THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 2315−2317

Electron Paramagnetic Resonance of Three-Spin Nitroxide−Copper(II)−Nitroxide Clusters Coupled by a Strong Exchange Interaction

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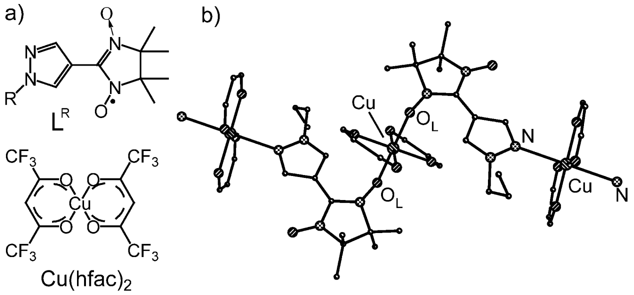
Received: December 19, 2005; In Final Form: January 13, 2006

The complex of Cu^{2+} hexafluoroacetylacetonate with two pyrazol-substituted nitronyl nitroxides represents an unusual exchange-coupled three-spin system. The antiferromagnetic exchange coupling, which already at $T < 150$ K is larger than the thermal energy kT, induces the transition from a total spin state $S = {}^3/_2$ to a state $S = {}^1/_2$ and produces static spin polarization. Anomalous electron paramagnetic resonance (EPR) spectra of an $S = {}^1/_2$ state were detected experimentally and described theoretically. The effective g factor of the three-spin system is smaller than 2, despite the fact that all the individual components have $g > 2$. The observed signals with $g < 2$ are highly informative and can be employed for determination of the sign and value of the exchange interaction in three-spin nitroxide−copper−nitroxide clusters.

Copper−nitroxide complexes are important systems in the area of molecular magnetism.[1] They are widely used as models for the investigation of magneto-structural correlations. The complex of Cu^{2+} hexafluoroacetylacetonate ($Cu(hfac)_2$) with two pyrazol-substituted nitronyl nitroxides (L^R) represents an unusual exchange-coupled three-spin system. The antiferromagnetic exchange interaction, which already at $T < 150$ K is larger than the thermal energy kT, induces the transition from a total spin state $S = {}^3/_2$ to a state $S = {}^1/_2$ and produces static spin polarization. We report on the anomalous electron paramagnetic resonance (EPR) spectra of the $S = {}^1/_2$ state detected experimentally and described theoretically and discuss novel aspects and potential applications.

Recently, a new family of heterospin polymer-chain complexes of the composition $Cu(hfac)_2L^R$ was discovered (Chart 1a).[2]

CHART 1: (a) Chemical Structure of $Cu(hfac)_2$ and the Nitroxide Ligand L^R and (b) Polymer-Chain Structure of $Cu(hfac)_2L^{Pr}$ Complexes



These complexes undergo structural rearrangements at low temperatures followed by magnetic effects analogous to spin-crossover. The character of magnetic anomalies is strongly dependent on the substituent R. In this work we use the nitroxide L^R with R = propyl. The polymer chains consist of alternating coordination units CuO_4N_2 and CuO_6, which contain one-spin $>N-Cu^{2+}-N<$ and three-spin $>N-{}^\bullet O-Cu^{2+}-O^\bullet-N<$ clusters, respectively (Chart 1b). The intercluster exchange coupling is smaller than the intracluster exchange by 2 orders of magnitude.[2] Magnetic susceptibility data revealed a considerable decrease of the value of effective magnetic moment $\mu_{eff}(T)$ between $T \approx 250$ K and ≈ 100 K associated with a transition in the exchange cluster $>N-{}^\bullet O-Cu^{2+}-O^\bullet-N<$ from an $S = {}^3/_2$ state to an $S = {}^1/_2$ state.[2] This transition is governed by an increase of the antiferromagnetic exchange coupling due to a temperature-dependent structural rearrangements. X-ray analysis showed that at room temperature the CuO_6 units represent octahedrons with elongated axes O_L-Cu-O_L ($Cu-O_L$ distance 2.315 Å). On lowering the temperature to 115 K, the $Cu-O_L$ distances gradually shorten by ≈0.3 Å, whereas the $Cu-O_{hfac}$ distances increase by ≈0.3 Å. Thus, the elongated (Jahn−Teller) axis of the octahedron is changed from O_L-Cu-O_L to $O_{hfac}-Cu-O_{hfac}$[2].

We have found that the EPR spectra are strongly temperature dependent, reflecting the structural and magnetic changes in $Cu(hfac)_2L^{Pr}$. Figure 1 shows continuous wave EPR spectra of polycrystalline powder measured at X-band (9.72 GHz) between 90 and 260 K. The spectrum at 260 K shows the usual pattern of Cu^{2+} ions in an octahedral environment ($g_\perp = 2.075$, $g_\parallel = 2.371$) superimposed by a broad and weak line with a negative wing which is visible at $g \approx 2$. We assign the former spectrum to the one-spin system $>N-Cu^{2+}-N<$ (CuO_4N_2 unit), and the latter one to the three-spin cluster $>N-{}^\bullet O-Cu^{2+}-O^\bullet-N<$ (CuO_6 unit). The most pronounced change at lower temperatures is the appearance of a new feature in the high-field region of

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10.1021/jp0573792 CCC: $33.50

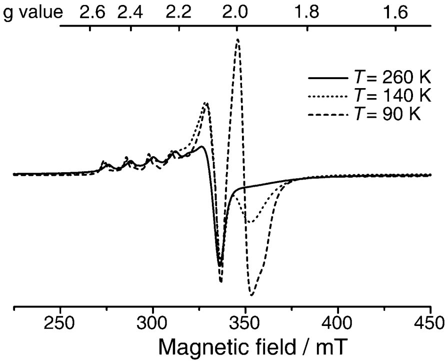

Figure 1. X-band EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at T = 90, 140 and 260 K.

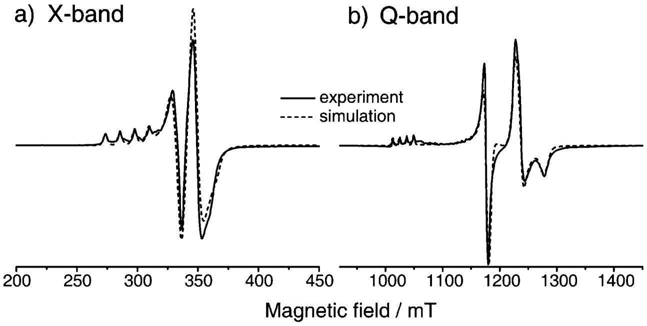

Figure 2. Experimental and simulated X-band (a) and Q-band (b) EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at T = 90 K. g values used in the simulations for the CuO$_4$N$_2$ unit: Cu^{2+}, $g_{\|} = 2.371$, $g_{\perp} = 2.075$. g values used in the simulations for the CuO$_6$ unit: L$^{\mathrm{R}}$, $g = 2.007$; Cu^{2+}, $g_x = 2.047$, $g_y = 2.097$, $g_z = 2.287$. $J = -115$ cm^{-1}.

the spectrum ($g \approx 1.85-2$). Because no significant structural changes occur in the CuO$_4$N$_2$ units[2], this new signal is unambiguously assigned to the three-spin system >N−$^{\bullet}$O−Cu^{2+}−O$^{\bullet}$−N< (in the CuO$_6$ unit) in the spin state $S = {}^1/_2$.

Figure 2 shows the X- and Q-band (34.17 GHz) EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at $T = 90$ K. The observed g values of the "$g < 2$ signals" coincide at both microwave frequencies. Thus, the positions of the spectral features are not influenced by exchange, dipole and other magnetic field independent interactions. At the same time, the "$g < 2$ signals" cannot be explained by either the g value of copper complex or of the nitroxide. It is well-known that nitroxides have g values close to g_{e} of free electron ($g = 2.007$ for L$^{\mathrm{Pr}}$), and that for Cu^{2+} ions in octahedral environment $g > 2$ for all three principal values of the tensor.[3] In some cases, for Cu^{2+} ions in tetrahedral environment $g < 2$,[3] but for Cu(hfac)$_2$L$^{\mathrm{Pr}}$ tetrahedral geometry is excluded by X-ray analysis.[2] Thus, the observation of signals with $g < 2$ needs further explanation.

The spin Hamiltonian for a three-spin system $^{\bullet}$O−Cu^{2+}−O$^{\bullet}$ can be written as

$$\hat{H} = g_1\beta B(\hat{S}_{1z} + \hat{S}_{3z}) + g_2\beta B\hat{S}_{2z} - 2J(\hat{S}_1 + \hat{S}_3)\hat{S}_2$$

where B is the static magnetic field and β is the Bohr magneton. Subscripts 1 and 3 correspond to the spins of the two nitroxides, and subscript 2 corresponds to the spin of the copper. The nitroxides are assumed to be equivalent with isotropic values g_1 and the same isotropic exchange coupling constant J with copper. For simplicity we assume that the g_2 value for the Cu^{2+} complex is isotropic. The assumption of zero exchange between the two nitroxides is justified by the linear geometry of the $^{\bullet}$O−Cu^{2+}−O$^{\bullet}$ chain.[2,4]

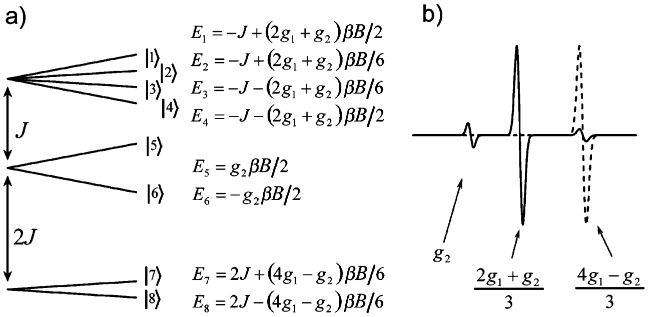

Figure 3. (a) Energy levels and energies of an exchange-coupled three-spin system with $|J| \gg B$, $J < 0$. (b) Calculated EPR spectrum for $|J| \ll kT$ (solid line) and $|J| \gg kT$ (dashed line).

Figure 3a shows the energy level scheme for the case $|J| \gg B$ and the energies considering only terms linear on B/J.

The eigenfunctions $|1\rangle$−$|4\rangle$ describe the quartet $S = {}^3/_2$ state, the eigenfunctions $|5\rangle$, $|6\rangle$ and $|7\rangle$, $|8\rangle$ describe the two doublet $S = {}^1/_2$ states. For $|J| \gg B$ five transitions with three different frequencies will be observed (Figure 3b): $|5\rangle \leftrightarrow |6\rangle$ with effective $g = (E_5 - E_6)/\beta B = g_2$, $|1\rangle \leftrightarrow |2\rangle$, $|2\rangle \leftrightarrow |3\rangle$ and $|3\rangle \leftrightarrow |4\rangle$ with effective $g = (E_i - E_j)/\beta B = (2g_1 + g_2)/3$ (i, j = 1, 2; 2, 3; 3, 4), and $|7\rangle \leftrightarrow |8\rangle$ with effective $g = (E_7 - E_8)/\beta B = (4g_1 - g_2)/3$. Note that in our case the transition $|7\rangle \leftrightarrow |8\rangle$ will have $g < 2$, because $g_1 \approx 2$ and $g_2 > 2$.

At this point it is important to consider the magnitude of the exchange interaction J. Referring to strong exchange interactions usually means $|J| \gg B$.[4] At the same time, in most of the practical situations, $|J| \ll kT$. The spectrum for this case is shown in Figure 3b (solid line). It is, however, very different from the experimentally observed spectra in Figures 1 and 2. A line with $g < 2$ is observed, but the much stronger central line with $g > 2$ is missing. If, on the other hand, the condition $|J| > kT$ is met, the lowest state will predominantly be populated. This is the case for Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at $T < 150$ K, where, on the basis of magnetic susceptibility measurements, the exchange interaction was estimated to be $J \approx -100$ cm^{-1} [2]. It is this strong exchange that forces the spin system to undergo an $S = {}^3/_2 \rightarrow {}^1/_2$ transition. For example, for $T = 100$ K and $J = -100$ cm^{-1} the Boltzman populations between the lower of the two states $S = {}^1/_2$ and state $S = {}^3/_2$ differ by a factor $\exp(3J/kT) \approx 75$. Thus, the spectrum is statically polarized and the EPR transitions within the upper $S = {}^1/_2$ state and the $S = {}^3/_2$ state are weak, whereas the transition within the lowest $S = {}^1/_2$ state is enhanced. As a result, virtually only this transition is observed (Figure 3b, dashed line). For a ferromagnetic exchange interaction ($J > 0$) the energy scheme in Figure 3a would be inverted and only the $S = {}^3/_2$ state would be populated. As a result, the signal with $g < 2$ would be very weak.

The pattern shown in Figure 3b with a dashed line describes very well the phenomenon that we only observe a strong peak with $g < 2$. The account of exchange coupling between equivalent nitroxides would only change the spacing between quartet and doublet states (Figure 3a), whereas the EPR frequencies within these states would remain unchanged. The g anisotropy of the copper complex will not change the basic characteristics as well but will lead to a splitting of the resonance lines. The experimental spectra in Figure 2 can be nicely simulated using a reasonable g tensor for the copper complex and taking polarization effects into account (dashed lines).[5]

In conclusion, we summarize the main features of the spectra and give an outlook for EPR applied to nitroxide−copper−nitroxide three-spin systems exchange-coupled with $|J| > kT$. A strong signal may be observed at effective $g < 2$ when the exchange coupling is antiferromagnetic. The proper g values can be obtained by including the polarization of the energy levels in the simulation of the spectra. In cases where essentially only "$g < 2$ signals" are observed (strong polarization), the exchange-coupled spin system has an effective $g < 2$, whereas all the individual components have $g > 2$. In the opposite case of a ferromagnetic exchange coupling, no signals at $g < 2$ would be observed. EPR is thus capable of determining the sign of J for three-spin systems with $|J| > kT$, which is not the case for two-spin systems or for $|J| < kT$. When the "$g < 2$ signals" are well separated from the rest of the spectrum (e.g., at high microwave frequencies), the measurement of their intensity versus temperature allows one to evaluate the absolute value of J, which is the subject of further investigation. Finally, all general features were demonstrated using a nitroxide–copper(II)–nitroxide cluster. A family of similar compounds has been studied over the past decade, with the ultimate aim to design molecular magnets.[2,6] As shown in this work, EPR on these compounds complements the magnetic susceptibility and X-ray techniques and represents an efficient method for studying exchange interactions and coordination modes; the EPR is much faster and does not require single crystals. In addition, the described phenomena explain the low g values often required in simulations of the $\mu_{\mathrm{eff}}(T)$ dependence of solids containing three-spin nitroxide–copper–nitroxide clusters.[2]

Acknowledgment. We are thankful to Ms. K. Maryunina and Dr. S. Fokin for providing us with a sample of $\mathrm{Cu(hfac)_2L^{Pr}}$ and for stimulating discussions. This work was supported by INTAS (M. Fedin YSF Nr.04-83-2669) and RFBR (Nr. 05-03-32264-a).

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