Contribution from the Department of Chemistry, University of Florence, Florence, Italy,
and Laboratoire de Chimie, Departement de Recherche Fondamentale, Centre d'Etudes Nucléaires, F 38041 Grenoble, France

Weak Exchange Interactions between Nitroxides and Copper(II) Ions Monitored by EPR Spectroscopy

C. Benelli,† D. Gatteschi,*† C. Zanchini,† J. M. Latour,‡ and P. Rey‡

Received January 17, 1986

EPR spectra and the temperature dependence of the magnetic susceptibility of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolidinyl-1-oxyato)copper(II) (I) are reported. The structure of I shows that the copper atom is bound to four different ligands in such a way that two different chains intersect at each copper ion. The magnetic data are interpreted by considering isolated clusters of three $S = {}^1/_2$ spins, one copper atom and two nitroxides, ferromagnetically coupled to give a quartet ground state with $J = -21.2$ cm^{-1} and $J' = -6.30$ cm^{-1}. The EPR spectra show only one signal for every crystal orientation, indicating that some averaging process is operative. Different broadening mechanisms are examined, and the angular and frequency dependences of line widths are studied.

Introduction

The complexes of transition–metal ions with stable organic radicals are being actively investigated at present[1–8] because of their relevance to some biological processes, such as those present in photosynthesis,[9] and also because they can form novel magnetic materials. In this frame the magnetic properties of Cu(hfac)$_2$TEMPOL (hfac = hexafluoroacetylacetonato; TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy),[10] which contains linear chains of copper ions octahedrally coordinated by two hfac ligands, one nitroxide, and one –OH group, were reported.[11,12] The magnetic data were interpreted with use of two different exchange coupling constants, one relative to the short copper–nitroxide interaction and the other relative to the interaction between the nitroxide and the nearest-neighbor copper ion. The former was found to be ferromagnetic, $J = -13 \pm 5$ cm^{-1},[2] while the latter was found to be much smaller, and antiferromagnetic, $J' = 0.0542$ cm^{-1}.[12] The EPR spectra of this complex at room temperature are typical of a triplet,[11] determined by the large J coupling, and the J' interaction only determines the appearance of the lines, washing out the hyperfine splitting.

Recently some of us reported the synthesis[13] and the X-ray structure[14] of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolidinyl-1-oxyato)copper(II) (I), which was found to possess the structure schematized in Figure 1.

The ligands bind the copper ions with the two chelate oxygen atoms in the equatorial plane while the tail (the nitroxide oxygen) binds a different copper ion in the axial position. The coordination around copper is distorted octahedral, with two nitroxides in axial positions and four oxygen atoms of the keto aldehydes in the equatorial positions. On the whole the copper atom is bound to four different 4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolidinyl-1-oxy ligands, yielding a structure in which two different chains intersect at each copper ion as shown in Figure 2.

As one looks at the crystal structure, it is apparent that several exchange pathways involving the nitroxides and the copper ion are available. Therefore, we decided to measure the magnetic susceptibility of I in the range 6–250 K as well as to study the EPR spectra of I because in principle these are best suited to monitor weak interactions and can provide information on the spin dimensionality of the compound.

Experimental Section

The compound I was prepared by a previously reported procedure.[13] Magnetic susceptibility data were measured between 6 and 300 K with an SHE superconducting susceptometer at a field strength of 0.5 T.

The crystals were oriented with a Philips PW1100 diffractometer and were found to correspond to the reported structure with prominent (100) and ($\bar{1}$00) faces. Single-crystal EPR spectra in the temperature range 140–300 K were recorded at X-band frequency with a Bruker ER-200 spectrometer and at Q-band with a Varian E9 spectrometer equipped with standard apparatus for variable-temperature measurements.

Results

The temperature dependence of the magnetic susceptibility of I is shown in Figure 3, in the form of χT vs. T. The high-temperature value, $\chi T = 1.263$ cm^3 K mol^{-1}, corresponds to that expected for three noninteracting spins, but when the temperature is lowered, χT increases, suggesting a dominant ferromagnetic coupling involving the three spins. At the lowest temperature χT is equal to 2.087 cm^3 K mol^{-1}, which corresponds well to a quartet ground state.

The polycrystalline powder EPR spectra of I recorded at room temperature show only an isotropic signal centered at $g = 2.06$. Single-crystal spectra show only one signal for every crystal orientation. The lines are Lorentzian to a good approximation, showing that exchange narrowing is operative between the two magnetically nonequivalent sites of the monoclinic cell. The **g** tensor is anisotropic: $g_1 = 2.035$, $g_2 = 2.048$, $g_3 = 2.099$. The largest g value is observed parallel to the b axis, while the two smallest are in the ac plane, with g_1 parallel to a^*. The spectra are slightly temperature-dependent. At 144 K the g values are $g_1 = 2.029$, $g_2 = 2.041$, $g_3 = 2.099$.

The line widths show angular, temperature, and frequency dependence. The maximum line width is observed parallel to b, where ΔH_{pp} is 288 G at room temperature and 205 G at 144 K at X-band frequency, while it is 255 G at room temperature at Q-band frequency.

The angular dependence of ΔH_{pp} at room temperature in the plane bc is slightly different at X-band and Q-band frequencies, as shown in Figure 4. In both cases the maxima are seen parallel to b and minima parallel to c. The data points at Q-band are lower than those at X-band. The rate of decrease of ΔH_{pp} on moving away from b is faster at Q-band than at X-band.

Discussion

The magnetic data of I can be interpreted with use of several

---

(1) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334.
(2) Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 798.
(3) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1983**, *22*, 1591.
(4) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677.
(5) Dickman, M. H.; Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 2595.
(6) Benelli, C.; Gatteschi, D.; Zanchini, C.; Dickman, M. H.; Doedens, R. J.; Porter, L. C. *Inorg. Chem.* **1986**, *25*, 3453.
(7) Grand, A.; Rey, P.; Subra, R. *Inorg. Chem.* **1983**, *22*, 391.
(8) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 2147.
(9) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.
(10) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417.
(11) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813.
(12) Benelli, C.; Gatteschi, D.; Carnegie, D. W., Jr.; Carlin, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2560.
(13) Espié, J. C.; Ramasseul, R.; Rassat, A.; Rey, P. *Bull. Soc. Chim. Fr.* **1981**, 33, Part II.
(14) Laugier, J.; Ramasseul, R.; Rey, P.; Espié, J. C.; Rassat, A. *Nouv. J. Chim.* **1983**, *7*, 11.

---

† University of Florence.
‡ Centre d'Etudes Nucléaires.

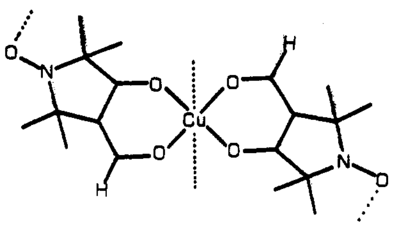

Figure 1. Schematic representation of the structure of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolinyl-1-oxyato)copper(II) (I).

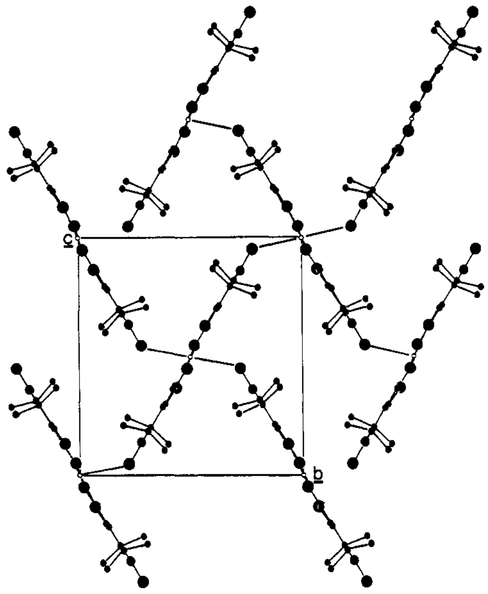

Figure 2. General view of the structure of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolinyl-1-oxyato)copper(II) (I) [(○) Cu, (•) C, (●) N, (⬤) O].

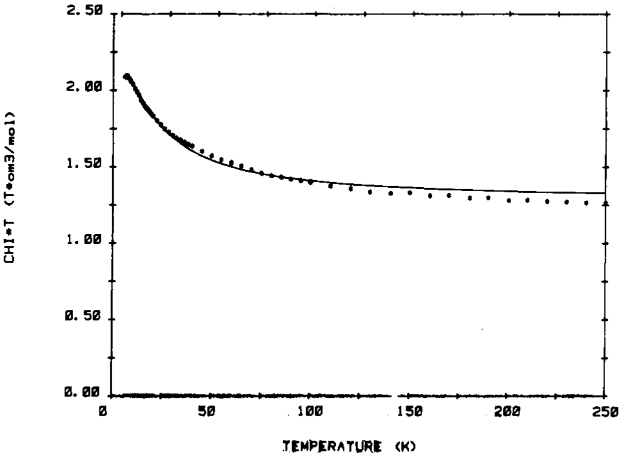

Figure 3. Temperature dependence of the magnetic susceptibility of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolidinyl-1-oxyato)copper(II) (I) in the form of χT vs. T.

different models. The simplest is that which considers only the interaction between one copper ion and two nearest-neighbor nitroxides, i.e. considering isolated clusters of three $S = {}^1/_2$ spins. The appropriate Hamiltonian is

$$H = J\hat{S}_{Cu}\cdot S_r + J\hat{S}_{Cu}\cdot S_{r'} + J'\hat{S}_r\cdot\hat{S}_{r'} \qquad (1)$$

where $\hat{S}_{Cu}$, $\hat{S}_r$, and $\hat{S}_{r'}$ refer to the copper and the two nitroxide spins, respectively. The energies of the three states are given by[15]

$$E(S = {}^3/_2) = J/2 + J'/4 \qquad (2)$$

$$E(S = {}^1/_2, 1) = -J + J'/4 \qquad (3)$$

$$E(S = {}^1/_2, 0) = -3J'/4 \qquad (4)$$

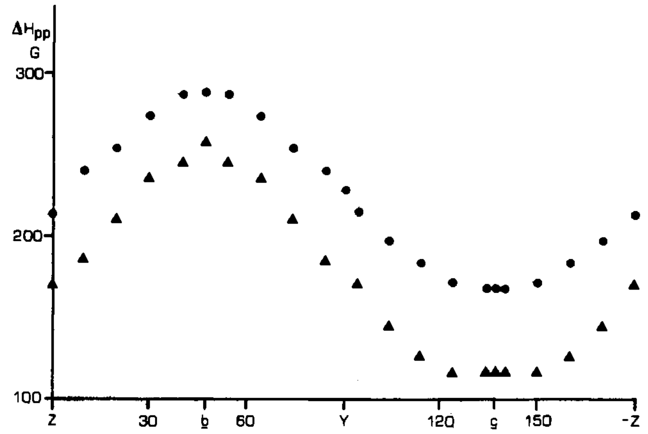

Figure 4. Angular dependence of ΔH_{pp} for the EPR single-crystal spectra of bis(4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolinyl-1-oxyato)copper(II) (I) at room temperature in the *bc* plane at X- (●) and Q-band (▲) frequencies.

The two $S = {}^1/_2$ states are labeled 1 and 0, indicating the intermediate spin obtained by coupling the two nitroxides first. The corresponding g values of these multiplets are

$$g(S = {}^3/_2) = {}^2/_3 g_r + {}^1/_3 g_{Cu} \qquad (5)$$

$$g(S = {}^1/_2, 1) = {}^4/_3 g_r - {}^1/_3 g_{Cu} \qquad (6)$$

$$g(S = {}^1/_2, 0) = g_{Cu} \qquad (7)$$

The experimental data were fit by using the appropriate equation for three $S = {}^1/_2$ spins[16] to give $J = -21.2$ cm^{-1}, $J' = -6.30$ cm^{-1}, $g_r = 2.01$, and $g_{Cu} = 2.12$. The corresponding curve is shown in Figure 3. As previously observed,[17-20] it is fairly difficult to obtain precise values of the coupling constants in the case of ferromagnetic coupling, and this is particularly true for trinuclear species. Therefore, we do not attach much meaning to the relatively large J' constant and interpret the parameters as indicating that a moderate ferromagnetic coupling is operative. The reasonably good fit of the experimental data shows that the single three-spin model is accurate enough.

The ferromagnetic coupling between a copper ion and an axial nitroxide is now well established and appears to be determined by the orthogonality of the copper xy and the radical magnetic orbitals.[12]

The model might be complicated by the introduction of additional exchange pathways which can yield extended magnetic interactions, but the reasonably good fit obtained for the temperature dependence of the magnetic susceptibility suggests that intermolecular interactions are indeed smaller than either J or J'.

According to the three-spin model one could expect to observe EPR signals from each spin multiplet. Since the crystals are monoclinic, one could further expect that each signal should generally split into two due to the presence of two magnetically nonequivalent sites. Since, however, only one signal was observed for every crystal orientation, it is apparent that some averaging process is operative.

In principle two distinct processes are possible: one is fast thermal rearrangement on the various spin multiplets, and the other is exchange narrowing.

---

(15) Gatteschi, D.; Bencini, A. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Gatteschi, D., Kahn, O., Willett, R. W., Eds.; Reidel: Dordrecht, Holland, 1985; p 241.

(16) Benelli, C.; Bunting, R. K.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 3074.

(17) Bencini, A.,; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 704.

(18) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877.

(19) Hatfield, W. E. *Inorg. Chem.* **1983**, *22*, 833.

(20) Carlin, R. L.; Burriel, R.; Corneliesse, R. M.; Van Duyneveldt, A. J. *Inorg. Chem.* **1983**, *22*, 831.

The first should contribute an averaged spectrum for each magnetically nonequivalent site but is not able alone to average the two sites. The second, on the other hand, can average completely to one single signal. Before proceeding further, it is convenient to look more into the detail of the crystal structure of the compound.

Each copper ion is bound to four different 4-formyl-3-oxo-2,2,5,5-tetramethylpyrrolidinyl-1-oxy ligands in such a way that two of them are bound to the metal ion through their aldo and keto oxygen atoms, leaving the nitroxide oxygen atoms 6.307 Å apart from the metal ion. The overall structure is formed by zigzag chains, which intersect at each copper ion. The shortest copper–copper distances are 7.822 Å along the *a* axis and 8.290 Å in the plane orthogonal to it.

It is apparent that several exchange pathways are actually available for the narrowing of the EPR lines and also that, although the CuO_2 spin clusters lie substantially in the *bc* plane, the exchange interactions orthogonal to this plane can be strong enough to suppress two-dimensional behavior, yielding Lorentzian lines.

Several different broadening mechanisms of the EPR lines are possible. The dipolar interactions can be accounted for by considering the shortest nonbonded Cu–O distances of 6.307 Å. These are expected to give a contribution to the line width of 200–300 G.[21,22] Other broadening mechanisms are due to the differences in the **g** tensors of the various spin multiplets.[23] If the **g** tensors of the three multiplets are further averaged out, the resulting **g** tensor is given by

$$\mathbf{g}_{av} = \tfrac{2}{3}\mathbf{g}_r + \tfrac{1}{3}\mathbf{g}_{Cu} \qquad (8)$$

This relation can be used to relate the experimental **g** tensor to the individual $\mathbf{g}_r$ and $\mathbf{g}_{Cu}$ tensors. $\mathbf{g}_r$ is expected to be quasi-isotropic and can be safely assumed to be given by

$$\mathbf{g}_r = 2.00\mathbf{e} \qquad (9)$$

where **e** is the unit matrix. Then with use of eq 5–7 it is possible to calculate the principal values of $\mathbf{g}_{Cu}$ as $g_{Cu,1} = 2.105$, $g_{Cu,2} = 2.144$, and $g_{Cu,3} = 2.297$ at room temperature. Considering that these are values averaged on the two magnetically nonequivalent sites, these are rather satisfactory. In fact, the largest *g* value is that parallel to *b*. Since the *z* axes of the two copper ions, defined by the Cu–O nitroxide bonds, make an angle of ~14° with *b*, the largest molecular *g* value must be larger than 2.30, a value which compares well with those of CuO_6 chromophores[24] and with the value found in Cu(hfac)$_2$TEMPOL.[11]

If we use the g_{Cu} values calculated above, we see that $g_z(S = {}^3/_2) = 2.099$, $g_z(S = {}^1/_2, 1) = 1.901$, and $g_z(S = {}^1/_2, 0) = 2.297$. The *g* anisotropy among the various multiplets therefore provides a broadening mechanism on the order of 600 G at X-band and of 2300 G at Q-band frequency. Along the other principal directions the anisotropies are smaller.

Another possible broadening mechanism is provided by the copper hyperfine splitting. Again this is expected to be largest along *z*. For a copper complex like this it is expected to be on the order of 130–150 G, so its contribution to the broadening should not exceed 50–60 G and should be negligible compared to the effects of the other mechanisms.

Finally, the other broadening mechanism is given by the zero-field splitting of the quartet state. For a three-spin cluster like the present one it is expected to be determined by the sum of exchange and dipolar contributions, which can be decomposed as[15]

$$\mathbf{D}_{3/2} = \tfrac{1}{3}\mathbf{D}_{Cu-r} + \tfrac{1}{6}\mathbf{D}_{r-r} \qquad (10)$$

where $\mathbf{D}_{Cu-r}$ is the contribution derived from the copper–radical interaction and $\mathbf{D}_{r-r}$ is that derived from the radical-radical interaction. An estimate of $\mathbf{D}_{3/2}$ can be made by considering the zero-field splitting observed in the triplet state of Cu(hfac)$_2$TEMPOL, $D_1 = 1690$ G.[12] Indeed, the copper–oxygen distances in the two complexes are comparable (2.59 Å in the present compound[14] and 2.44 Å in Cu(hfac)$_2$TEMPOL[10]) and also the *g* values are similar, so that the dipolar component of $\mathbf{D}_{Cu-r}$ should not vary substantially. Since D_1 is expected to be ${}^1/_2\mathbf{D}_{Cu-r}$ and $\mathbf{D}_{3/2}$ is related to it by $\mathbf{D}_{3/2} = {}^1/_3\mathbf{D}_{Cu-r}$, we can estimate $\mathbf{D}_{3/2}$ on the order of 1000 G.

Finally, the contribution from the anisotropy of the two magnetically nonequivalent sites can be neglected compared to the previous ones, given the favorable orientation of the copper octahedron in the unit cell.

From the above considerations it is apparent that the two most important broadening mechanisms are the difference in the *g* values of the various multiplets and the zero-field splitting of the ground quartet. The former is frequency-dependent and is expected to yield broader lines at Q-band than at X-band frequency. Now the experimental data show that ΔH_{pp} is consistently smaller in the 35-GHz as compared to the 9-GHz spectra. Therefore, it must be concluded that this broadening mechanism is quenched in the present compound. This effect may be determined by fast thermal averaging on the three total spin multiplets, or even by fast thermal averaging on the two spin doublets only, since they are the ones whose *g* values differ from the average as shown by eq 5–7.

On this basis the narrowing of the lines as the Zeeman frequency is increased must be attributed to the different weights of secular and nonsecular terms at 9 and 35 GHz, respectively. Since the line widths do not show a large angular dependence, we may attempt to guess the frequency dependence using the expression valid for powder average[21]

$$\Delta H_{pp} \propto 1 + \tfrac{5}{3}\exp[-\tfrac{1}{2}(\omega_0/\omega_e)^2] + \tfrac{2}{3}\exp[-2(\omega_0/\omega_e)^2] \qquad (11)$$

where ω_0 is the Zeeman and ω_e is the effective exchange frequency. Since the ratio of the line widths at Q- and X-band frequencies is close to 0.9, ω_e is estimated to be 0.13 cm^{-1}. This value compares well with the value of 0.05 cm^{-1} we recently obtained for the analysis of the magnetic susceptibility data for Cu(hfac)$_2$TEMPOL, for the interaction between a nitroxide with a copper ion to which it is not directly bound.[11] It also compares well with other solution data on the interaction between copper and nitroxides.[25]

Registry No. I, 85646-32-8.

---

(21) Kubo, R.; Tomita, K. *J. Phys. Soc. Jpn.* **1954**, *9*, 888.

(22) Anderson, P. V.; Weiss, P. R. *Rev. Mod. Phys.* **1953**, *25*, 269.

(23) Yokota, M.; Koide, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 953.

(24) Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*N. Y.*) **1982**, *8*, 1.

(25) DuBois, D. L.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 2624.