to the copper acetate monohydrate complex, $\Delta E_{x^2-y^2,xy}$ was found to be close to 12 000 cm^{-1} and the $\Delta E_{x^2-y^2,xz}$ and $\Delta E_{x^2-y^2,yz}$ values were around 15 500 cm^{-1}. One should notice that the experimental $\Delta E_{x^2-y^2,z^2}$ value is around 10 000 cm^{-1}, whereas our theoretical estimate is centered around 13 000. This difference may be attributed to the stronger ligand field produced by the pyrazine ligand in comparison to the water molecule.

Table 3. ZFS Parameters (in cm^{-1}) Extracted from Either SOC or SSC Calculations Separately or Combining Both SOC and SSC in the SI Matrix[a]

method	D_{SSC}	D_{SOC}	$D_{\mathrm{SSC+SOC}}$	E_{SSC}	E_{SOC}	$E_{\mathrm{SSC+SOC}}$
CASSCF	−0.118	−0.017	−0.137	0.000	0.001	0.000
NEVPT2	−0.118	−0.026	−0.144	0.000	0.003	0.003
DDCI1	−0.118	+0.005	−0.115	0.000	0.001	0.003
DDCI2	−0.118	−0.172	−0.291	0.000	0.002	0.002
DDCI3	−0.118	−0.200	−0.319	0.000	0.006	0.006
experiment (ref 10)			−0.335			0.01

[a] Wave functions are the CAS(18,10)SCF ones, whereas the energies used in the SI matrix are those of the indicated methods. E is conventionally defined positive.

Table 4. ZFS Parameters (in cm^{-1}) Extracted from Separate SOC or SSC Calculations or from Combining SOC and SSC in the SI Matrix[a]

method	D_{SSC}	D_{SOC}	$D_{\mathrm{SSC+SOC}}$	E_{SSC}	E_{SOC}	$E_{\mathrm{SSC+SOC}}$
DDCI1	−0.117	−0.008	−0.112	0.000	0.002	0.003
DDCI2	−0.100	−3.321	−3.442	0.000	0.066	0.006
DDCI3	−0.091	−2.303	−2.394	0.000	0.052	0.052

[a] Correlated energies and wave functions of the indicated methods are used in the SI matrix.

Having established the accuracy of the different methods for the calculation of the relevant spin−orbit free quantities, we now extract the ZFS parameters using the effective Hamiltonian theory as described in ref 31. The results reported in Table 3 are obtained with either CASSCF or post-CASSCF energies on the diagonal of the state interaction matrix, whereas CASSCF wave functions are used to calculate the off-diagonal matrix elements. The state interaction matrix contains both SOC and SSC contributions.

One may first notice that the SSC contribution to the ZFS parameters is very well described at the first order of perturbation theory. The SOC contribution to the ZFS parameters is, as expected, very sensitive to electron correlation. The comparison between theory and experiment demonstrates the very good agreement of both the axial and rhombic parameters at the DDCI3 level. The D_{SOC} contribution is underestimated at lower levels of correlation due to the underestimation of the excited-state magnetic couplings. One should also notice that the computed values $D_{\mathrm{SSC+SOC}}$ and $E_{\mathrm{SSC+SOC}}$ are almost identical to the sum of the SOC and SSC contributions calculated separately (values only differ by 2.1×10^{-3} cm^{-1} at most), thus validating the approximations made in eq 5.

To address the question to what extent the lack of dynamic electron correlation effects in the wave functions influences the ZFS parameters, we have replaced the CASSCF wave function with DDCI wave functions in the calculation of the off-diagonal SI matrix elements. The results reported in Table 4 show that the D_{SOC} and E_{SOC} parameters calculated in this way are strongly overestimated. At first sight, this effect may be surprising since the DDCI wave functions are in principle closer to the exact solution than the CASSCF wave functions. However, when using a truncated correlated wave function the SOC extradiagonal elements are also truncated. For instance, the contribution of the spin−orbit interactions between 1h−2p (2h−1p) and the 2h−2p (which are not introduced in the CI), are missing and

Table 5. SOC Contributions to the ZFS Parameters Calculated with Equations 14 and 15 with $J_{x^2-y^2,n}$ and $\Delta E_{x^2-y^2,n}$ Obtained through CASSCF, NEVPT2, DDCI2, and DDCI3[a]

method	D_{SOC} (eq 14)	D_{SOC} (ab initio)	E_{SOC} (eq 15)	E_{SOC} (ab initio)
CASSCF	0.047	−0.017	0.005	0.001
NEVPT2	0.025	−0.026	0.003	0.003
DDCI2	−0.143	−0.172	0.005	0.001
DDCI3	−0.179	−0.200	0.003	0.006

[a] Results are compared with the ab initio ZFS parameters. All values are given in cm^{-1}.

Table 6. $\Delta E_{x^2-y^2,n}$, $J_{x^2-y^2,n}$ and Their Contributions to D_{SOC} Decomposed into Contributions Arising from the Different Excited States[a]

n	$\Delta E_{x^2-y^2,n}$	$J_{x^2-y^2,n}$	$D_{SOC}(n)$
xy	12280	−29.9	−0.276
z^2	13313	−359.0	0.000
xz	15090	−64.0	+0.048
yz	15510	−63.9	+0.045
total			−0.179
ab initio			−0.200

[a] Spin-free quantities are obtained at the DDCI3 level. All values are given in cm^{-1}.

this leads to an unbalanced treatment of the off-diagonal elements. On the contrary, when CASSCF wave functions are used all the spin−orbit interactions between the states involved in the SI are calculated, since the CASSCF wave functions are solutions of a full configuration interaction in the active space.

Validity of the D_{SOC} and E_{SOC} Analytical Expressions. In order to check the relevance of the analytical expressions of the SOC contributions to the ZFS parameters, we have calculated estimates of the D_{SOC} and E_{SOC} parameters from eqs 14 and 15 using the $J_{x^2,y^2,n}$ and $\Delta E_{x^2-y^2,n}$ values reported in Table 2. The SOC constant of the Cu^{2+} ion is used for ζ, and results are compared to the ab initio results in Table 5. The good agreement between the ab initio results and those obtained with eqs 14 and 15 demonstrates the validity of the analytical expressions of D_{SOC} and E_{SOC}. It is also interesting to see how the use of underestimated values for $\Delta E_{x^2-y^2,n}$ and $J_{x^2-y^2,n}$ may lead to positive values of D_{SOC}. Additional insight on the physical origin of magnetic anisotropy in the copper acetate molecule is provided by the decomposition of the D_{SOC} parameter in its different contributions. Table 6 reports the estimates of D_{SOC} obtained at the DDCI3 level by each couple of singlet and triplet excited states $\Phi^{S,T}_{x^2-y^2,n}$ having the same spatial configuration. Although the symmetry of the complex slightly deviates from D_{2h} symmetry, one may first confirm that the $\Phi^{S,T}_{x^2-y^2,z^2p}$ excited states do not contribute to the D_{SOC} parameter since the ab initio SOC between these states and the ground state is negligible. This result legitimates the neglect of the participation of these states to the analytical expressions derived above. Since both the $J_{x^2-y^2,n}$ and $\Delta E_{x^2-y^2,n}$ values are of the same order of magnitude for all the excited states, the D_{SOC} parameter is dominated by the contribution of the $\Phi^{S,T}_{x^2-y^2,x,y}$ states, as expected from eq 14.

Having established that eq 14 covers the main physics of the axial anisotropy, it is interesting to discuss some previous studies in order to understand why a correct analytical expression led to a wrong sign of the axial D parameter of copper acetate compounds. Note first that it is important that, although the D_{SSC} contribution to the overall D parameter is non-negligible, the D_{SOC} contribution is dominant. The D_{SOC} value is governed by the magnitude of the magnetic couplings of excited states, and consequently a precise value of these couplings is required for an accurate determination of D.

In their first study of the copper acetate monohydrate compound,[2] Bleaney and Bowers presented an analytical expression of D_{SOC} similar to that of eq 14. However, the authors assumed that all the $J_{x^2-y^2,n}$ magnetic couplings were equal to the ground-state coupling $J_{x^2-y^2,x^2-y^2}$. As seen in Tables 1 and 3, the magnetic coupling of the ground state is antiferromagnetic, whereas those of the ungerade excited states are ferromagnetic. As a consequence, these incorrect values of the magnetic couplings led to a wrong sign of the D parameter.

A second important study concerned the copper acetate pyrazine compound.[9] As mentioned before, this molecule has a similar structure as the monohydrate compound, and hence, the formula presented in eq 14 applies. The authors analyzed in great detail the polarized absorption and magnetic circular dichroism spectra to determine the precise energy level diagram. They found an antiferromagnetic value close to 50 cm^{-1} for the $J^{g}_{x^2-y^2,x,y}$ coupling from the energy difference between the $^3A_{2g}$ and the $^1A_{2g}$ states. Assuming that this coupling is identical to the magnetic coupling $J^{u}_{x^2-y^2,x,y}$ between ungerade states (which provides the leading contribution to D_{SOC}), they also concluded that D was positive. The expressions of the singlet and triplet of gerade symmetry (indicated in upper-index) are

$$|\Phi^{T}_{xy},1\rangle_g = \frac{1}{\sqrt{2}}[|d_{xy}(a)d_{x^2-y^2}(b)\rangle - |d_{x^2-y^2}(a)d_{xy}(b)\rangle]$$

$$\begin{aligned}|\Phi^{S}_{xy},0\rangle_g = \frac{1}{2}[&|d_{xy}(a)\bar{d}_{x^2-y^2}(b)\rangle - |\bar{d}_{xy}(a)d_{x^2-y^2}(b)\rangle \\ &+ |d_{x^2-y^2}(a)\bar{d}_{xy}(b)\rangle - |\bar{d}_{x^2-y^2}(a)d_{xy}(b)\rangle] \qquad (17)\end{aligned}$$

The different signs in comparison with the ungerade states result in a different expression of their energy difference:

$$\begin{aligned}\Delta E^{ST}_{g} = J^{g}_{x^2-y^2,xy} &= 2\langle d_{x^2-y^2}(a)d_{xy}(b)|r_{12}{}^{-1}|d_{xy}(b)d_{x^2-y^2}(a)\rangle \\ &\quad + 2\langle d_{xy}(a)d_{x^2-y^2}(b)|r_{12}{}^{-1}|d_{x^2-y^2}(a)d_{xy}(b)\rangle \\ &= 2K_{x^2-y^2,xy} + 2\langle d_{xy}(a)d_{x^2-y^2}(b)|r_{12}{}^{-1}|d_{x^2-y^2}(a)d_{xy}(b)\rangle \qquad (18)\end{aligned}$$

The second integral appears with a positive sign, whereas it appeared with a negative sign in the expression of the magnetic coupling between the ungerade states for symmetry reasons (see eq 16). On the basis of the assumption that the second integral can be neglected, the coupling between gerade and ungerade states was expected to be similar.[9] However, as we have seen in the previous section, these interactions depend strongly on the dynamic electron correlation treatment and are not negligible. In fact, they govern the magnitude of the excited-state couplings and are responsible for the ferromagnetic interaction between the ungerade $\Phi^{S,T}_{x^2-y^2,x,y}$ states.

■ CONCLUSION

The determination of the ZFS parameters of copper acetate is a difficult problem, both experimentally and theoretically. The quantities to be extracted are very small and require the use of state-of-the-art methods. Despite the broad interest of the scientific community in these compounds, the sign of the axial ZFS parameter was only determined experimentally in 2008,[10] more than 50 years after the pioneering work of Bleaney and Bowers.[2] The theoretical determination presented in this work also required the use of precise ab initio calculations. Several conclusions have emerged from this work:

- The SSC contribution to the axial ZFS parameter is far from being negligible, $D_{SSC} \simeq D/3$, and should therefore be included in the calculation. It is completely described at the first order of perturbation theory, i.e., including only the lowest triplet state in the SI matrix. The calculated value slightly differs from the one obtained using the point dipole approximation ($D_{SSC} = -0.171$ cm^{-1}).[10]
- The SOC contributions to the ZFS parameters are dominated by the magnetic couplings of excited states and their mean energy difference to the lowest triplet state. Because of the sensitivity of the excited states' magnetic couplings to electron correlation, the magnitude and nature of the SOC parameters are also strongly dependent on the level of theory. The computationally demanding DDCI3 method, which is considered to be the most accurate method for the determination of magnetic couplings, was used to determine the low-energy spectrum of the complex.
- Using analytical expressions of the D_{SOC} and E_{SOC} parameters, it is possible to reproduce the main contributions to the SOC parameters using the SOC of the Cu^{2+} ion and the spin-free ab initio energies of the excited states. The agreement between the so-calculated SOC parameters and the ab initio ones demonstrates the validity of these analytical expressions.
- The reason why the use of a similar analytical expression of D_{SOC} has led to a wrong sign of the D parameter in previous works can be attributed to the use of incorrect values of the excited states' magnetic couplings.

Although this work is devoted to the determination of the anisotropy parameters of the copper acetate monohydrate complex, it also provides some interesting information concerning the theoretical description of the spin-free excited-state spectrum and also on the theoretical treatment of the ZFS using MRCI energies and wave functions. The magnetic coupling between the excited states increases with the level of electron correlation. The decomposition of the physical factors contributing to these ferromagnetic couplings will be the subject of a further investigation. We have also seen that, although very accurate results are obtained using correlated energies and CASSCF wave functions, the results get damaged when using the correlated wave functions to compute the SOC matrix. Although arguments have been put forward to rationalize this behavior, a detailed explanation of this observation will require more methodological work that is outside the scope of this paper.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Representative matrix of the multispin Hamiltonian in the $|S, M_S\rangle$ basis in an arbitrary axes frame, representative matrix of the giant spin Hamiltonian in the $|M_S\rangle$ components of the lowest-lying triplet state basis in an arbitrary axes frame, representative matrix of the giant spin Hamiltonian in the magnetic axes frame, matrix elements of the SOC operator between the lowest triplet state components and the excited states' components, matrix elements of the effective model Hamiltonian obtained at the second-order of perturbation, and intermediate steps in the calculation of the D and E analytical expressions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: nathalie.guihery@irsamc.ups-tlse.fr.

■ ACKNOWLEDGMENT

Financial support has been provided by the Spanish Ministry of Science and Innovation (project CTQ2008-06644-C02-01), the Generalitat de Catalunya (project 2009SGR462 and Xarxa d'R+D+I en Qumica Teòrica i Computacional, XRQTC), and the Agence Nationale de la Recherche (ANR) (project TEMAMA ANR-09-BLAN-0195-01). F.N. thanks the Sonderforschungsbereich 813 ("Chemistry at Spin Centers"), the University of Bonn, and the Max-Planck Society (fellow program) for financial support of this work.

■ REFERENCES

(1) Guha, B. C. *Proc. R. Soc. London, Ser. A* **1951**, *206*, 353–373.
(2) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451–465.
(3) Van Niekerk, J. N.; Schoenig, F. R. L. *Acta Crystallogr.* **1953**, *6*, 227–232.
(4) Ross, I. G. *Faraday Soc.* **1959**, *55*, 1058–1063.
(5) Ross, I. G. *Faraday Soc.* **1959**, *55*, 1064–1069.
(6) Gerloch, M.; Harding, J. H. *Proc. R. Soc. London, Ser. A* **1978**, *360*, 211–227.
(7) Gregson, A. K.; Martin, R. L.; Mitra, S. *Proc. R. Soc. London, Ser. A* **1971**, *320*, 473–486.
(8) Gribnau, M. C. M.; Keijzers, C. P. *Inorg. Chem.* **1987**, *26*, 3413–3414.
(9) Ross, P. K.; Allendorf, M. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 4009–4021.
(10) Ozarowski, A. *Inorg. Chem.* **2008**, *47*, 9760–9762.
(11) Webb, S. P.; Gordon, M. S. *J. Chem. Phys.* **1998**, *109*, 919–927.
(12) Pederson, M. R.; Jackson, K. A. *Phys. Rev. B* **1990**, *41*, 7453–7461.
(13) Jackson, K. A.; Pederson, M. R. *Phys. Rev. B* **1990**, *42*, 3276–3281.
(14) Pederson, M. R.; Khanna, S. N. *Phys. Rev. B* **1999**, *60*, 9566–9572.
(15) Baruah, T.; Pederson, M. R. *Int. J. Quantum Chem.* **2003**, *93*, 324–331.
(16) Kortus, J.; Pederson, M. R.; Baruah, T.; Bernstein, N.; Hellberg, C. S. *Polyhedron* **2003**, *22*, 1871–1876.
(17) Park, K.; Pederson, M. R.; Richardson, S. L.; Aliaga-Alcalde, N.; Christou, G. *Phys. Rev. B* **2003**, *68*, 020405.
(18) Ribas-Ariño, J.; Baruah, T.; Pederson, M. R. *J. Chem. Phys.* **2005**, *123*, 044303.
(19) Ribas-Ariño, J.; Baruah, T.; Pederson, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 9497–9505.
(20) Ruiz, E.; Cirera, J.; Cano, J.; Alvarez, S.; Loose, C.; Kortus, J. *Chem. Commun.* **2008**, 52–54.
(21) Neese, F.; Solomon, E. I. *Inorg. Chem.* **1998**, *37*, 6568–6582.
(22) Vahtras, O.; Loboda, O.; Minaev, B.; Ågren, H.; Ruud, K. *Chem. Phys.* **2002**, *279*, 133–142.
(23) Malmqvist, P.-Å.; Roos, B. O.; Schimmelpfennig, B. *Chem. Phys. Lett.* **2002**, *357*, 230–240.

(24) Roos, B. O.; Malmqvist, P.-Å. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2919–2927.

(25) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222–239.

(26) de Graaf, C.; Sousa, C. *Int. J. Quantum Chem.* **2006**, *106*, 2470–2478.

(27) Petit, S.; Pilet, G.; Luneau, D.; Chibotaru, L.; Ungur, L. *Dalton Trans.* **2007**, 4582–4588.

(28) Chibotaru, L.; Ungur, L.; Aronica, C.; Elmoll, H.; Pilet, G.; Luneau, D. *J. Am. Chem. Soc.* **2008**, *130*, 12445–12455.

(29) Chibotaru, L.; Ungur, L.; Soncini, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4126–4129.

(30) Soncini, A.; Chibotaru, L. *Phys. Rev. B* **2008**, *77*, 220406.

(31) Maurice, R.; Bastardis, R.; de Graaf, C.; Suaud, N.; Mallah, T.; Guihéry, N. *J. Chem. Theory Comput.* **2009**, *5*, 2977–2984.

(32) Maurice, R.; Guihéry, N.; Bastardis, R.; de Graaf, C. *J. Chem. Theory Comput.* **2010**, *6*, 55–65.

(33) Maurice, R.; de Graaf, C.; Guihéry, N. *Phys. Rev. B* **2010**, *81*, 214427.

(34) Maurice, R.; de Graaf, C.; Guihéry, N. *J. Chem. Phys.* **2010**, *133*, 084307.

(35) Maurice, R.; Pradipto, A. M.; Guihéry, N.; Broer, R.; de Graaf, C. *J. Chem. Theory Comput.* **2010**, *6*, 3092–3101.

(36) Gilka, N.; Taylor, P. R.; Marian, C. M. *J. Chem. Phys.* **2008**, *129*, 044102.

(37) Ganyushin, D.; Neese, F. *J. Chem. Phys.* **2008**, *128*, 114117.

(38) Neese, F. *ORCA—an ab Initio, Density Functional and Semiempirical Program Package*, version 2.6; University of Bonn, Bonn, Germany, 2008.

(39) Ganyushin, D.; Neese, F. *J. Chem. Phys.* **2006**, *125*, 024103.

(40) Neese, F. *J. Am. Chem. Soc.* **2006**, *128*, 10213–10222.

(41) Neese, F. *J. Chem. Phys.* **2007**, *127*, 164112.

(42) Ganyushin, D.; Gilka, N.; Taylor, P. R.; Marian, C. M.; Neese, F. *J. Chem. Phys.* **2010**, *132*, 144111.

(43) Sinnecker, S.; Neese, F. *J. Phys. Chem. A* **2006**, *110*, 12267–12275.

(44) Duboc, C.; Phoeung, T.; Zein, S.; Pécaut, J.; Collomb, M.-N.; Neese, F. *Inorg. Chem.* **2007**, *46*, 4905–4916.

(45) Ganyushin, D.; Neese, F. *J. Chem. Phys.* **2008**, *128*, 114117.

(46) Zein, S.; Duboc, C.; Lubitz, W.; Neese, F. *Inorg. Chem.* **2008**, *47*, 134–142.

(47) Zein, S.; Neese, F. *J. Phys. Chem. A* **2008**, *112*, 7976–7983.

(48) Liakos, D. G.; Ganyushin, D.; Neese, F. *Inorg. Chem.* **2009**, *48*, 10572–10580.

(49) Neese, F. *J. Chem. Phys.* **2005**, *122*, 034107.

(50) Ganyushin, D.; Gilka, N.; Taylor, P.; Marian, C.; Neese, F. *J. Chem. Phys.* **2010**, *132* (14), 144111.

(51) Boča, R. *Theoretical Foundations of Molecular Magnetism*; Elsevier: Amsterdam, The Netherlands, 1999.

(52) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(53) Moriya, T. *Phys. Rev.* **1960**, *120*, 91–98.

(54) Buckingham, A. D.; Pyykko, P.; Robert, J. B.; Wiesenfeld, L. *Mol. Phys.* **1982**, *46*, 177–182.

(55) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Dover Publications: Dover, NY, 1986.

(56) Harriman, J. E. In *Theoretical Foundations of Electron Spin Resonance*; Loebl, E. M., Ed.; Academic Press: New York, 1978.

(57) Riplinger, C.; Kao, P. Y.; Rosen, G. M.; Kathirvelu, V.; Eaton, G. R.; Eaton, S.; Kutaleadze, A.; Neese, F. *J. Am. Chem. Soc.* **2009**, *131*, 10092–10106.

(58) Brown, G. M.; R., C. *Acta Crystallogr.* **1973**, *B29*, 2393–2403.

(59) Hess, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. *Chem. Phys. Lett.* **1996**, *251*, 365–371.

(60) Llusar, R.; Casarrubios, M.; Barandiarán, Z.; Seijo, L. *J. Chem. Phys.* **1996**, *105*, 5321–5330.

(61) Barandiarán, Z.; Seijo, L. *J. Chem. Phys.* **2003**, *118*, 7439–7456.

(62) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. *Chem. Phys. Lett.* **2001**, *350*, 297–305.

(63) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. *J. Chem. Phys.* **2002**, *117*, 9138–9153.

(64) Angeli, C.; Pastore, M.; Cimiraglia, R. *Theor. Chem. Acc.* **2007**, *117*, 743–754.

(65) Miralles, J.; Daudey, J.-P.; Caballol, R. *Chem. Phys. Lett.* **1992**, *198*, 555.

(66) Miralles, J.; Castell, O.; Caballol, R.; Malrieu, J.-P. *Chem. Phys.* **1993**, *172*, 33–43.

(67) Neese, F. *J. Chem. Phys.* **2003**, *128*, 9428.

(68) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(69) Bloch, C. *Nucl. Phys.* **1958**, *6*, 329–347.

(70) des Cloizeaux, J. *Nucl. Phys.* **1960**, *20*, 321–346.

(71) Cabrero, J.; Calzado, C. J.; Maynau, D.; Caballol, R.; Malrieu, J. P. *J. Phys. Chem. A* **2002**, *106*, 8146–8155.

(72) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 2728.

(73) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 3985.

(74) Calzado, C. J.; Angeli, C.; Taratiel, D.; Caballol, R.; Malrieu, J.-P. *J. Chem. Phys.* **2009**, *131*, 2009.

(75) Elmali, A. *Turk. J. Phys.* **2000**, *24*, 667–672.