to $\psi_{\rm SA}$, are decreased. A further consequence of replacing the propane-1,3-diylidene (**1**) by the ethanediylidene bridging group (**6**) is an almost perfect alignment of the C15–Hβ and C16–Hβ bonds with the 2p$_z$ axes at the adjacent bridged centers (cf. *yz* projection). The hyperconjugative interaction of $\psi_{\rm AS}$ with a σ orbital of the bridging group is thus enhanced, leading to an increased destabilization of this perimeter HOMO relative to $\psi_{\rm SA}$.

The "orbital switch" on passing from **1** to **6** can accordingly be rationalized as follows (Figure 4). *In **1**, the effect of homoconjugation overrides that of inductive and hyperconjugative perturbations*, so that $\psi_{\rm AS}$ is lowered in energy relative to $\psi_{\rm SA}$. It is therefore a $\psi_{\rm SA}$-like orbital which is singly occupied in $\mathbf{1}^{+\cdot}$. On the other hand, owing to a weaker homoconjugation and a stronger hyperconjugation, *the effect of inductive and hyperconjugative perturbations is dominant in **6***. As a consequence, $\psi_{\rm AS}$ is raised in energy above $\psi_{\rm SA}$, and the singly occupied orbital in $\mathbf{6}^{+\cdot}$ is $\psi_{\rm AS}$-like.

The very large coupling constant ($a_{\rm H15,16}$ = 2.815 mT) of the two β protons in the 15,16-positions of $\mathbf{6}^{+\cdot}$ is perfectly in line with the single occupancy of an $\psi_{\rm AS}$-like orbital and a strong hyperconjugative interaction between $\psi_{\rm AS}$ and a σ orbital of the bridging ethanediylidene group. Since each of the β-proton-bearing carbon atoms (15 and 16) is linked to two bridged centers (μ and μ'), the appropriate relationship is[32]

$$a_{\rm H15,16} = B(c_{{\rm AS},\mu} + c_{{\rm AS},\mu'})^2 \cos^2 \theta$$

where $c_{{\rm AS},\mu}$ and $c_{{\rm AS},\mu'}$ are the pertinent LCAO coefficients and θ stands for the dihedral angle between the C15–Hβ or C16–Hβ bonds and the 2p$_z$ axes at μ and μ'. In $\mathbf{6}^{+\cdot}$, $\mu = 1$ and $\mu' = 6$ for C15–Hβ (i.e., Hβ is H15) and $\mu = 8$ and $\mu' = 13$ for C16–Hβ (i.e., Hβ is H16); moreover, $c_{\rm AS,1} = c_{\rm AS,6} = 0.368$ and $c_{\rm AS,8} = c_{\rm AS,13} = -0.368$. Taking the proportionality factor B as +5 to +6 mT,[33] and θ as 10° (Figure 5, *yz* projection for **6**), one obtains $a_{\rm H15,16}$ = +2.6 to +3.2 mT, in good agreement with the observed value of 2.815 mT.

The prerequisites for the large coupling constant of the β protons in $\mathbf{6}^{+\cdot}$ are thus (i) the single occupancy of an orbital exhibiting at the bridged centers μ and μ' large coefficients of the same sign and (ii) a far-reaching alignment of C15–Hβ and C16–Hβ bonds with the 2p$_z$ axes at μ and μ'.[34] Such prerequisites are missing in $\mathbf{1}^{+\cdot}$. In particular, the nodal properties of the singly occupied orbital preclude a hyperconjugative interaction between this $\psi_{\rm SA}$-like MO and a σ orbital of the propanediylidene bridging group (the relevant coefficients have opposite signs: $c_{\rm SA,1} = -c_{\rm SA,6}$ and $c_{\rm SA,8} = -c_{\rm SA,13}$). Accordingly, the coupling constant of the two β protons in the 15,16-positions of $\mathbf{1}^{+\cdot}$ is relatively small ($a_{\rm H15,16}$ = 0.140 mT) and must be due to another mechanism of spin transfer, presumably to spin polarization. It is interesting to note that the coupling constant of the two γ protons in the 17-position of $\mathbf{1}^{+\cdot}$ has (within the limits of experimental error) the same value as $a_{\rm H15,16}$. This value ($a_{\rm H17}$ = 0.140 mT) is rather large for γ protons, since such protons generally give rise to coupling constants which are by 1 order of magnitude smaller than those of β protons.[6c] Closer examination of the geometry of **1** (cf. *xz* projection in Figure 5) indicates that the C17–Hγ bonds are in almost planar W arrangement with the 2p$_z$ axes at the bridged centers. Such an arrangement leads to appreciable γ-proton coupling constants when C–Hγ bonds lie in an antinode of the singly occupied orbital,[36] as this is the case for the HOMO $\psi_{\rm SA}$ in $\mathbf{1}^{+\cdot}$.

Concluding Remark. The important aspect of the present work is the striking effect of a relatively slight structural change on the energetic sequence of the frontier orbitals. It is gratifying that this effect can be rationalized in terms of a simple MO model of a π perimeter which is perturbed by the introduction of the bridging group.

Acknowledgment. We thank the Swiss National Science Foundation for financial support. Our thanks are also due to Professors E. Vogel and K. Müllen, Köln, for the generous gift of the compounds **1**–**8** and for their interest in this work.

Registry No. 1, 25835-57-8; **2**, 91491-85-9; **3**, 91491-86-0; **4**, 31575-22-1; **5**, 91491-87-1; **6**, 38765-94-5; **7**, 91491-88-2; **8**, 55647-83-1.

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[34] A closely analogous example is the large coupling constant (1.910 mT) found for the two β protons in the radical anion of *trans*-10b,10c-dihydropyrene (=1,5:8,12-ethanediylidene[14]annulene).[35]

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Exchange Interactions in Bis(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy)copper(II): A Nitroxyl Radical Complex of Copper(II)

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Abstract: The single-crystal EPR spectra and the temperature dependence of the magnetic susceptibility of bis(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy)copper(II) (Cu(hfac)$_2$(TEMPOL)) have been measured. The compound has a linear chain structure, with a TEMPOL ligand bridging two Cu(hfac)$_2$ moieties, but the EPR spectra are typical of a triplet state, showing that magnetically the compound is a chain of weakly coupled metal–radical pairs. The magnetic coupling between the two spins is ferromagnetic, with a singlet–triplet separation of −13 ± 5 cm^{-1}. The single-crystal EPR spectra show that **g** and **D** are practically parallel to each other. The principal values are the following: g_x = 2.057, g_y = 2.013, g_z = 2.157, D_x = 88 × 10^{-4} cm^{-1}, D_y = −1140 × 10^{-4} cm^{-1}, D_z = 1052 × 10^{-4} cm^{-1}, with *z* roughly parallel to the Cu–O(TEMPOL) bond direction. The **g** tensor has been decomposed into the copper and radical contributions, yielding information on the nature of the magnetic orbital localized on copper. The zero-field splitting tensor has been decomposed into the sum of a dipolar and an exchange component.

Nitroxyl radicals are widely used as spin probes in biological systems,[1-6] but they are now actively studied also as ligands toward transition-metal ions.[7-10] We found particularly interesting those compound where a Lewis acid/base interaction is present between

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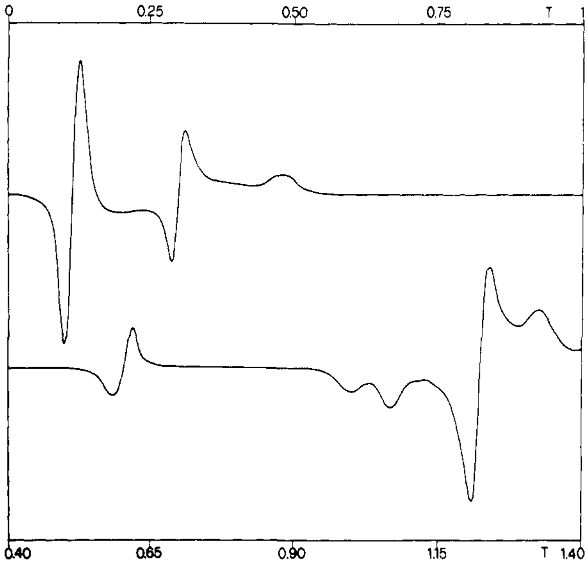
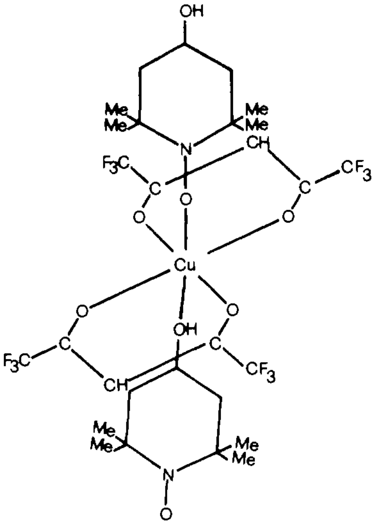


Figure 1. Polycrystalline powder EPR spectra of Cu(hfac)$_2$(TEMPOL) at room temperature and X- (upper) and Q-band frequencies (lower).

the metal ion and the oxyl group of the radical. Drago et al. also showed the possibilities of using the interaction of nitroxyl radicals with diamagnetic complexes in order to study the nature of the Lewis acid-base interaction.[11,12] The use of a paramagnetic ligand, such as a nitroxide, gives the opportunity of obtaining first-hand information on the metal-ligand interaction, monitored by the magnetic coupling with the metal electrons. In fact in pairs of metal ions the exchange mechanism is generally determined by the overlap of the two magnetic orbitals on the two different metal ions through the intervening ligands (Anderson's superexchange),[13] while in the interaction of organic radicals with transition-metal ions, direct exchange should be operative. This means that the extent of coupling is directly determined by the overlap of the metal and ligand magnetic orbitals.

We have long been interested in the characterization of exchange interactions involving pairs of similar or dissimilar metal ion.[14,15] In particular studying EPR spectra it is possible to have information not only on the exchange interaction between the ground states, through the temperature dependence of the line intensities, but also on the interaction between one ground state and an excited state, through the analysis of the dipolar and exchange contribution to the zero-field splitting.[15-19] Therefore we decided to study the EPR spectra of complexes of transition-metal ions with nitroxide ligands[20] in order to collect information on the bonding interactions not only between the two ground magnetic orbitals but also those involving excited orbitals.

Recently Anderson reported the crystal structure determination of bis(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy)copper(II) (Cu(hfac)$_2$(TEMPOL)).[21] The compound is formed of polymeric chains of square-planar Cu(hfac)$_2$ units bridged by TEMPOL ligands. Each copper ion is hexacoordinated by four oxygen atoms of two hfac$^-$ ions, one OH and one NO atom of two different TEMPOL ligands, as shown below. Only the room temperature magnetic susceptibility



was reported, which showed that the effective magnetic moment does not differ much from the value expected for two independent $S = {}^1/_2$ spins.[21] We wish to report here the single-crystal EPR spectra of Cu(hfac)$_2$(TEMPOL) in order to fully characterize the nature of the interaction of the radical with the metal ion. Magnetic susceptibility data in the range 4.2-300 K will also be used to describe the nature of the ground state.

Experimental Section

Anhydrous Cu(hfac)$_2$ was prepared by literature methods.[22] The ligand 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPOL) (Molecular Probes) was used without purification. The complex was prepared according to the reported procedure.[21] Dichroic brown green crystals were obtained from methylene chloride solutions by cooling in a refrigerator overnight. The crystals were oriented with a Philips PW 1100 diffractometer. They were found to correspond to the reported structure,[21] with prominent $(0\bar{1}1)$ and $(01\bar{1})$ faces.

Polycrystalline powder and single-crystal EPR spectra were recorded with a VARIAN E-9 spectrometer equipped with standard X- (9 GHz) and Q-band (35 GHz) facilities. At X band the crystal was mounted on a Perspex rod and rotated in the static magnetic field by using a one circle goniometer. At Q-band frequency the magnet was rotated around the crystal again mounted on a Perspex rod. The symmetry properties of the crystal were used to check the alignment in the magnetic field. Low-temperature spectra were recorded using Oxford Instruments ESR9 and ESR35 cryostats.

Magnetic susceptibility measurements were performed with a Faraday balance equipped with a Bruker electromagnet operating at 2.7 T and a R-100 Cahn microbalance. The cooling apparatus was a CF 200 flow cryostat from Oxford Instruments Co.

Results

Polycrystalline powder EPR spectra of Cu(hfac)$_2$(TEMPOL) at room temperature at X- and Q- band frequencies are shown in Figure 1. They are typical triplet spectra showing three main

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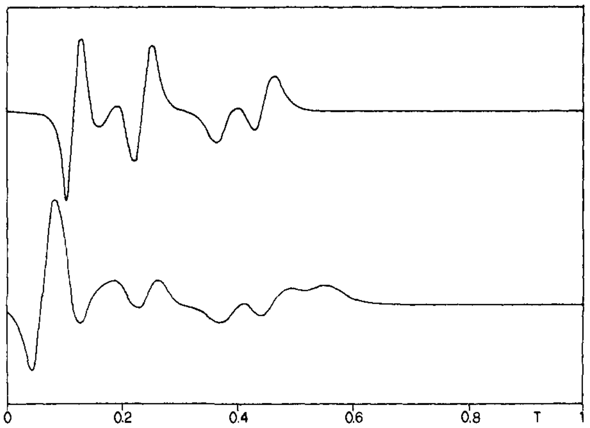

Figure 2. Single-crystal EPR spectra of Cu(hfac)$_2$(TEMPOL) at X-band frequencies with the static magnetic field in the *YZ* plane making an angle of 50° with *b*: (upper line) room temperature, (lower line) liquid helium temperature.

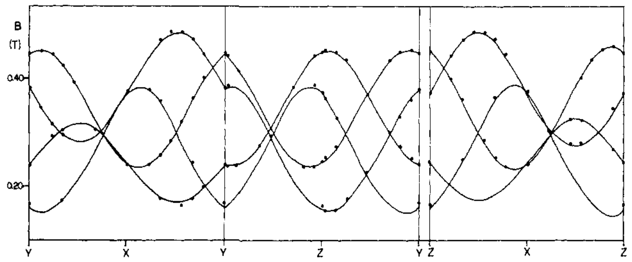

Figure 3. Angular dependence of the transition fields at X-band frequencies at room temperature.

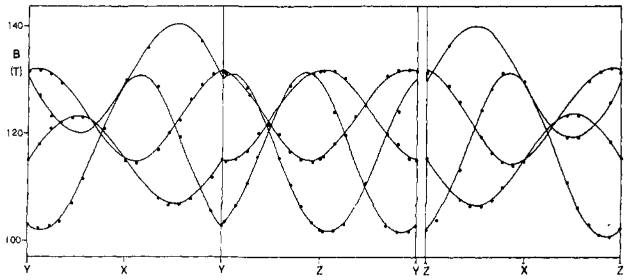

Figure 4. Angular dependence of the transition fields at Q-band frequencies at room temperature.

features at X band and five features at Q-band frequency. The signal at 0.6 T at 35 GHz is clearly the $\Delta M = 2$ transition, which has its X-band counterpart at 0.12 T, although to this feature more than one transition may contribute. The $\Delta M = 1$ transitions in the Q-band spectra are assigned on the basis of a first-order analysis: the two *z* transitions are at 1 and 1.32 T, the *y* transitions at 1.07 T and beyond the range available on our instrument. The two *x* transitions are coincident at 1.22 T. The corresponding transitions at X-band frequency are the following: *z* at 0.12 and 0.47 T, *y* at 0.12 and 0.47, and the *x* transitions coincident at 0.3 T. The fact that the fine-structure transitions parallel to *x* are coincident is indicative of $E/D \simeq {}^1/_3$. From the reported formulas[23] a satisfactory agreement was reached with

$$g_x = 2.05 \qquad g_y = 2.03 \qquad g_z = 2.15 \qquad D = 0.16\ \text{cm}^{-1}$$

$$E/D \cong 1/3$$

The fairly large calculated *D* value explains why the $\Delta M = 2$ transition is observed at lower than "half"-field.

This assignment was confirmed through single-crystal spectra at both X- and Q-band frequencies. The spectra were recorded by rotating the crystals around three axes labeled as *X*, *Y*, and *Z*, which are defined as follows: *X* is parallel to *a*, *Y* is orthogonal to the $(0\bar{1}1)$ face. A typical spectrum is shown is Figure 2. In Figures 3 and 4 are given the angular dependences of the transition fields at X- and Q-band frequency. Due to the monoclinic nature of the crystals,[21] symmetry in the spectra is expected only rotating around *X*.

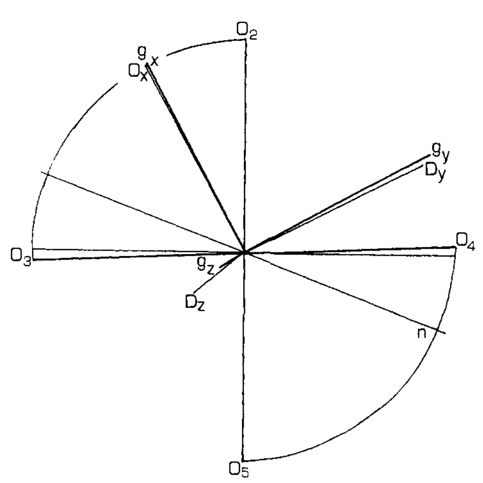

Figure 5. Principal direction of **g** and **D** tensors for site I (see text) of Cu(hfac)$_2$(TEMPOL).

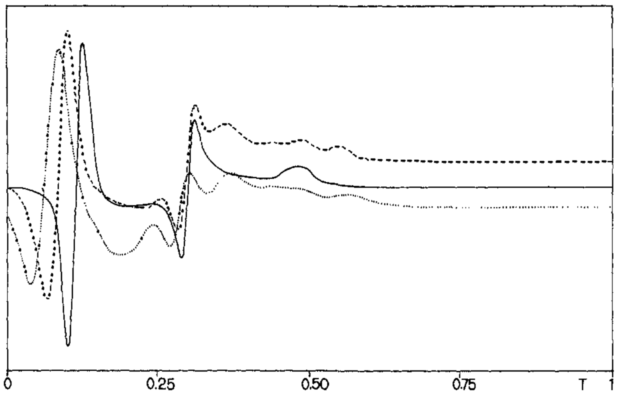

Figure 6. Polycrystalline powder EPR spectra of Cu(hfac)$_2$(TEMPOL) at room temperature (—), 73 K (----), 4.2K (···) and X-band frequency.

In a general orientation of the crystal in the static magnetic field four $\Delta M = 1$ and two $\Delta M = 2$ transitions are expected for two magnetically nonequivalent sites in the monoclinic unit cell.[24] This makes unravelling the individual transition field from the experimental spectra rather difficult in many orientations.

However, we found that in general at X band it is easier to follow the high-field transitions, while at Q band the low-field transitions are better resolved, since in this case they do not overlap with the $\Delta M = 2$ transition.

The fitting procedure used the transition fields which could be safely obtained at both frequencies. The program we used diagonalizes the hamiltonian matrix and minimizes the least-squares residuals according to a procedure previously described.[25] The program allows for not parallel **g** and **D** tensors. The fitting procedure was repeated independently for the two magnetically not equivalent sites. The calculated spin hamiltonian parameters for sites I and II, the principal values, and directions of the **g** and **D** tensors are shown in Table I. The **g** and **D** tensors of each site are within error parallel to each other, and within error they are symmetry related. In Figure 5 we show the orientation of the **g** and **D** tensors for site I. The view is orthogonal to the CuO$_4$ plane (O$_4$ being the four hexafluoroacetylacetonate oxygen atoms). g_{zz} and D_{zz} are very close to the perpendicular to this plane (they

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Table I. Calculated Spin Hamiltonian Parameters and Principal Values and Directions of **g** and D Tensors for Sites I and II[a]

	site I	site II		site I	site II
g_{xx}	2.045 (3)	2.048 (3)	D_{xx}	−0.0479	−0.047
g_{xy}	−0.014(4)	0.036 (4)	D_{xy}	−0.0587 (9)	0.029 (1)
g_{xz}	−0.035 (3)	0.012 (4)	D_{xz}	−0.0335 (9)	0.061 (1)
g_{yy}	2.040 (2)	2.136 (2)	D_{yy}	−0.0497 (7)	0.0940 (7)
g_{yz}	−0.028 (3)	−0.034 (3)	D_{yz}	−0.0189 (9)	−0.030 (1)
g_{zz}	2.141 (2)	2.040 (3)	D_{zz}	0.0979 (6)	−0.0470 (7)

site I			site II			
g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	
2.057 (4)	2.013 (4)	2.157 (3)	2.056 (4)	2.012 (4)	2.156 (3)	
−0.70 (3)	0.65 (3)	0.27 (2)	−0.74 (3)	0.60 (4)	0.28 (3)	β_{ix}[b]
0.70 (3)	0.68 (3)	0.20 (2)	0.05 (3)	0.37 (2)	0.927 (8)	β_{iy}
−0.05 (3)	0.33 (2)	−0.941 (7)	−0.66 (4)	−0.70 (3)	−0.24 (2)	β_{iz}

site I			site II			
D_{xx}	D_{yy}	D_{zz}	D_{xx}	D_{yy}	D_{zz}	
0.008 (1)	−0.114 (1)	0.1052 (7)	0.014 (1)	−0.116 (1)	0.1024 (8)	
−0.684 (4)	0.701 (4)	0.197 (7)	−0.707 (4)	−0.693 (4)	0.136 (9)	β_{ix}
0.721 (4)	0.691 (4)	0.044 (7)	−0.00 (1)	0.195 (4)	0.9807 (9)	β_{iy}
−0.104 (9)	0.172 (4)	−0.979 (1)	−0.706 (4)	0.693 (4)	−0.140 (9)	β_{iz}

[a] Estimated errors in parentheses. [b] Direction cosines of the principal directions of **g** and **D** tensors in the laboratory frame defined in the text.

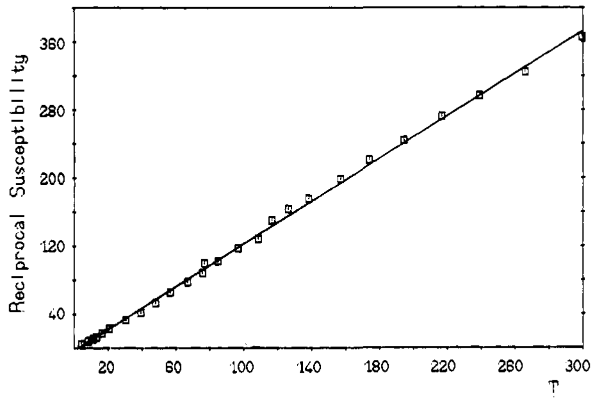

Figure 7. Temperature dependence of reciprocal magnetic susceptibility of Cu(hfac)$_2$(TEMPOL) in the range 4.2–300 K.

make an angle of 8° and 18°, respectively); g_{xx} and D_{xx} make an angle of 28.3° and 28.6° with the Cu–O2 bond direction. In Figure 5 we show also the projection of the perpendicular to the TEMPOL plane, *n*, on the CuO$_4$ plane.

The EPR spectra are found to be temperature dependent as shown in Figure 6. The features tend to move to higher and lower fields suggesting an increase in the value of the zero-field splitting tensor. We recorded single-crystal spectra at liquid helium temperature and found an increase in the number of the signals, suggesting that a phase transition occurred (see Figure 2). The transition is reversible because on warming the crystal the spectra recorded at room temperature are identical with those recorded before the cooling cycle. The spectra at low temperature are very complicated, with many overlapping bands, and we felt it was not advisable to attempt a detailed interpretation, lacking structural data.

The electronic spectra in the solid state show one broad band in the visible region, with a maximum at 14 700 cm^{-1}, which is typical of copper(II) acetylacetonate complexes with substantial axial interaction.[26,27]

The temperature dependence of the reciprocal magnetic susceptibility of Cu(hfac)$_2$(TEMPOL) is given in Figure 7. The magnetic susceptibility follows a Curie–Weiss law with $\theta = -3.9°$ indicating weak ferromagnetic interactions.

Discussion

The most plausible explanation of the room temperature EPR spectra is that the triplets originate from the interaction between the copper ions and the unpaired electron on the nitroxide radical. In principle also other exchange interactions are possible, e.g., the one between a nitroxyl group and a further copper ion bound to the hydroxyl group of TEMPOL and interchain interactions, but these must be smaller and determine only the line widths of the EPR signals. In this respect the present compound is similar to the pyrazine adduct of copper acetate, which behaves as a chain of dinuclear species.[28]

The magnetic susceptibility data of Cu(hfac)$_2$(TEMPOL) show that the coupling between the copper and the radical spins is fairly small and predominantly ferromagnetic in nature. The EPR spectra at 4.2 K, which show the presence of a paramagnetic species, agree with either a ground triplet or a ground singlet with a triplet separated by only a small energy gap.

Although in principle Cu(hfac)$_2$(TEMPOL) may behave like an alternating chain compound,[29-33] the room temperature EPR spectra show that the interactions in the chain are weak, so that at least a first approximation of the magnetic data may come from a simple Bleaney–Bowers treatment;[34] i.e., considering the system as a set of noninteracting pairs of coupled spins. By fixing the *g* value at the average *g* of the EPR spectra, $g = 2.076$, the best fit to the $\chi(T)$ function is obtained for $J = -13$ cm^{-1} (we use the spin hamiltonian in the form $H = J\mathbf{S}_1 \cdot \mathbf{S}_2$). We estimate an error of about ±5 cm^{-1} on this value, due to the quality of the data and to the intrinsic difficuly in estimating *J* values for ferromagnetically coupled compounds.[35,36]

Our *J* value is in substantial agreement with a recent report of an analogous copper(II) complex with a nitroxide biradical, bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)bis(pivaloylacetato)-copper(II), Cu(pac)$_2$(TEMPOL),[37] in which two oxyl donors are in the axial position of a distorted octahedral structure, where the observed coupling constant was also found to be ferromagnetic,[38]

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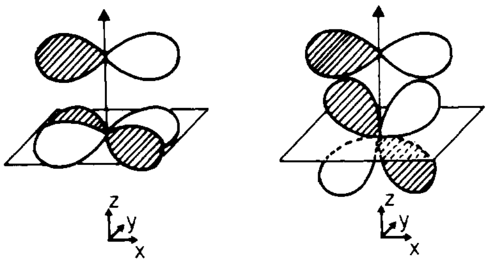

Figure 8. Scheme for the overlap of the magnetic orbital localized on copper atom and on the nitroxide ligand: (left) *xy* on copper, *x* on oxygen; (right) *xz* on copper, *x* on oxygen.

$J = -19.8$ cm^{-1}. In that case[39] the Cu–O bond distances are larger than in our case (258.3 vs. 243.9 pm) and the Cu–O–N angle is smaller (158.5° vs. 170.1°).

The *g* values can be used to describe the nature of the magnetic orbitals of Cu(hfac)$_2$(TEMPOL) assuming that J is larger than $h\nu$ and D. In this case[14]

$$\mathbf{g}_c = \frac{1}{2}\mathbf{g}_{Cu} + \frac{1}{2}\mathbf{g}_r \qquad (1)$$

where $\mathbf{g}$ is the $\mathbf{g}$ tensor for the complex $\mathbf{g}_{Cu}$ and $\mathbf{g}_r$ are those for the copper ion and the radical, respectively. Assuming that $\mathbf{g}_r$ is isotropic and equal to 2.00 is certainly a minor assumption. Consequently from (1), using the experimental $\mathbf{g}_c$ tensor one finds for $\mathbf{g}_{Cu}$ the principal values $g_{Cu,x} = 2.12$, $g_{Cu,y} = 2.02$, and $g_{Cu,z} = 2.31$ with the principal directions defined in Figure 5. This pattern of g values is typical for a ground xy orbital[40] where x and y bisect the equatorial bonds, although the large in-plane anisotropy, if it is not due to experimental error, indicates a substantial involvement of the z^2 orbital as well.[41] The large g_{zz} value is in agreement with a substantial effect of the axial ligands on the energy levels.

In Figure 8, is shown a possible scheme for the overlap of the magnetic orbital localized on copper, which for the sake of simplicity has been depicted as the xy orbital, and that on the nitroxide ligand, which must be a linear combination of nitrogen and oxygen p_x. Considering the nitroxide ligand to occupy an axial coordination site in a distorted octahedron around the copper ion, as seen in the crystal structure,[21] the overlap between the metal and ligand magnetic orbitals must be zero, since xy and z^2 have σ symmetry and p_x has π. Therefore, to this approximation, no antiferromagnetic contribution would be expected. On the other hand the ferromagnetic coupling also must be relatively small since the magnetic orbitals are far from each other to the extent that the overlap density is anticipated to be not too large.[42] In any case both in Cu(hfac)$_2$(TEMPOL) and Cu(pac)$_2$(TEMPOL)$_2$ a weak ferromagnetic interaction appears to dominate.

Another copper nitroxide complex that has been fully characterized is Cu(hfac)$_2$(TEMPO) (TEMPO is 2,2,6,6-tetramethypiperidinyl-*N*-oxy).[10,43] In this case the nitroxide occupies an equatorial position of a square pyramid,[10] and the complex is essentially diamagnetic at room temperature, indicating a coupling between the metal and ligand orbitals[43] such that $J > 500$ cm^{-1}. We recorded the EPR spectra of this complex, but no signal could be detected. The strong coupling in this case is supported by structural data.[10] In fact the TEMPO ligand is coordinating in such a way to the copper ion that the p_x orbitals of N and O are not orthogonal to the metal xy orbital: i.e., the p_x orbital is not π bonding, but it has a substantial σ character toward the metal orbital.

In discussing the structural data which are relevant to the description of the electronic structure of the complex, it must be recalled that extremely large and highly anisotropic thermal ellipsoids were found for the atoms of the TEMPOL ligand.[21] It was observed that the preferred direction of motion for all atoms of the TEMPOL ligand is approximately perpendicular to the mean plane of the radical ligand ring. Also the conformation of the ring is unusual, being almost flat in contrast with the chair conformation seen in structures of similar radical species.[44,45] On this basis, and on the basis of the fact that the bond lengths seen within the ring are abnormal, it was suggested that the atoms of the radical ligand are disordered on a static or dynamic basis between two different ring conformations.[21] Our room temperature EPR data concord with the crystal structure data, in the sense that two magnetically not equivalent sites are revealed, as expected for a monoclinic unit cell.[24] This may mean that either the disorder is static, but it does not affect the EPR spectra, or the disorder is dynamic. The second hypothesis seems the most reasonable, and it finds some confirmation also from the low-temperature data, which show that the number of sites is increased as compared to room temperature. This might be due to freezing out of the two distortions, whose interconversion becomes slow on the EPR time scale. The fact that the changes in the EPR spectra are reversible also agrees with a dynamic distortion.

The observed zero-field splitting of Cu(hfac)$_2$(TEMPOL) also deserves attention. In a two-spin system the zero-field splitting tensor is given by a sum of terms,[46] which for individual $S = {}^1/_2$ states reduces[15] to

$$\mathbf{D} = \mathbf{D}^{ex} + \mathbf{D}^{dip} \qquad (2)$$

where $\mathbf{D}^{ex}$ and $\mathbf{D}^{dip}$ are the exchange and through-space component, respectively. In practice $\mathbf{D}^{dip}$ is usually evaluated through some simple classic electrostatic treatment, and if $\mathbf{D}$ is found to differ noticeably from this calculated value, the difference is attributed to $\mathbf{D}^{ex}$. This term depends on the mechanism of exchange involving excited states of the two separate spin systems.[16]

Usually $\mathbf{D}^{dip}$ is evaluated through the point dipolar approximation; i.e., the two spins are approximated as two classical point dipoles, and the zero-field splitting is evaluated as the energy of these two dipoles.[47] In the present case the dipolar approximation is hardly applicable for several reasons. First, while it is reasonable to assume that one unpaired spin is on the copper ion, the spin of the nitroxyl ligand may be delocalized on both the oxygen and on the nitrogen donor atom.[48] Second, the oxygen-to-metal distance is not very large,[21] so that the extension of the dipoles is not small enough compared to their separation to consider them as point dipoles. Recent calculations concerning the delocalization of unpaired spin density on hexaaquo metal complexes indeed showed deviations from the values expected for point dipoles centered on metal ions and water oxygen atoms.[49] However, the model can be used as a first approximation using g_{Cu} and g_r obtained from the above analysis and the distance seen in the crystal structure.[21] Attempts were made to calculate $\mathbf{D}^{dip}$ allowing for both the possibility of delocalization of the spin on both the nitrogen and the oxygen atoms with a parameter α, such that for $\alpha = 1$ the unpaired spin is completely on the oxygen, while for $\alpha = 0.5$ it is equally shared by the oxygen and the nitrogen, and for the spatial extention of the orbitals which contain the unpaired spin, according to a procedure that is well established for organic biradicals[50,51] and for metal complexes.[52] In any case we found that the largest $\mathbf{D}^{dip}$ component is expected roughly parallel to

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the Cu–O(TEMPOL) direction and could not account for a large component parallel to *y*.

These results seem to indicate that the dipolar contribution alone is not sufficient to explain the experimental **D** tensor. We are forced therefore to take into consideration the anisotropic exchange contribution. This is expected to be determined by the spin-orbit mixing of excited states into the ground state. Neglecting low-symmetry components the diagonal elements are given[16,46] by

$$\mathbf{D}_{ii}^{ex} = J(e_{Cu},g_r)\sum_{e_{Cu}}\frac{|\langle g_{Cu}|L_{Cu,i}|e_{Cu}\rangle|^2}{\Delta_{Cu}^2}\lambda_{Cu}^2 + J(g_{Cu},e_r)\sum_{e_r}\frac{|\langle g_r|L_{r,i}|e_r\rangle|^2}{\Delta_r^2}\lambda_r^2 \quad (3)$$

where $|g\rangle$ and $|e\rangle$ represent the ground and excited state, respectively, r indicates the radical, Δ_{Cu} and Δ_r are the energy differences between the ground and the excited state, λ is the spin-orbit coupling constant, L is the orbital angular momentum operator, and $i = x, y, z$, $J(e,g)$ are the coupling constants between the ground and one excited magnetic orbital. Of the two terms it seems reasonable to consider only the first, since the second depends on the spin-orbit coupling constant on the radical, which is smaller than that of the copper ion.

In order to estimate the possible contribution to $\mathbf{D}^{ex}$ it is convenient to use a slightly idealized symmetry of the Cu–O(TEMPOL) moiety. In particular it is convenient to neglect the small deviations (~20°) of the perpendicular to the nitroxide ring, *n*, from the bisector of the hfac chelates.[21] As it is shown in Figure 8 then a very strong π interaction might be operative between the copper *xz* orbital with ligand p_x orbital containing the unpaired electron. It is therefore conceivable that in eq 3 the dominant term is that relative to $J(xz_{Cu},x_r)$. Since *xz* can be coupled to the ground *xy* orbital through L_y, eq 3 predicts a large contribution to **D** orthogonal to the plane of the π overlap.

If now we go back to the real complex, we can expect that the largest $\mathbf{D}^{ex}$ component will be roughly orthogonal to *n*, and in fact the largest **D** component is observed along the *y* direction, which makes an angle of 64.8° with *n*. The deviation may be due to off-diagonal terms which are more difficult to evaluate.

Conclusions

The analysis of the magnetic susceptibility and of the EPR spectra of Cu(hfac)$_2$(TEMPOL) has confirmed that the extent of coupling of the metal and organic radical spins depends on the relative geometry of the magnetic orbitals localized on the two paramagnetic centers. In particular when the radical ligand occupies axial positions in tetragonally elongated copper(II) complexes the coupling is weak and ferromagnetic. The interactions between excited states of the metal ion and the ground state on the radical have a large influence on both the principal directions and the principal values of the zero-field splitting tensor.

Registry No. Cu(hfac)$_2$(TEMPOL), 91738-58-8.

Structure and Bonding in Dilithiomethane

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Abstract: Electron density analysis shows singlet CH$_2$Li$_2$ structures to be largely C$^-$Li$^+$ in character with a small amount of three-center bonding. Three-center bonding is less important for the triplets, which have, instead, significant Li–Li bonding. A simple but effective model of triplet CH$_2$Li$_2$ results from excitation of one electron from the HOMO (lone pair) of the singlet into the LUMO (Li–Li bonding) and then allowing relaxation to optimize the geometry and minimize the energy. The anomalous reversed dipole moment of the triplet results from decreased positive charge placed on the lithium atoms due to charge transfer into a Li–Li bonding orbital. To a useful approximation, triplet CH$_2$Li$_2$ may be modeled in part as a simple summation of triplet methylene and Li$_2$. This model aids particularly in explaining the reversal of the dipole moment.

In the search for a planar four-coordinate carbon atom, Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople[1] found that lithium was an excellent substituent for stabilizing the planar carbon presumably because of both donor and acceptor characteristics. The simplest molecule with a stabilized four-coordinate planar carbon was found to be dilithiomethane. Four minimum energy structures were obtained—singlet and triplet planar and tetrahedral—with the triplet states of lower energy. The triplet tetrahedral state was of lowest energy, yet the triplet planar state was only 3 kcal mol^{-1} higher in energy. Since the single determinant Hartree–Fock approximation does not treat singlets and triplets equivalently, the actual ground state was not determined conclusively. However, the indication is clear that the four states are very close in energy.

Schaefer and Laidig[2] continued this work by fully optimizing the geometry for all four states using a double-ζ-plus polarization (DZ+P) basis set. They found the triplet tetrahedral state to be only 0.8 kcal mol^{-1} more stable than the triplet planar state. Inclusion of all single and double excitations gave CI energies which, after being corrected for unlinked clusters, shows the singlet tetrahedral state to be the ground state. However, all four states are within 6 kcal mol^{-1} of each other. These results are summarized in Table I.

Examination of the optimized structures reveals a few interesting features. The triplet states have significantly longer C–Li bonds and narrower Li–C–Li bond angles than do the singlets. Particularly noteworthy is that the Li–Li distance in the triplets is actually smaller than the Li–Li bond in Li$_2$ (2.93 Å).[3]

Perhaps the most remarkable aspects of these systems are their dipole moments. The singlet states have large dipole moments with polarity C$^-$Li$^+$ as expected, but the triplet states have small dipole moments of opposite polarity, i.e., C$^+$Li$^+$. The purpose of this work is to determine the nature of the bonding occurring in these systems by use of electron density functions and to rationalize the unusual dipole moments of the triplets.

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