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Orbital Symmetries and Magnetic Interaction between Copper(II) Ions and the *o*-Semiquinone Radical. Magnetic Studies of (Di-2-pyridylamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate and Bis(bis(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II))

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Magnetic susceptibility and electron paramagnetic resonance studies are reported for two Cu(II) semiquinonato compounds, for which the molecular structures have been previously described. These compounds are [Cu(NH(py)₂)(DTBSQ)](ClO₄) (1) and [Cu(DTBSQ)₂] (2), with NH(py)₂ = di-2-pyridylamine and DTBSQ = 3,5-di-*tert*-butyl-*o*-semiquinonato. In compound 1, the magnetic behavior reveals an exceptionally strong ferromagnetic interaction with a triplet ground state stabilized by ca. 200 cm⁻¹ with regard to the singlet excited state. This behavior results from the strict orthogonality of the σ magnetic orbital of the copper(II) chromophore and the π^* magnetic orbital of the semiquinone radical. In compound 2, the Cu(II)-semiquinone interaction is found weakly antiferromagnetic, so that the semilocal ground state within the Cu(DTBSQ)₂ mononuclear unit is a doublet. This reversal of the sign of the coupling is attributed to the tetrahedral distortion around copper(II), which mixes the σ and π^* symmetries. In addition, the two Cu(DTBSQ)₂ units are coupled antiferromagnetically and the ground state of the compound as a whole is a singlet, with a triplet excited state at 7.9 cm⁻¹ above the singlet state.

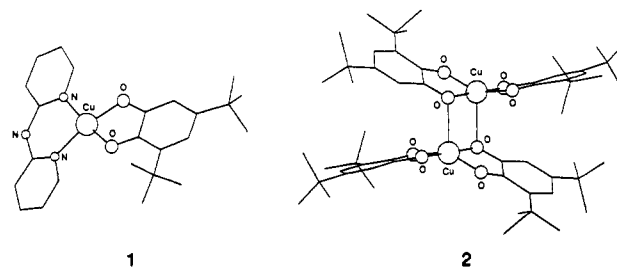
Introduction

Exchange interaction between magnetic centers is a general phenomenon in coordination and bioinorganic chemistry.² Numerous studies are now available in which the nature and magnitude of the interaction are related to the molecular structure of the system. Recently, a new step has been reached: the design and synthesis of new polymetallic systems with predictable magnetic properties.³ This approach is based upon a few key concepts, the main one being that the nature of the interaction between two unpaired electrons originates from a "competition" between a ferromagnetic and an antiferromagnetic contribution, favoring the triplet and the singlet states, respectively. When the orbitals describing those unpaired electrons, called magnetic orbitals, overlap, the antiferromagnetic contribution usually dominates. When those magnetic orbitals are orthogonal, or quasi-orthogonal, the antiferromagnetic contribution vanishes and the ground state is the triplet state. The strategy of orthogonality between the magnetic orbitals has been applied successfully to the design of ferromagnetically coupled dinuclear compounds.^{4,5}

Most of the studies devoted to the exchange interaction deal with compounds in which the magnetic centers are metal ions. Those devoted to the interaction between paramagnetic metal ions and organic radicals are relatively rare;⁶⁻¹⁶ a few reviews about

this interesting group of compounds are available.^{6,16} The biological relevance of such systems has also been realized at an early stage. For instance, in high-valent porphyrins, an interaction between the Fe(III) ion and a radical residing on the porphyrin ring might be occurring and in fact has already been characterized in some model compounds. Further, the copper-A site in cytochrome oxidases exhibits properties suggesting a coordinated sulfur ligand with radical character.¹⁷ Also, in many intermediates arising from the oxidation of organic molecules through copper enzymes, organic radicals coordinated to copper(II) ions are likely involved.

Recently, the magnetic and EPR properties of several copper(II)-radical compounds have been investigated and in some cases rationalized in light of the symmetry rules summarized above.^{10,12-14,16} In this paper, we report on a study of this kind, where the nature of the interaction between organic radical and copper(II) ion is related to the relative symmetries of the interacting magnetic orbitals. This study concerns two crystallographically characterized copper(II) compounds with the radical ligand 3,5-di-*tert*-butyl-*o*-semiquinone: [Cu(NH(py)₂)(DTBSQ)](ClO₄) (1), where NH(py)₂ = di-2-pyridylamine and DTBSQ = 3,5-di-*tert*-butyl-*o*-semiquinonato,¹⁸ and [Cu(DTBSQ)₂] (2), in which two Cu(DTBSQ)₂ units are related through a symmetry center to give a copper(II) dimer with a total of six unpaired electrons.¹⁹



Experimental Section

Syntheses. Both compounds were synthesized as described earlier¹⁸⁻²⁰ and checked for purity by spectroscopic and analytical methods.

Measurements. ESR spectra were recorded on Varian instruments at temperatures between 4 and 300 K. Magnetic susceptibilities were

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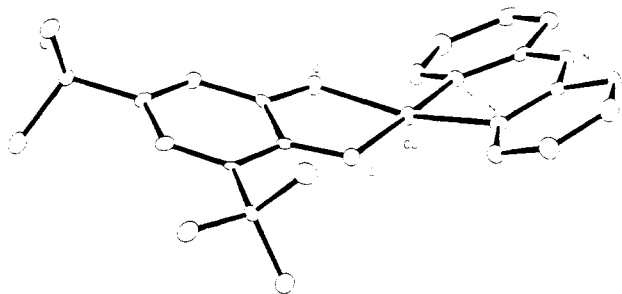


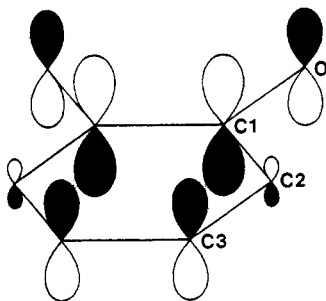
Figure 1. Perspective view of the $[\text{Cu}(\text{NH}(\text{py})_2)(\text{DTBSQ})]^+$ cation in **1**.

measured with a Faraday type magnetometer equipped with a helium continuous-flow cryostat, in the 4.2–300 K temperature range. For both **1** and **2**, independence of the susceptibility from the applied magnetic field was checked at room temperature. Mercuric tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections were estimated as $-228 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **1** and $-514 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **2**.

Results

[Cu(NH(py)₂)(DTBSQ)](ClO₄) (1). The structure of the $[\text{Cu}(\text{NH}(\text{py})_2)(\text{DTBSQ})]^+$ cation in **1** is redrawn in Figure 1.¹⁸ Copper(II) ion is in a 4 + 2 distorted octahedral environment with two nitrogen atoms of $\text{NH}(\text{py})_2$ and the two oxygen atoms of DTBSQ in the basal plane and two oxygen atoms of the perchlorate group in the apical positions with apical bond lengths above 2.4 Å. In addition, the cupric ion is slightly displaced from the basal plane toward one of the apical sites, so that the molecular skeleton is not rigorously planar. If one neglects this weak bending of the magnetic cation, the symmetry is very close to C_{2v} . When one considers this bending, the symmetry is C_s with a mirror plane σ perpendicular to the pseudomolecular plane.

The unpaired electron from the copper(II) ion is described by a magnetic orbital ϕ_{Cu} pointing along the Cu–N and Cu–O bonds in the basal plane. ϕ_{Cu} is antisymmetric with regard to the mirror plane σ and transforms as b_1 in C_{2v} and a'' in C_s . The unpaired electron of the *o*-semiquinone radical is found from elementary molecular orbital theory to occupy the π^* orbital noted ϕ_{sq} and schematized as follows:



This orbital transforms as b_2 in C_{2v} and a' in C_s and is, indeed, symmetric with regard to the mirror plane σ . It follows that, even by taking into account the slight deviation of the $[\text{Cu}(\text{NH}(\text{py})_2)(\text{DTBSQ})]^+$ unit from planarity, ϕ_{Cu} and ϕ_{sq} are strictly orthogonal and the interaction is expected to be purely ferromagnetic with a triplet ground state.⁴ It has been shown that in such a case the magnitude of the ferromagnetic interaction is governed by the extrema of the overlap density $\rho(i)$ defined by²¹

$$\rho(i) = \phi_{\text{Cu}}(i) \phi_{\text{sq}}(i) \quad (1)$$

Indeed, the S–T singlet–triplet splitting J may then be written as

$$J = 2 \int \int_{\text{space}} \frac{\rho(i) \rho(j)}{r_{ij}} d\tau(i) d\tau(j) \quad (2)$$

and the more pronounced and the more concentrated the extrema

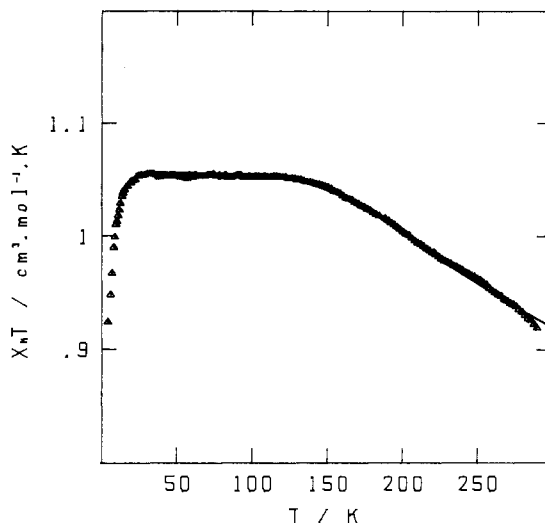
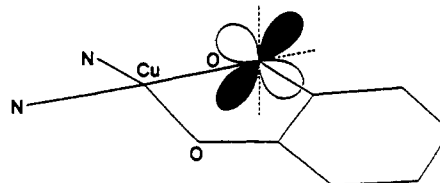


Figure 2. Experimental (Δ) and calculated (—) temperature dependences of $\chi_M T$ for **1**. The calculated curve does not take into account the Weiss correction introduced to fit the data below 20 K (see text).

of ρ , the more positive the two-electron exchange integral of the right-hand term of (2). ϕ_{Cu} is significantly delocalized toward the oxygen atoms of the *o*-semiquinone radical. Concerning ϕ_{sq} , it has significant density on the same oxygen atoms. An extended Hückel calculation gives the following spin densities: O, 0.136; C₁, 0.196; C₂, 0.024; C₃, 0.144. It follows that the overlap density exhibits two positive and two negative lobes around each oxygen atom of the *o*-semiquinone, with extrema located in the plane containing the Cu–O bond and the direction perpendicular to the pseudomolecular plane, schematized as follows:



To sum up these theoretical considerations, the interaction in compound **1** is expected to be ferromagnetic with a rather large singlet–triplet (S–T) energy gap.

The molar magnetic susceptibility χ_M of **1** has been measured in the $4.2 \leq T/\text{K} < 300$ temperature range. Figure 2 shows the results in the form of the $\chi_M T$ versus T plot. $\chi_M T$ is equal to $0.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature, smoothly increases upon cooling, reaches an extended plateau between 150 and 20 K with $\chi_M T = 1.053 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and finally slightly decreases below 20 K, reaching $0.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 4.2 K. This behavior is quite characteristic of a strong intramolecular ferromagnetic interaction. The plateau corresponds to the temperature range where only the triplet ground state is thermally populated; the magnetic susceptibility then follows a Curie law $\chi_M T = 2N\beta^2 g^2 / 3k$, and the average g factor deduced from the magnetic data in this 150–20 K range is found equal to 2.052. g may be related to the average local g factors g_{Cu} and g_{sq} of the copper(II) ion and the semiquinone, respectively, by

$$g = \frac{1}{2}(g_{\text{Cu}} + g_{\text{sq}}) \quad (3)$$

The value found for g is consistent with $g_{\text{Cu}} \approx 2.10$ and $g_{\text{sq}} \approx 2.00$.

Above 150 K, the excited singlet state begins to be thermally populated. The singlet–triplet energy gap J can be estimated by comparing the experimental data to the theoretical expression

$$\chi_M T = \frac{2N\beta^2 g^2}{k} \left[3 + \exp\left(-\frac{J}{kT}\right) \right]^{-1} \quad (4)$$

By least-squares fitting, J is found equal to 220 cm^{-1} . As has already been mentioned,²² the accuracy on J in case of strong

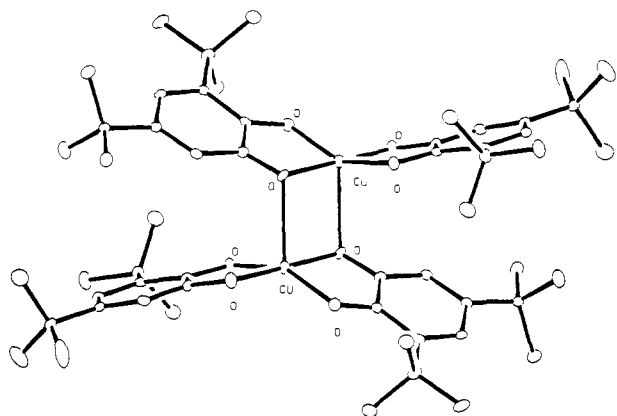


Figure 3. Perspective view of $[\text{Cu}(\text{DTBSQ})_2]_2$ (2).

ferromagnetic interaction is rather poor. In the present case, it is more appropriate to say that the singlet-triplet energy gap is of the order of 200 cm^{-1} .

The slight decrease of $\chi_M T$ below 20 K could be due to the combined effect of very weak intermolecular interactions through the perchlorate groups that bridge the mononuclear units to form infinite chains¹⁸ and the zero-field splitting within the triplet state (vide infra). The magnetic data below 20 K may be fitted with a Curie-Weiss law

$$\chi_M = \frac{C}{T - \theta} \quad (5)$$

and a Weiss constant $\theta = -0.78 \text{ K}$. In absence of zero-field splitting, such a Weiss constant would correspond in a molecular field treatment to intermolecular antiferromagnetic interactions characterized by $zJ' = -0.8 \text{ cm}^{-1}$. In fact, owing to the zero-field splitting, this value has to be considered as an upper limit (in absolute value).

The EPR properties of the compound substantiate the ferromagnetic interaction. If the two local doublets did not interact, the spectrum at any temperature would be essentially the superposition of the spectra associated with the local doublets. In particular, the characteristic spectrum of the organic radical with very sharp features should be easily detectable. Actually, the compound that had first been reported in frozen THF solution as EPR silent at 77 K,¹⁸ in fact, when recorded as a powder, does show some broad features at 77 K, covering the magnetic field range up to 6000 G. Although such a poorly resolved spectrum cannot be analyzed quantitatively, it is rather typical of some coupled systems with a triplet ground state and a large zero-field splitting within this triplet.²²

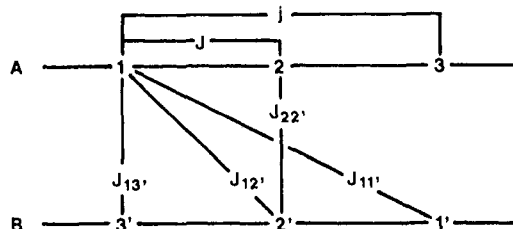
$[\text{Cu}(\text{DTBSQ})_2]_2$ (2). The crystal structure of 2 is redrawn in Figure 3.¹⁹ Each copper(II) ion is coordinated to four oxygen atoms from two DTBSQ ligands in a geometry that is slightly distorted from a planar arrangement toward a tetrahedral one. This tetrahedral distortion was essentially absent in 1. In addition, two $\text{Cu}(\text{DTBSQ})_2$ units are related through a symmetry center to form a dimeric species.

Within each $\text{Cu}(\text{DTBSQ})_2$ unit, the interaction between the metal ion and the two organic radicals leads to two doublets and a quartet of low-lying states, of which the relative energies are 0, $-J + j$, and $-3J/2$, where J refers to the Cu(II)-semiquinone interaction and j to the interaction between the terminal semiquinone groups. In absence of the tetrahedral distortion, the Cu(II)-semiquinone interaction would be ferromagnetic (and J positive as in 1) but, owing to the distortion, the orthogonality of the ϕ_{Cu} and ϕ_{SQ} magnetic orbitals is destroyed. The problem at hand is to know whether the overlap $\langle \phi_{\text{Cu}} | \phi_{\text{SQ}} \rangle$ arising from the distortion is large enough to reverse the sign of J . As for the interaction between the terminal semiquinone groups, it is certainly antiferromagnetic ($j < 0$), because it involves two magnetic orbitals

of the same π^* symmetry. To sum up, it does not seem possible to predict the nature of the ground state—either a doublet or a quartet—within the $\text{Cu}(\text{DTBSQ})_2$ unit from symmetry considerations.

If we now consider the dimeric unit as a whole, the situation is even more complicated. Two approaches are possible:

(i) The first one involves treating the dimeric unit as a whole, with six unpaired electrons. The low-lying states are then five singlets, nine triplets, five quintets, and one sextet. In the frame of the Heisenberg-Dirac-Van Vleck (HDVV) formalism, the relative energies of these states will depend on the six interaction parameters, as shown in the following diagram:



where 1, 1', 3, 3' refer to the semiquinone radicals and 2, 2' to the metal ions. Although calculation of these relative energies does not present any conceptual difficulty, it is rather tedious. The best way is to work successively in the $M_s = 3, 2, 1$, and 0 subspaces. A calculation of this kind has already been carried out in several cases, particularly for the magnetic chains.^{23,24} To obtain the exact expression of the molar magnetic susceptibility deduced from the spin Hamiltonian

$$\mathcal{H} = -\sum_{i,j>i} J_{ij} \hat{S}_i \hat{S}_j + \sum g_i \hat{S}_i H \quad (6)$$

it is also necessary to calculate the g factors associated with the different magnetic states from the local g_{Cu} and g_{SQ} and then to apply the Van Vleck relationship. If we neglect the difference $g_{\text{Cu}} - g_{\text{SQ}}$, the spin state does not couple through the Zeeman perturbation and only the first-order Zeeman coefficients intervene in the expression of the susceptibility. Such a complete approach is obviously the most satisfying from a theoretical viewpoint, but it suffers from overparametrization, so that it is not possible to know unambiguously the nature of the Cu(II)-semiquinone interaction (i.e., the sign of J).

(ii) An alternative approach consists of assuming that the Cu(II)-semiquinone interaction within the $\text{Cu}(\text{DTBSQ})_2$ unit is significantly stronger than any other interaction between local doublets belonging to two symmetry-related units. If so, the magnetic properties will be essentially sensitive to the energy gaps arising from the interaction between the ground states of the $\text{Cu}(\text{DTBSQ})_2$ units and much less to the energy gaps arising from the interaction between the ground state of a unit and an excited state of the other or between two excited states. It is then possible to write two approximate expressions for the magnetic susceptibility of $[\text{Cu}(\text{DTBSQ})_2]_2$, the former valid if the ground state within the mononuclear unit is a doublet and the latter valid if this ground state is the quartet. The hope is then that one of these expressions will fit the experimental data much better than the other one. These expressions are

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [\exp(J_{\text{AB}}/4kT) + 2 \exp(\Delta_1/kT) + \exp(2\Delta_1/kT) + 12 \exp(\Delta_2/kT) + 12 \exp((\Delta_1 + \Delta_2)/kT) + 20 \exp(2\Delta_2/kT)] / [\exp(-3J_{\text{AB}}/4kT) + 3 \exp(J_{\text{AB}}/4kT) + 8 \exp(\Delta_1/kT) + 4 \exp(2\Delta_1/kT) + 16 \exp(\Delta_2/kT) + 16 \exp((\Delta_1 + \Delta_2)/kT) + 16 \exp(2\Delta_2/kT)] \quad (7)$$

where Δ_1 is the ground doublet-excited doublet and Δ_2 the ground

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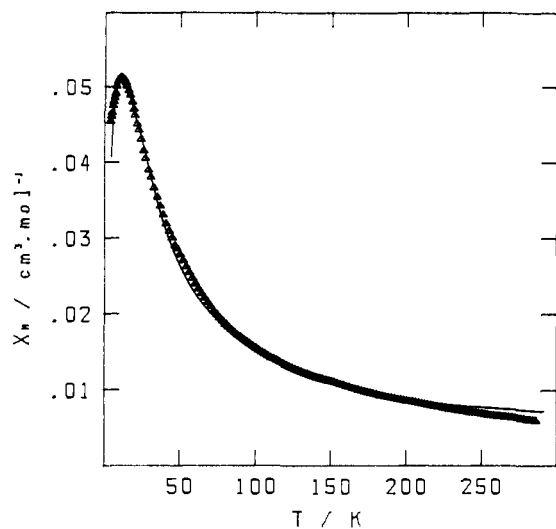


Figure 4. Experimental (Δ) and calculated (—) temperature dependences of χ_M for **2**.

doublet-excited quartet energy gap within the mononuclear unit, and

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [\exp(-11J_{AB}/4kT) + 5 \exp(-3J_{AB}/4kT) + 14 \exp(9J_{AB}/4kT) + 12 \exp(\Delta_1/kT) + 12 \exp(\Delta_2/kT) + \exp(2\Delta_1/kT) + 2 \exp((\Delta_1 + \Delta_2)/kT) + \exp(2\Delta_2/kT)] / [\exp(-15J_{AB}/4kT) + 3 \exp(-11J_{AB}/4kT) + 5 \exp(-3J_{AB}/4kT) + 7 \exp(-9J_{AB}/4kT) + 16 \exp(\Delta_1/kT) + 16 \exp(\Delta_2/kT) + 4 \exp(2\Delta_1/kT) + 8 \exp((\Delta_1 + \Delta_2)/kT) + 4 \exp(2\Delta_2/kT)] \quad (8)$$

where Δ_1 and Δ_2 are now the two ground quartet-excited doublet energy gaps. In both (7) and (8), J_{AB} is the interaction parameter of the spin Hamiltonian

$$\mathcal{H} = -J_{AB} \hat{S}_A \cdot \hat{S}_B \quad (9)$$

where \hat{S}_A and \hat{S}_B are the spin operators associated with the ground states of the $\text{Cu}(\text{DTBSQ})_2$ units; $S_A = S_B = 1/2$ in (7) and $S_A = S_B = 3/2$ in (8). We also assumed in (7) and (8) that all magnetic states had the same average g factor.

The magnetic behavior of **2** is shown in Figure 4. The χ_M versus T plot exhibits a rounded maximum at 11 K, which is characteristic of a coupled system with a diamagnetic ground state and a first-excited magnetic state close in energy to this ground state. At 300 K, the product $\chi_M T$ (χ_M being the molar magnetic susceptibility per dimeric unit) is equal to $1.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. If all the molecular states arising from the interaction between the six magnetic centers were statistically populated at this temperature, $\chi_M T$ would be about $2.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($= 3N\beta^2 g^2 / 2k$). We attempted to fit the experiment magnetic data with both (7) valid for $S_A = S_B = 1/2$ and (8) valid for $S_A = S_B = 3/2$. No physically acceptable solution was found with (8) whereas, with (7), we obtained a rather satisfying solution ($R = \sum [\chi^{\text{obsd}}]^2 - (\chi^{\text{calcd}})^2 / \sum (\chi^{\text{obsd}})^2 = 3 \times 10^{-4}$ for 153 experimental points) with $g = 1.95$, $J_{AB} = -7.9 \text{ cm}^{-1}$, $\Delta_1 = -23 \text{ cm}^{-1}$, and $\Delta_2 = -46 \text{ cm}^{-1}$. Therefore, within the $\text{Cu}(\text{DTBSQ})_2$ unit, the ground state is a doublet and the most excited state the quartet. Hence, J is negative and the $\text{Cu}(\text{II})$ -semiquinone interaction antiferromagnetic. The spectra of the low-lying states in $\text{Cu}(\text{DTBSQ})_2$ and in the dinuclear species **2**, as deduced from the magnetic data, is schematized in Figure 5. The frozen-solution EPR spectrum¹⁹ of **2** was reported to be typical for weakly coupled dimers, but the bands were very broad. The X-band powder EPR spectrum of **2** is also badly resolved. At 11 K, the temperature of the maximum of χ_M , it exhibits four broad features between 1000 and 7000 G that could correspond to the H_{z1} , H_{x2} , H_{y2} , and H_{z2} resonant fields for a triplet state split in zero-field with an axial zero-field-splitting parameter larger than the incident quantum

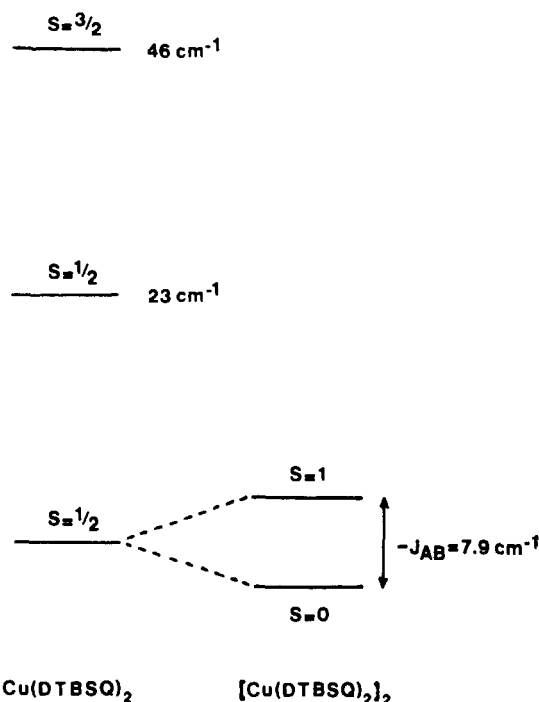


Figure 5. Low-lying states in **2**, as deduced from the magnetic data.

(0.3 cm^{-1}).^{22,25} Upon cooling down at 4.2 K, the intensity of those features decreases as expected for resonances in an excited state. In addition, at any temperature, the spectrum shows the typical features of an isolated copper(II) ion in tetragonally elongated surroundings with a well-resolved hyperfine structure. This copper(II) spectrum most likely belongs to an impurity.

Discussion

So far, the stabilization of the state of highest spin multiplicity through a ferromagnetic interaction has been observed in relatively few compounds with more than one magnetic center. For instance, a survey through the literature dealing with copper(II) dinuclear compounds indicates that less than 4% of them have been reported to have a triplet ground state. One can recall here that, a few years ago, the compounds of this kind were still so rare that some authors expressed skepticism of their existence.²⁶ In fact, the stabilization of a triplet state in a magnetic system with two unpaired electrons opposes the concept of the chemical bond, according to which those two electrons tend to pair in a molecular orbital of low energy. A key to obtain such a ferromagnetic interaction is the orthogonality of the magnetic orbitals. Rassat et al.²⁷ have probably been the first ones to point out that such an orthogonality in an organic diradical of D_{2h} symmetry led to a triplet ground state, and to our knowledge, there is no counterexample; when all the involved magnetic orbitals have different symmetries, the ground state has the highest spin multiplicity. Although this orthogonality is apparently a sufficient condition, it is not always necessary; other mechanisms like spin-polarization effects may also lead to a ferromagnetic interaction.²⁸

Maybe also, there are more ferromagnetically coupled compounds than those actually reported. Indeed, it is much more difficult to give evidence of a ferromagnetic interaction than of an antiferromagnetic one, and even when it is clear that the ground state has the highest spin multiplicity, the energy gaps between the low-lying states cannot be determined very accurately from the magnetic data. This is due to the fact that the temperature

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dependence of the magnetic susceptibility is much more sensitive to small variations of J for J negative than for J positive.²⁹

Compound **1** provides quite a pedagogical example of ferromagnetic interaction driven by the symmetry rules. The σ and π^* orbitals describing the unpaired electrons around the copper(II) ion and the semiquinone ligand, respectively, cannot be combined to give rise to a molecular orbital of low energy through which those electrons could pair; Hund's rule thus holds and the ground state is the triplet.

The EPR properties of **1** are consistent with a ferromagnetic interaction between the cupric ion and the *o*-semiquinone ligand. It was first reported that **1** was EPR silent, resulting from strong antiferromagnetic interaction.¹⁸ A similar interpretation was given³⁰ for another Cu(II)-DTBSQ compound, whose structure is likely to be similar to that of **1**. In fact, when such a large stabilization of the singlet state does occur, the EPR spectrum always exhibits some nicely resolved structures from dilute uncoupled impurities. In contrast, when the triplet state is the ground state, the EPR spectrum is very poorly resolved owing to a large zero-field splitting and/or the magnetic concentration, which averages and broadens the signals. As described above, the EPR spectrum of **1** consists of very broad, poorly resolved features. The only case reported to date of a copper(II) dimer with a triplet ground state and a well-resolved EPR spectrum is a complex in which some magnetic isolation has been obtained by using very bulky diamagnetic ligands.³¹ In the present case, the intermolecular interactions may also be favored by the out-of-plane π^* character of the spin density around the semiquinone group.

The antiferromagnetic nature of the copper(II)-semiquinone interaction in **2**, in contrast with the situation encountered in **1**, may be explained by the breakdown of the strict orthogonality of the ϕ_{Cu} and ϕ_{SQ} magnetic orbitals, due to the tetrahedral distortion around the copper atom. Such a difference between **1** and **2** confirms the key role of the orbital symmetry. In the present case, the tetrahedral distortion sufficiently mixes the σ and π^* symmetries to make the antiferromagnetic contribution preponderant. J , defined as $2\Delta_2/3$, is found equal to -30.7 cm^{-1} . This value has to be compared with $J \approx +200 \text{ cm}^{-1}$ found in **1**. As for the coupling between the mononuclear units, it is largely due to the overlap between the π^* orbitals of the face-to-face semiquinone groups. Such a rather large interaction between

planar organic radicals in a face-to-face configuration has already been reported, for instance in the $(\text{TCNQ})_2^{2-}$ dimers.^{32,33}

Finally, we discuss briefly the magnetic properties of the metal-*o*-semiquinone compounds already described in light of the orbital symmetry considerations emphasized in this paper. Buchanan et al. found^{34,35} that the ground state of the $\text{M}(\text{SQ})_3$ compounds (SQ = *o*-semiquinonato; M = V(III), Cr(III), Fe(III)) had the lowest spin multiplicity (i.e. $S = 1/2$ for V(III), $S = 0$ for Cr(III), and $S = 1$ for Fe(III)), due to antiferromagnetic coupling of spins between the trivalent metal ion and the organic radical. It is easy to see that in none of these compounds is the orthogonality of the magnetic orbitals achieved. Indeed in the tris(*o*-semiquinonato) compounds, the metal center has a distorted octahedral environment with a symmetry very close to C_3 . The *d*-type metal orbitals arising from the t_{2g} set transform as a $+e$ in C_3 , whereas those from the e_g set transform as e . The three symmetry-adapted combinations of the singly occupied π^* semiquinone orbitals transform as a $+e$. Whatever the trivalent metal ion may be (V(III), Cr(III), Fe(III)), the magnetic orbitals on the metal cannot be orthogonal to all the semiquinone magnetic orbitals. Overlap of orbitals with the same symmetry stabilizes the state of lowest spin multiplicity.

Weak antiferromagnetic interaction was also detected in two $\text{Ni}(\text{py})_2(\text{SQ})_2$ compounds, which can be rationalized again from symmetry arguments.³⁶ Tetrameric species of the form $\text{Ni}_4(\text{SQ})_8$ were also obtained and their magnetic properties interpreted by using a procedure rather similar to that used for **2**. In conclusion, it is worth noting that recently³⁷ the compound $\text{Cu}(\text{bpy})(\text{DTBcat})$, with $\text{bpy} = 2,2'$ -bipyridine and $\text{DTBcat} = 3,5$ -di-*tert*-butylcatecholato, was reported. The molecular skeleton is essentially planar as **1**, but of course there is just one unpaired electron, and hence no copper-radical interaction. In the solid state, this compound can dimerize and present an interaction between the metal ions, which has been detected from EPR studies.³⁷

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