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Crystal and Molecular Structure and Magnetic Exchange Properties of Bis(di-μ-ethoxo-bis(3,5-di-*tert*-butylsemiquinonato)dicopper(II)) Complex. A Synergy between DFT and Experimental Magnetochemistry

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The compound bis(di-μ-ethoxo-bis(3,5-di-*tert*-butylsemiquinonato)dicopper(II)) has been synthesized and its structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group *C*2/*c*, with $a = 37.736(8)$ Å, $b = 9.173(2)$ Å, $c = 23.270(5)$ Å, $\beta = 122.24(3)°$. The structure can be described as a Lewis adduct between two dinuclear $[Cu(DBSQ)(C_2H_5O)]_2$ units (DBSQ = 3,5-di-*tert*-butylsemiquinonato). The temperature dependence of the magnetic susceptibility was efficiently analyzed by a combined DFT/experimental approach, showing that a rather strong ferromagnetic interaction exists between the $DBSQ^-$ and the copper(II) ions modulated by an antiferromagnetic interaction between the two copper(II) ions of the dinuclear units. Weak antiferromagnetism between the two units in the unit cell was measured.

Introduction

The common approach to the investigation of the magnetic properties of insulating solids such as normal molecular magnets consists of partitioning the magnetic interaction in spin–spin interactions between adjacent magnetic centers, i.e., between atoms or molecular groups onto which the unpaired electron(s) are reasonably well localized. The interaction energy is computed by using a spin Hamiltonian[1] of the type

$$H = \sum J_{ik}\mathbf{S}_i\mathbf{S}_k \qquad (1)$$

where $\mathbf{S}_{i,k}$ are the spins associated with the different paramagnetic centers, and J_{ik} are called the isotropic magnetic exchange coupling constants and are parameters to be determined from experiments. The eigensolutions of H are eigenstates of $\mathbf{S}^2$, the total spin S being $\mathbf{S} = \sum_i \mathbf{S}_i$. In a high symmetric molecule in which all the spins and interactions are equal, the exchange coupling constant, J, has the simple physical meaning obtained by the expression of the Heisenberg spin ladder: $JS = E(S) - E(S - 1)$, where $E(S)$ is the energy of the spin state S. In more complex cases, the eigenstates of the Hamiltonian of eq 1 must be obtained from diagonalization of the Hamiltonian matrix computed on the S space, and no analytic expression for the eigenstates can be obtained.[2] Thus the Heisenberg Hamiltonian defines a family of states and then the electronic ground state of the paramagnetic system. Therefore, within this model the magnetic properties of a molecular magnet are defined by the simple interactions between the magnetic moments associated with the spins of the separated paramagnetic centers without any changes in their electronic properties. Since the spins $\mathbf{S}_i$ are chosen on the basis of the oxidation number formalism, there is no doubt that this model represents a useful, but simplified, view of the physical problem.

This approach to the description of the magnetic properties of molecular materials is expected to work well when, in a given derivative containing more than one paramagnetic center, the wave functions describing the electron spins are similar to those of the independent different counterparts. In other words this occurs when electron spin density is localized onto different parts of the molecules, the paramagnetic centers. On the other hand, it is common among magnetochemists to use the spin Hamiltonian approach to describe the magnetic properties of molecules in which extensive delocalization occurs, i.e., organic biradicals or transition

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(2) Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Springer-Verlag: Heidelberg, Germany, 1990.

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metal complexes with paramagnetic ligands, by assigning local spins by chemical intuition.[3] Quantum chemical calculations of the electronic ground states and next excited states of the systems are in these cases the only way of giving a meaning to the spin Hamiltonian parameters. This synergy between experiment and theory is quite peculiar to magnetochemistry, and becomes still more important when the complexity of the system under investigation increases.[4]

In the most common practice, the exchange coupling constants in eq 1 are obtained by least-squares fitting the measured temperature dependence of the molar magnetic susceptibility with the energies obtained by the diagonalization of eq 1. The J_{ik} are the parameters of the fitting procedure (together with the Zeeman g factor and a few other parameters, depending on the physical system under consideration). When the symmetry of the system is low, the number of parameters to be included in the fit can be rather high, and it can happen that the variance/covariance (or error) matrix has large out-of-diagonal elements. These are related to the covariance of couples of parameters that are, therefore, no longer independent. There is no doubt that this fact constitutes an obstacle for the correct analysis of the experimental data. This problem was already been considered in the past literature,[5-7] but the proposed approaches cannot be considered to offer an unambiguous general solution of the problem. We will show in the present paper the effect of the correlation between the spin Hamiltonian parameters in a four-spin system and how the use of DFT calculations can provide interesting suggestions to lead the chemists toward a reasonable interpretation of both the fitting procedure and the chemical sense of the obtained results.

We have found that a compound of analytical formula $Cu(DBSQ)(C_2H_5O)$ (DBSQ = 3,5-di-*tert*-butyl-semiquinonato) can be isolated from basic ethanolic solutions containing copper(II) salts and 3,5-di-*tert*-butylcatechol in a 1:1 ratio. The X-ray crystal structure shows that the solid compound contains a tetranuclear $[Cu(DBSQ)(C_2H_5O)]_4$ species, which can be described as a Lewis adduct between two dinuclear $[Cu(DBSQ)(C_2H_5O)]_2$ units. The chemical phenomenology of this result is rather well-known,[8,9] since when 3,5-di-*tert*-butyl-*o*-dioxolene is used, several polynuclear 3d-semiquinonato metal complexes are formed. This can be attributed to the presence of a not sterically conditioned oxygen donor in the 1-position of the dioxolene ring. A full analysis of the magnetic properties of these polynuclear complexes has never been attempted, presumably because of the high complexity of these systems. The temperature dependence of the magnetic susceptibility of the copper semiquinonato cluster we describe here was fitted by using the spin Hamiltonian of eq 1, but a meaningful set of parameters was obtained only by using the results of DFT calculations that allowed us to determine a priori the relative values of the exchange coupling constants.

Table 1. Crystal Data and Structure Refinement for $[Cu(DBSQ)(C_2H_5O)]_2$

fw	657.80
temp	150(2) K
wavelength	1.54178 Å
cryst syst, space group	monoclinic, *C*2/*c*
unit cell dimens	$a = 37.736(8)$ Å
	$b = 9.173(2)$ Å
	$c = 23.270(5)$ Å
	$\alpha = 90.000°$
	$\beta = 122.24°$
	$\gamma = 90.000°$
vol	6812(2) Å^3
Z	8
calcd density	1.283 mg/m^3
abs coeff	1.841 mm^{-1}
F(000)	2784
cryst size	0.6 × 0.2 × 0.2 mm^3
θ range for data collection	2.10° to 57.74°
limiting indices	$-38 \leq h \leq 38$
	$-8 \leq k \leq 9$
	$-25 \leq l \leq 25$
reflns collected/unique	6553/3470 [R(int) = 0.0603]
completeness to θ	57.95−73.1%
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3470/0/375
GOF on F^2	1.009
final R indices [$I > 2\sigma(I)$]	R1 = 0.0633
	wR2 = 0.1534
R indices (all data)	R1 = 0.1034

Experimental Section

Synthesis of $Cu(DBSQ)(C_2H_5O)$. A solution of copper(II) perchlorate hexahydrate (1 mmol) in ethanol (40 mL) was mixed with a solution of 3,5-di-*tert*-butylcatechol (1 mmol) in dichloromethane (30 mL). Triethylamine (0.5 mL) was then added and the resulting solution was gently warmed for 0.5 h and allowed to stand. Green-brown crystals were obtained after several hours. These crystals were filtered, washed with ethanol, and then air-dried. (Anal. Found: C 58.85; H 7.74; $C_{16}H_{25}CuO_3$ requires C 58.42; H 7.66.) The reaction conditions are very similar to those usually followed in the oxidation of catechols to quinones with copper salts in pyridine−methanol mixtures.[10] Here we have replaced pyridine with triethylamine and no copper(I) complexes were isolated. However, the presence of a small quantity of quinone as a reaction product was evidenced by TLC.

Crystal Structure Determination. X-ray data were collected on a CCD-1K three circles Bruker diffractometer, using Cu Kα radiation and a Göbel mirrors monochromator. Intensities were corrected for absorption (SADABS). The structure was solved by direct methods (SIR97),[11] which gave the position of all non-

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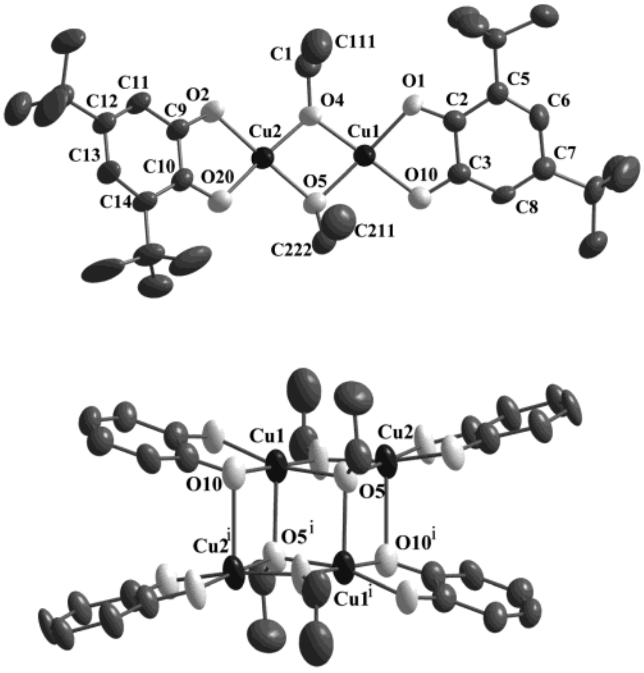

Figure 1. Top: ORTEP view of the asymmetric unit of $[Cu(DBSQ)(C_2H_5O)]_2$ with the atom numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 30% probability. Bottom: ORTEP view of one of the centrosymmetric units appearing in the unit cell.

hydrogen atoms, and was refined by Fourier difference syntheses, using SHELXL97[12] with the full-matrix least-squares method. During the final iterations, hydrogen atoms were added in calculated positions assuming idealized bond geometries. Anisotropic thermal parameters were applied for all non-hydrogen atoms. Details of data collection and structure refinement are given in Table 1.

Physical Measurements. Temperature dependence of the magnetic susceptibility was measured on polycrystalline powders of $[Cu(DBSQ)(C_2H_5O)]_2$ with a Cryogenic S600 SQUID magnetometer in the temperature range of 2−300 K with a magnetic field of 0.1 and 1 T. Measurements were corrected for the diamagnetic contribution calculated from Pascal's constants,[13] and for a temperature-independent paramagnetic contribution $\chi_{TIP} = 180 \times 10^{-6}$ $cm^3\ K\ mol^{-1}$.[3]

Polycrystalline powder EPR spectra were recorded at X-band on a Varian E-9 spectrometer equipped with an Oxford Instrument helium flux cryostat. HF-EPR spectra were recorded on a home-build spectrometer at the L.C.M.I.-C.N.R.S. in Grenoble (France).

Results and Discussion

Structural Characterization. The compound $[Cu(DBSQ)(C_2H_5O)]$ crystallizes in the monoclinic, centrosymmetric, *C*2/*c* space group. The crystal structure is shown in Figure 1. Selected bond distances and angles are reported in Tables 2 and 3. The asymmetric unit is formed by the dinuclear system bis(3,5-di-*tert*-butyl-semiquinonato)-di-μ-ethoxo-dicopper(II), in which two copper(II) ions are bridged by two μ_2-ethoxo ions. The coordination of the two copper(II) ions is completed by two oxygen atoms of the DBSQ ligands in an approximately square-planar environment (maximum deviations from the least-squares plane formed by the donor atoms are 0.24 and 0.14 Å for Cu(1) and Cu(2), respectively). In addition, both the copper(II) ions of the asymmetric unit experience a further interaction with two oxygen atoms of a second $Cu_2(DBSQ)_2(C_2H_5O)_2$ molecule. The unit cell content shows that these two units are related by an inversion center to form dimers of bis(3,5-di-*tert*-butyl-semiquinonato)-di-μ-ethoxo-dicopper(II) units, whose structure is also shown in Figure 1. The interaction between these two units occurs through bridging oxygen atoms in the axial positions. As a matter of fact, two shorter contact distances between Cu(1) and the centrosymmetric related ethoxo oxygen, $O(5)^i$ ($i = -x + 0.5, -y + 0.5, -z$) (2.342 Å), and Cu(2) and one centrosymmetric semiquinonato oxygen atom, $O(10)^i$ (2.561 Å), were observed, in such a way that the Cu(II) ion coordination results in a five-coordinated square pyramid. This type of interaction is often found in square-planar copper(II) complexes as a result of the relatively strong Lewis acidity of the metal centers. The crystal structure of the $Cu(DBSQ)_2$ shows the existence of a similar interaction leading to a dimeric $[Cu(DBSQ)_2]_2$ compound.[9e]

Table 2. Selected Bond Lengths [Å] for $[Cu(DBSQ)(C_2H_5O)]_2$

O(1)−Cu(1)	1.952(4)	O(5)−Cu(1)^i	2.342(5)
O(4)−Cu(1)	1.883(5)	C(9)−O(2)	1.309(8)
O(10)−Cu(1)	1.949(5)	C(10)−O(20)	1.275(9)
O(5)−Cu(1)	1.977(4)	O(1)−C(2)	1.261(7)
O(20)−Cu(2)	1.945(5)	O(10)−C(3)	1.294(7)
O(2)−Cu(2)	1.934(5)	C(3)−C(2)	1.477(9)
O(4)−Cu(2)	1.891(5)	O(10)−Cu(2)	2.561(4)
Cu(1)−Cu(2)	2.939(2)	C(9)−C(10)	1.444(9)
O(5)−Cu(2)	1.944(4)		

Table 3. Selected Bond Angles [deg] for $[Cu(DBSQ)(C_2H_5O)]_2$

O(1)−Cu(1)−O(5)	165.1(2)	O(20)−C(10)−C(14)	124.6(6)
O(4)−Cu(1)−O(10)	178.8(2)	O(1)−C(2)−C(5)	126.1(6)
O(4)−Cu(2)−O(20)	170.8(2)	O(10)−C(3)−C(8)	123.3(6)
O(2)−Cu(2)−O(5)	178.2(2)	O(4)−Cu(1)−Cu(2)	38.9(1)
O(2)−C(9)−C(11)	123.6(6)	O(5)−Cu(1)−Cu(2)	41.0(1)

The average value of the Cu−O bond distances in the $[Cu(DBSQ)(C_2H_5O)]_2$ units is 1.945 Å. The Cu_2O_2 group is planar and asymmetric. The Cu−O−Cu angles at the bridging ethoxide ligands are 102.3° and 97.1° for O(4) and O(5), respectively, and consequently the Cu−O bond lengths are shorter for O(4) than for O(5) while the Cu(1)−O(4) and Cu(2)−O(5) bond distances (1.883 and 1.945 Å, respectively) are slightly shorter than the corresponding Cu(2)−O(4) and Cu(1)−O(5) lengths (1.945 and 1.891 Å). The observed 1.285 Å average value for the C−O bond length is in the range usually found for 3d metal−semiquinonato complexes.[8] Similar conclusions can be reached through the inspection of the C−C bond lengths whose average value of 1.46 Å is again strongly indicative of the radical character of the ligand.

Magnetic Properties. $[Cu(DBSQ)(C_2H_5O)]_2$ is EPR silent at the X-band frequency. HF-EPR experiments show a broad signal that does not show any significant feature. The χT vs T dependence in the temperature range 2−300 K is shown in Figure 2. At room temperature the χT value is 1.42 $cm^3{\cdot}K{\cdot}mol^{-1}$, and, on decreasing the temperature, it monotonically decreases reaching 0.01 $cm^3{\cdot}K{\cdot}mol^{-1}$ at 2 K,

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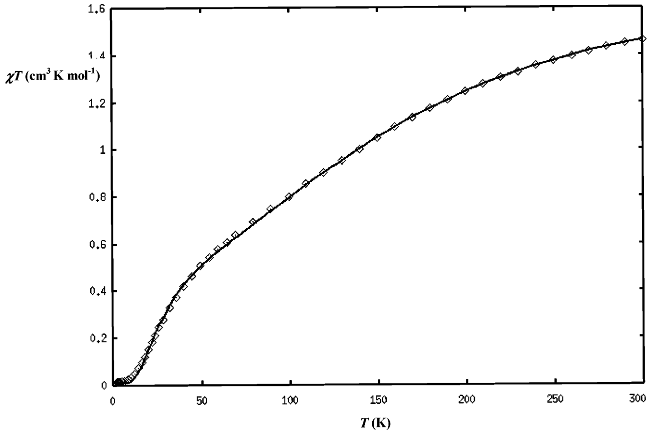

Figure 2. χT vs T curve for complex $[Cu(DBSQ)(C_2H_5O)]_2$ (open diamonds) and best fit curve (continuous line).

indicating that magnetic interactions yield a singlet ground state. The deviation of χT from zero at 4.2 K can be ascribed to some paramagnetic impurities.

Two approaches are possible to analyze the experimental data. In the first one, the two centrosymmetric molecules found in the unit cells are considered as a whole. In this case we are dealing with a system containing eight interacting electron spins (i.e. $\{[Cu(DBSQ)(C_2H_5O)]_2\}_2$), whose magnetic characterization would require at least the use of six independent spin Hamiltonian parameters. Although such an approach is the most satisfying one from a theoretical point of view, it suffers from overparametrization, as already pointed out by Kahn et al.[5] In the second approach, the magnetic interactions between the two centrosymmetric $[Cu(DBSQ)(C_2H_5O)]_2$ units are considered to be much smaller than those occurring within the $[Cu(DBSQ)(C_2H_5O)]_2$ molecule. It is indeed well-known from previous studies on 1:1 copper(II)−semiquinonato complexes that the two paramagnetic centers experience a strong ferromagnetic interaction according to orthogonality of the magnetic orbitals ($\sigma(d_{x^2-y^2})$ for the copper(II) ion and π^* for the DBSQ ligand,[5,8,10,14] if a local reference system with the x and y axis pointing toward the methoxy ligands is assumed. It has also been shown that the magnetic interaction between two copper(II) ions bridged by two μ-oxo donors is strongly dependent by the magnitude of the Cu−O−Cu angle.[15] In the present case a strong antiferromagnetic interaction between the two in-plane ethoxo-bridged copper(II) ions is expected. On the other hand, weak exchange interactions have always been measured between square-pyramidal five-coordinated distorted copper(II) complexes bridged by apical donor atoms.[5,16] In this model the exchange interactions within the $[Cu(DBSQ)(C_2H_5O)]_2$ unit are accounted for by the spin Hamiltonian[17]

$$\mathbf{H} = J_1\mathbf{S}_1\cdot\mathbf{S}_2 + J_2\mathbf{S}_3\cdot\mathbf{S}_4 + J_3\mathbf{S}_2\cdot\mathbf{S}_3 \tag{2}$$

where $\mathbf{S}_1$ and $\mathbf{S}_4$ are the spin operators of the semiquinonato ligands, and $\mathbf{S}_2$ and $\mathbf{S}_3$ those of the copper(II) ions, and the smaller interdimer interactions are accounted for by a molecular field approach.

Susceptibility data were fit by minimizing the sum of the squares of the deviation of the computed χT values from the experimental ones, using the MINUIT program package.[18] Theoretical susceptibilities were calculated by full diagonalization of the spin Hamiltonian (2) applying a Boltzmann distribution to populate the spin states.[3] As usually done in the literature, the variation of g with the total spin state was neglected, to reduce the number of free parameters in the fit, and only one value was used. The presence of paramagnetic impurities was introduced through eq 3[3]

$$\chi_\rho = \chi(1-\rho) + \left[\frac{N\mu^2 g_i^2 S_i(S_i+1)}{3kT}\right]\rho \tag{3}$$

where g_i, S_i, and ρ are the g, S, and the amount of the impurity, respectively. Interdimer spin interactions were included through eq 4[13]

$$\chi_i = \frac{\chi}{1+\theta\chi} \tag{4}$$

where θ is the parameter that takes into account the intermolecolar spin interactions in the Weiss molecular field approximation: $\theta = zJ/Ng^2\mu_B^2$. Putting z, the number of nearest neighbors, equal to 1, θ gives the interdimer interaction.

A fixed impurity with $S_i = {}^1/_2$, $g_i = 2.08$, and $\rho = 2\%$ was assumed, and, to reduce the number of parameter in the fit, we used constant g values ($g = 2.08$) in all the equations. The number of free parameters used in the least-squares fit of χT was 4. The best-fit parameters values were $J_1 = -371.9(5)$ cm^{-1}, $J_2 = 287.8(1)$ cm^{-1}, $J_3 = -370.9(5)$ cm^{-1}, and $\theta = 5.07(6)$ cm^{-3} mol ($J = 5.72$ cm^{-1}) with the agreement factor

$$R = \frac{\sum_i |\chi_{obsd}(i)T_i - \chi_{calcd}(i)T_i|}{\sum \chi_{calcd}(i)T_i} = 0.00891 \tag{5}$$

The agreement with the experimental data is excellent, notwithstanding the various approximations introduced and the computed standard deviations on the parameters are low. The best fit curve is compared to the experimental one in Figure 2.

As expected from the previous qualitative consideration the exchange interaction between the copper(II) centers and DBSQ is strongly ferromagnetic and J_2 is strongly antiferromagnetic. It must also be noted that the Hamiltonian of eq 2 is invariant with respect to the permutation of the copper(II) centers, i.e., J_1 can be assigned either to Cu1 or

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[17] The spin Hamiltonian used in this paper has the form $H = J\mathbf{S}_1\cdot\mathbf{S}_2$.

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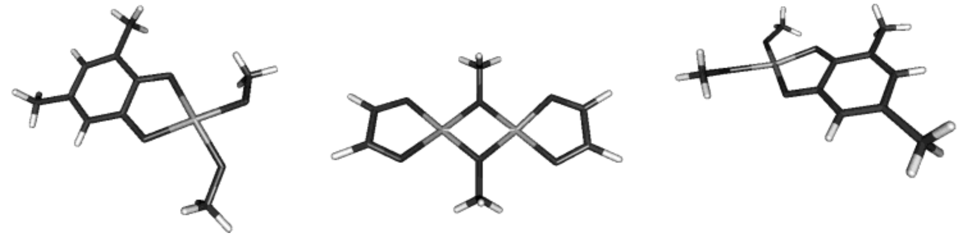

DM_1 **DM_2** **DM_3**

Figure 3. Model structures used throughout the calculations.

to Cu2. DFT calculations can, in principle, solve this ambiguity and give a quantitative estimate of the exchange interactions.

DFT Calculations. All the calculations were performed with the Gaussian98 program package.[19] Copper core electrons were replaced with the LANL2DZ effective core potential and the LANL2 basis sets[20] were applied to all the atoms. The Becke's hybrid functional with the LYP correlation functional[21] (B3LYP) was used. In polynuclear complexes the exchange interactions between paramagnetic centers are generally computed on dinuclear systems that mimic as much as possible the geometries seen in the whole cluster.[22] In the present case the compound $[Cu(DBSQ)(C_2H_5O)]_2$ contains four paramagnetic centers in a linear arrangement, and three model dinuclear units that mimic the couples of adjacent paramagnetic centers of the asymmetric unit are needed, namely **DM_1** (SQ(1),Cu(1)), **DM_2** (Cu(1),Cu(2)), and **DM_3** (SQ(2),Cu(2)), shown in Figure 3.

The three magnetic exchange coupling constants to be computed are $J_{SQ(1)Cu(1)} = J_1$, $J_{Cu(2)SQ(2)} = J_2$, $J_{Cu(1)Cu(2)} = J_3$. SQ(1) and SQ(2) are the semiquinonato ligands bonded to Cu(1) and Cu(2), respectively (see Figure 1). In **DM_1** and **DM_3**, the 3,5-di-*tert*-butyl-*o*-semiquinonato ligands were substituted by 3,5-di-methyl-*o*-semiquinonato ligands, and methoxo groups were used instead of the ethoxo ones. In **DM_2**, the 3,5-di-*tert*-butyl-*o*-semiquinonato ligands were modeled by two diamagnetic (*Z*)-ethylene-1,2-diol ligands. Ligand modeling is a common practice in the calculation of the magnetic properties of transition metal dinuclear systems for the purpose of accelerating the SCF convergence.[23] It has been shown,[24] however, that this modeling can have important effects on the absolute values of the *J*'s to be compared with experiment, and therefore, only a qualitative agreement between experimental and computed data could be expected. Any other better result can be considered as fortuitous.

The approach commonly used for computing the magnetic exchange coupling constant between two $S = {}^1/_2$ systems requires the calculation of the energies of two Slater determinants, i.e., two separate unrestricted SCF calculations. The first determinant represents the state with the maximum spin multiplicity, $S_{max} = 1$, the ferromagnetic state; the second determinant, the Broken Symmetry (BS) determinant, is a state with mixed spin and space symmetry.[25] The BS wave functions are a useful representation of the magnetic orbitals.[23] The energy of the singlet, $S = 0$, state can be obtained from that of the BS state by using spin projection techniques, and the relevant equation for computing the exchange coupling constant, *J*, is

$$J = E_{S_{max}} - E_{S=0} = \frac{E_{S_{max}} - E_{BS}}{1 - a^2} \qquad (6)$$

where $a^2 = \langle \Psi_{BS} | \underset{\sim}{S}^2 | \Psi_{BS} \rangle / 2$. In the *active electron approximation*[3] this value is related to the overlap between the magnetic orbitals, $|S_{ab}^{\alpha\beta}|^2$, according to

$$\langle \Psi_{BS} | \underset{\sim}{S}^2 | \Psi_{BS} \rangle = 1 - |S_{ab}^{\alpha\beta}|^2 \qquad (7)$$

The *J* value computed with eq 6 contains the correction for the overlap between the magnetic orbitals.[24,26]

It has been commonly found in the literature that *J* values computed with use of eq 6 are much larger than the experimental ones, and a procedure used by some authors[27] was to avoid the spin projection and to consider the BS state

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Table 4. The Computed Exchange Parameters, J, the S^2 Values, and the Local Spin Densities

	J_{exp}, cm^{-1}	J,[a] cm^{-1}	J,[b] cm^{-1}	S^2	$d_A(A)$	$d_B(A)$	$d_A(B)$	$d_B(B)$
DM_1	−456	−1152	−584	0.9860	0.821	0.073	0.179	0.927
DM_2	319	572	295	0.9694	0.926[c]/0.911[d]	0.100[c]/0.090[d]	0.074[c]/0.088[d]	0.900[c]/0.910[d]
DM_3	−322	−740	−416	0.8748	0.729	0.106	0.271	0.894

[a] Computed with eq 6: $J = E_{S_{max}} - E_{BS}/1 - a^2$. [b] Computed with eq 8: $J = E_{S_{max}} - E_{BS}$. [c] O(5) is assigned to fragment B while O(4) to fragment A. [d] O(4) is assigned to fragment B while O(5) to fragment A.

as a pure singlet state, using, therefore, the equation

$$J = E_{S_{max}} - E_{BS} \tag{8}$$

Equation 6 reduces indeed to eq 8 when the overlap between the magnetic orbitals, $|S_{ab}^{\alpha\beta}|^2$, is 1 (strong covalent bonding). J values computed with the two different approaches can differ by a factor 2. In this paper we will use both eqs 6 and 8 for computing the J values.

A qualitative analysis of the magnetic interactions was attempted with use of the local spin density analysis developed by Bertrand[28] for symmetric dinuclear magnetic systems and extended by us to asymmetric complexes.[29] In this framework, the extent of a magnetic interaction is related to the amount of spin density transferred from one magnetic center to the other, namely $d_A(B)$ and $d_B(A)$. $d_A(A)$ and $d_B(B)$ represent spin density localized onto the A and B magnetic centers. In transition metal dimers, the magnetic centers are associated to the metal atoms, since a large part of the spin density is found around the metal. In the case of organic radical ligands the assignment of the magnetic center is not obvious, since the electronic and spin densities are delocalized over a large part of the molecule. If not otherwise mentioned, we defined the magnetic centers according to the spin distribution computed with the Mulliken population analysis (Mulliken spin populations) for the BS wave function. Atoms with positive spin densities were assigned to fragment A in all cases. In the **DM₁** and **DM₃** systems A represents, therefore, the semiquinonato magnetic fragment, and the copper-centered one is fragment B. In **DM₂**, the A fragment belongs to the Cu(1) and the B fragment to the Cu(2).

The J values computed with eqs 6 and 8 are collected in Table 4. Ferromagnetic interactions were computed for the semiquinonato-copper(II) dimers, in agreement with the literature results,[5,8,14] while the interaction between the two copper(II) centers was found antiferromagnetic.[15] As expected, the J values computed with eq 8 are smaller that those obtained with eq 6. Although eq 8 is valid if the BS state is a pure singlet state, and in the present case the average values of $\mathbf{S}^2$, $\langle \mathbf{S}^2 \rangle_{BS} = 2a_2 \cong 1$, computed for **DM₁** and **DM₃** (Table 4) show that it is a 50% admixture of the triplet and singlet in both cases, nevertheless they will be taken as the values to compare with experiment, following the suggestion of some authors.[27] This is the well-known drawback of the BS approach. J_1 and J_3 differ in absolute value ($|J_1| > |J_3|$) due to the differences in the geometrical parameters of the two dinuclear complexes. These differences are apparent from the form of the magnetic orbitals of **DM₁** and **DM₃** shown in Figure 4, and from the calculated spin densities for the magnetic fragments, which are reported in Table 4. It should be mentioned that the obtained results are in full agreement with those of a computational study concerning the semiquinonate anion.[30]

One magnetic electron is mainly localized on one semiquinonato π^* orbital with a not negligible delocalization onto the copper ion; the other magnetic electron is localized on the $d_{x^2-y^2}$ orbital on the copper center with a negligible delocalization onto the aromatic ring, but with large delocalization onto the methoxy oxygen atoms. This delocalization is larger for **DM₃** and a larger overlap between the magnetic orbitals with respect to **DM₁** is, therefore, expected: this rationalizes the computed smaller ferromagnetic interaction. Along with this, the coordination geometry of **DM₃** causes the magnetic orbital on Cu(II) to move away from the coordination plane. The overlap between the magnetic orbitals computed through eq 6 is 0.12 and 0.35 for **DM₁** and **DM₃**, respectively, and justifies, within the active electron approximation, the smaller ferromagnetism of **DM₃**. The same qualitative conclusions can be reached looking at the local spin densities shown in Table 4, relative to the semiquinonato fragment, A, and copper(II) centered fragment, B. For **DM₃**, the spin density transferred from the copper-centered fragment to the catechol one ($d_B(A)$) and vice versa ($d_A(B)$) are larger than those computed for **DM₁**, due the larger electron delocalization onto the two methoxy oxygen atoms computed for **DM₃**. The antiferromagnetism of the **DM₂** dimer agrees with the value of the Cu−O−Cu angles (97.1° and 102.3°), which is in the range observed for the antiferromagnetic di-μ-alkoxo bridged complexes.[15] The rather large value of the transferred spin density (Table 4) rationalizes the quite large value of J_2. It has to be noted that the assignment of the bridging oxygens to Cu(1) or to Cu(2) is not unique. In fact, their spin densities in the BS state are slightly negative (O(4) = −0.00671 and O(5) = −0.00236), their value different from zero being due to the asymmetry of Cu−O−Cu bridges. We assigned one bridged oxygen per copper ion, and in Table 4 two values of $d_k(l)$ are shown corresponding to the two possible partitionings of the density.

Sinergy Fitting Parameters − DFT Calculation Results. The parameter values obtained by fitting the experimental data were compared with those calculated with the above-described DFT procedure. Although the fit of the experimental data is apparently good, the computed values of the parameters do not compare well with those computed with

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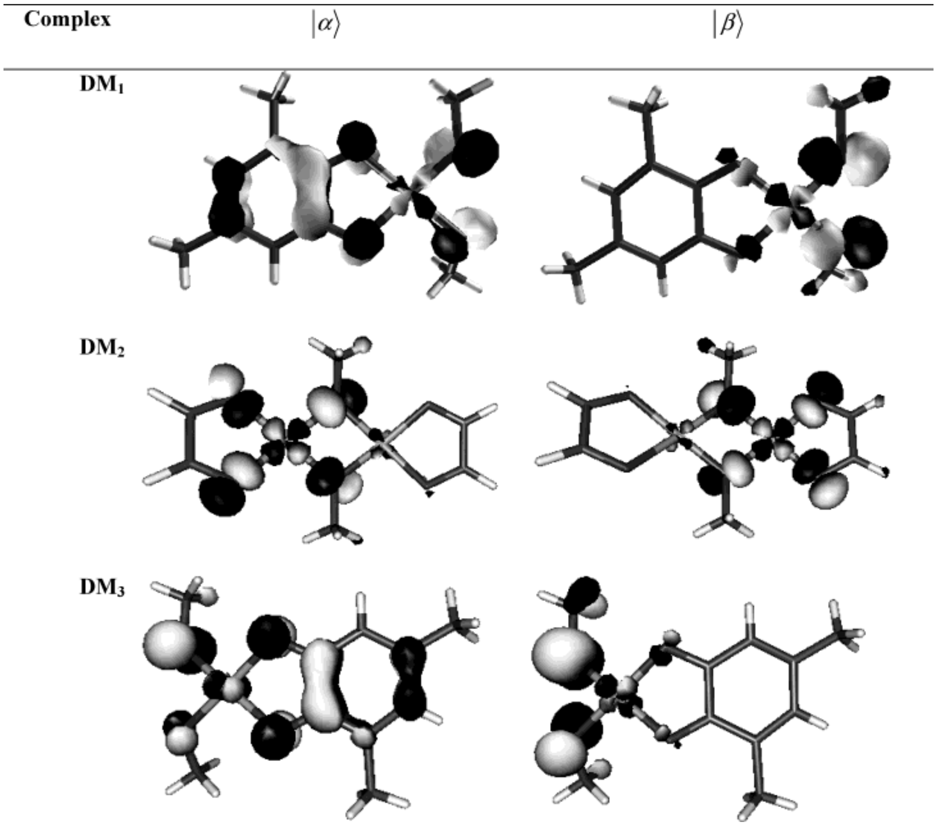

Figure 4. The computed magnetic orbitals for all the model complexes. Isodensity surfaces for $\Psi = 0.05$ au.

DFT. In particular J_1 and J_3, even if ferromagnetic, are almost equal, while the computed ratio J_1/J_3 is 1.40, better respecting the structural differences between the two semiquinonato-copper(II) moieties. An indication of the quality of a fitting procedure, which is unfortunately most often ignored among magnetochemists, is, along with the R value, the variance/covariance matrix. An inspection of the covariance of our parameters showed that J_1 and J_3 have a correlation coefficient, $\rho(J_1J_3)$, of 0.997. This means that the two parameters are not independent. We encountered the same situation with other spin complex systems,[31] and we found that several minima are possible with equivalent R factors. We have therefore performed a series of least-squares fits by fixing the value of J_1 while letting the other three parameters vary. The minimization function was found to be a flat surface on the (J_1, J_3) space and a number of different sets of parameters were found that well reproduce the experimental data. Among them, we chose the following set: $J_1 = -450$ cm^{-1} $J_2 = 288.3(1)$ cm^{-1}, $J_3 = -316.0(2)$ cm^{-1} and $\theta = 5.06(8)$ cm^{-3} mol (5.70 cm^{-1}) with $R = 0.00893$. With this set of parameters the ratio between J_1 and J_3 is 1.42, in good accord with the computed value of 1.40. It must also be noted that in the present case, since the interacting spins are all equal to $^1/_2$, the spin Hamiltonian, see eq 2, is symmetric in J_1 and J_3. Using the last set of data we would not be able to assign J_1 and J_3 to actual couples in the cluster. Only with the results of the calculations that show that **DM$_1$** has a larger coupling constant than **DM$_3$** is this assignment possible.

Conclusions

Fit of magnetic susceptibility data of clusters of spins can be questionable if the variance/covariance matrix, or error matrix, is not calculated and examined. Unfortunately this practice is often ignored in magnetochemistry. We offer here the second example of the importance of DFT calculations in the interpretation of the magnetic susceptibility data in linear clusters. In the present case a number of equivalent fits were possible, since the two exchanged coupling constants, J_1 and J_3, were strongly correlated, and only the relative signs of the interactions, J_1, $J_3 < 0$; $J_2 > 0$ could be obtained from the fit of the temperature variation of the magnetic susceptibility. The J_1 and J_3 values computed with DFT allowed us to establish the relative strength of the interactions, $J_1/J_3 \cong 1.4$, and with these values the best fit parameters $J_1 = -450$ cm^{-1}, $J_2 = 288.3(1)$ cm^{-1}, $J_3 = -316.0(2)$ cm^{-1} and $\theta = 5.06(8)$ cm^{-3} mol (5.70 cm^{-1}) were obtained.

The approach presented in this paper should be followed in all cases in which strong correlation is found between the magnetic parameters used to fit magnetic susceptibility data.

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