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Electron Spin Exchange Processes in Strongly Coupled Spin Triads

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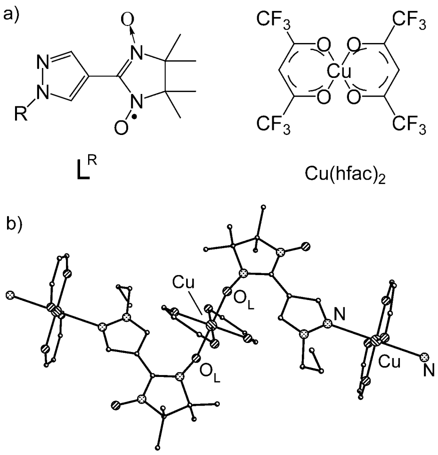
The complexes of Cu^{2+} hexafluoroacetylacetonate with two pyrazol-substituted nitronyl nitroxides are the choice systems to study the spin dynamics of strongly exchange-coupled spin triads. The large values of exchange coupling (ca. 100 cm^{-1}) and high-resolution electron paramagnetic resonance (EPR) at Q- and W-bands (35 and 94 GHz) allowed us to observe and interpret specific characteristics of these systems. An electron spin exchange process has been found between different multiplets of the spin triad, which manifests itself as a significant shift of the EPR line position with temperature. We propose that the spin exchange process is caused by the modulation of exchange interaction between copper and nitroxides by lattice vibrations. The estimations of the rate of exchange process and model calculations essentially support the observed phenomena. The studied characteristics of strongly coupled spin triads explain previously obtained results, agree with literature, and should be accounted for in future investigations of similar spin systems.

Introduction

Three-spin systems coupled by a strong exchange interaction are one of the simplest building blocks of more complicated multispin clusters. In particular, during previous decades, these systems drew a significant interest in the field of molecular magnetism.[1−3] The bridging of transition metals by nitroxide ligands is one of the approaches used in design of molecular magnets,[4] which may lead to formation of strongly coupled spin triads. Recently, a new family of multispin compounds based on copper(II) hexafluoroacetylacetonates ($Cu(hfac)_2$) and pyrazol-substituted nitronyl nitroxides (L^R) has been found (Chart 1).[5,6] The polymer chains of $Cu(hfac)_2L^R$ contain alternating one- and three-spin systems and exhibit low-temperature structural rearrangements, leading to magnetic effects analogous to a spin-crossover.[5,6] During these processes, the ratio between $S = 3/2$ and $S = 1/2$ total spin state populations of a spin triad changes, leading to a change of the effective magnetic moment.

In our recent work, the EPR study of a strongly coupled symmetric spin triad in $Cu(hfac)_2L^{Pr}$ (propyl-substituted compound) has been reported.[7] The unusual EPR signals of $Cu(hfac)_2L^{Pr}$ with g-factors $g < 2$ have been observed at low temperatures (ca. 100 K). The shapes and g-values of these signals were explained by the static multiplet polarization in spin triad, which occurs due to a large value of exchange coupling ($J \sim 100$ cm^{-1} corresponding to $\sim$140 K). If the exchange interaction is antiferromagnetic, the lower spin state $S = 1/2$ with $g < 2$ is predominately populated at $kT < |J|$, giving rise to the strong signals in the high-field region of EPR spectra. We have proposed that the observation of these signals is a highly important and useful characteristic of strongly coupled linear three-spin systems, as it allows for the determination of the sign and provides information on the absolute value of intracluster (i.e., within a triad) exchange interaction.

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



In this paper, we continue the characterization of strongly coupled spin triads. Using the high-resolution EPR at 35 and 94 GHz, we study the spin dynamics in a triad, which is connected to the appearance of signals with $g < 2$. The electron spin exchange process between different multiplets of a spin triad has been observed, which manifests itself as a significant shift of the EPR line position with temperature. The possibilities of such processes and some experimental indications have been discussed in literature previously.[3,8−10] In this work, we report the unambiguous experimental manifestation and a theoretical consideration of these processes in a family of compounds $Cu(hfac)_2L^R$.

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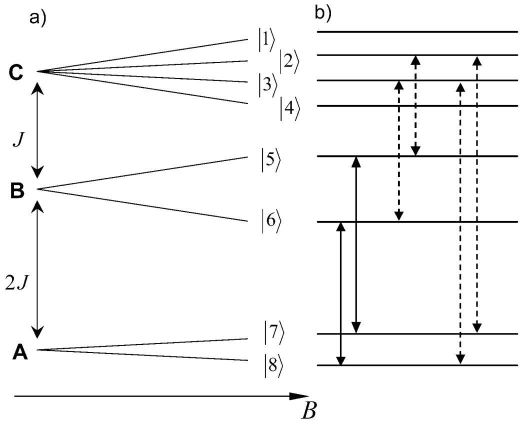

Figure 1. (a) Energy level diagram of a spin triad described by spin-Hamiltonian (eq 1) for the case $|J| \gg B$, $J < 0$. (b) Transitions induced by the modulation of isotropic (solid lines) and anisotropic (dashed lines) exchange interaction.

Experimental Methods

The experiments were carried out at a commercial W-band (94 GHz) EPR spectrometer (Bruker Elexsys E680) and at a home-built Q-band (35 GHz) EPR spectrometer[11] in continuous wave mode.

The synthesis and magnetic susceptibility dependences of the compounds Cu(hfac)$_2$L^R were discussed previously in refs 5−6. The compounds Cu(hfac)$_2$L^{Pr} and Cu(hfac)$_2$L^{Bu}/orthoxylene (Chart 1) were kindly provided by Ksenia Maryunina (International Tomography Center, ITC) as polycrystalline powders. To obtain the powder pattern EPR spectra, the polycrystalline powder was additionally crushed. The severe crushing produced defects in polymer-chain structure, leading to an appearance of signals from free nitroxides ($g = 2.007$). Because this was undesired, an optimum between the strength of the nitroxides' signals and the quality of the EPR powder pattern was adjusted. In addition, EPR spectra at several sample orientations were usually recorded and summed up in order to obtain the satisfactory powder pattern.

The alignment of microcrystals along the strong field of the W-band magnet has been found to be essential. This occurs because the compounds Cu(hfac)$_2$L^R used are undiluted (magnetically concentrated). It was possible to obtain nearly 100% oriented samples by introducing them into a magnetic field of 3−4 T. It was also possible to get rid of the orientation effect by mixing the polycrystalline powder Cu(hfac)$_2$L^R with a well-crushed diamagnetic quartz powder. In the latter case, the alignment was diminished due to the mechanical hindrance of the particles reorientations. Therefore, we could measure both oriented (one certain position) and disordered spectra of Cu(hfac)$_2$L^R at W-band. The alignment effects at Q-band were found to be insignificant.

Results and Discussion

1. General Remarks. Spin-Hamiltonian of the exchange-coupled linear spin triad nitroxide−copper(II)−nitroxide can be written in the following form

$$\hat{H} = \beta \mathbf{B} \mathbf{g}^{R}(\mathbf{S}^{R1} + \mathbf{S}^{R2}) + \beta \mathbf{B} \mathbf{g}^{Cu} \mathbf{S}^{Cu} - 2J(\mathbf{S}^{R1} + \mathbf{S}^{R2})\mathbf{S}^{Cu} \quad (1)$$

where superscripts R1 and R2 correspond to the two nitroxides and Cu to the copper, $\mathbf{g}^R$ and $\mathbf{g}^{Cu}$ are the corresponding g-tensors. The nitroxides are assumed equivalent with an isotropic g-factor g^R, i.e., $\mathbf{g}^R = g^R\, \hat{\mathbf{1}}$, where $\hat{\mathbf{1}}$ is the unity matrix. $\mathbf{B} = [0,0,B]$ is the magnetic field along the z-axis, and J is the exchange interaction between each nitroxide and copper ($J < 0$ corresponds to the antiferromagnetic coupling). The exchange coupling between two nitroxides is neglected, which is a good approximation for a linear geometry of spin triad.

The energy level scheme of a spin triad for the case $|J| \gg B, J < 0$ is shown in Figure 1a. The corresponding eigenfunctions for $B = 0$ in the basis $|S_z^{R1} S_z^{Cu} S_z^{R2}\rangle$ ($\alpha = +1/2$, $\beta = -1/2$) can be found as

$$\begin{aligned}
|1\rangle &= |\alpha\alpha\alpha\rangle \\
|2\rangle &= (|\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle + |\alpha\beta\alpha\rangle)/\sqrt{3} \\
|3\rangle &= (|\alpha\beta\beta\rangle + |\beta\beta\alpha\rangle + |\beta\alpha\beta\rangle)/\sqrt{3} \\
|4\rangle &= |\beta\beta\beta\rangle \\
|5\rangle &= (|\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle)/\sqrt{2} \\
|6\rangle &= (|\alpha\beta\beta\rangle - |\beta\beta\alpha\rangle)/\sqrt{2} \\
|7\rangle &= (|\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle - 2|\alpha\beta\alpha\rangle)/\sqrt{6} \\
|8\rangle &= (|\alpha\beta\beta\rangle + |\beta\beta\alpha\rangle - 2|\beta\alpha\beta\rangle)/\sqrt{6}
\end{aligned} \quad (2)$$

The effective g-tensors of the three multiplets A ($S = 1/2$), B ($S = 1/2$), and C ($S = 3/2$) can be found as[8]

$$\begin{aligned}
\mathbf{g}^{A} &= (4g^{R}\hat{\mathbf{1}} - \mathbf{g}^{Cu})/3 \\
\mathbf{g}^{B} &= \mathbf{g}^{Cu} \\
\mathbf{g}^{C} &= (2g^{R}\hat{\mathbf{1}} + \mathbf{g}^{Cu})/3
\end{aligned} \quad (3)$$

2. Experimental Study of Temperature-Dependent EPR Spectra. The spectrum of Cu(hfac)$_2$L^{Pr} at temperatures below the spin transition ($T = 90$ K) was explained by us earlier in terms of static multiplet spin polarization, where basically only the lower spin state $S = 1/2$ with an effective $\mathbf{g}^A < 2$ is populated (Figure 1a). However, the following studies at higher temperatures showed that the position, intensity, and shape of this signal is temperature dependent at $T > 100$ K. This means that the additional processes operate at $T > 100$ K, which need a closer examination. While the dependences of intensity and line shape on temperature are expected due to the temperature-dependent Boltzman factor and electron spin relaxation, the explanation of the line position shift is not so straightforward.

Figure 2a shows the polycrystalline powder spectra of Cu(hfac)$_2$L^{Pr} at Q-band at $T = 50-200$ K. Each spectrum is a superposition of the EPR signals of isolated copper ion in CuN$_2$O$_4$ units (low-field part $B < 1.24$ T, $g > 2$) and the signals of the three-spin cluster in CuO$_6$ units (high-field part $B > 1.24$ T, $g < 2$).[7] The signals of the one-spin unit remain virtually temperature-independent except for the line width ($g_{||} = 2.371$, $g_{\perp} = 2.075$[7]), while the signals of spin triads change drastically with temperature. At $T > 100$ K, the "$g < 2$ line" starts to shift toward higher g-factors with increasing temperature, getting broadened at the same time. At $T \sim 150$ K, its position already corresponds to $g \sim 2$ and at higher temperatures to $g > 2$. One possible explanation of the EPR line shift could be the gradual change of the g-tensor of copper with temperature. This might happen due to the temperature-dependent geometry changes in octahedral units CuO$_6$.[5,6] X-ray data has shown that, on lowering the temperature from 293 to 115 K, the elongated octahedrons containing spin triads transform to the flattened ones (e.g., at $T = 203$ K) and then again to the elongated ones with another long axis.[5,6] The main values of g-tensor of Cu(II) ion can be

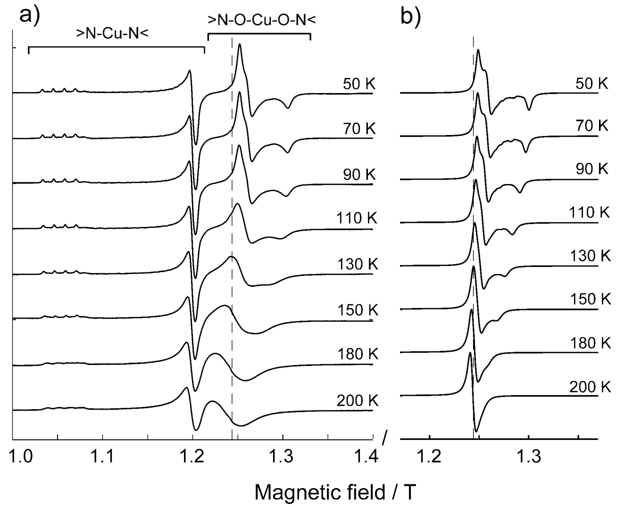

Figure 2. (a) Experimental polycrystalline powder EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at Q-band ($\nu_{\mathrm{mw}} = 34.83$ GHz); $g_{\mathrm{eff}} = 2$ corresponds to $B \sim 1.24$ T (dashed line). (b) Model calculations of EPR spectra of spin triad including the electron spin exchange process. The parameters used are: $\mathbf{g}^{\mathrm{Cu}} = [2.047, 2.097, 2.287]$, $J = -100$ cm^{-1}, $\omega_1 = 0.01$ MHz, $\nu_{\mathrm{mw}} = 34.835$ GHz, $T_2^{\mathrm{A}} = T_2^{\mathrm{B}} = 2$ ns, $T_2^{\mathrm{C}} = 0.5$ ns, $K = 5 \times 10^{11}$ s^{-1}, $\Delta J/J = 5 \times 10^{-2}$. The temperatures are indicated on the right. The curves are normalized.

estimated as $g_{||} \approx 2 + 8\delta$, $g_{\perp} \approx 2 + 2\delta$ for the case of elongated and $g_{||} \approx 2$, $g_{\perp} \approx 2 + 6\delta$ for the case of flattened octahedrons ($0 < \delta \ll 1$).[12] However, the mean g-value is the same in both cases, and thus the "center of mass" of the EPR line should not change due to the geometry changes; thus, this effect cannot explain the experimental observations.

Alternatively, the observed behavior can be well understood in terms of spin exchange process between different multiplets of the three-spin system (A, B, and C). To avoid confusion between spin exchange process and the intracluster exchange interaction J, we will always use the words "process" for the first (dynamic) case and "interaction" for the second (static) case below. Qualitatively, when the lower $S = 1/2$ spin state A ($\mathbf{g}^{\mathrm{A}} < 2$) is predominately populated at $kT \ll |J|$, the electron spin exchange process with two other states B and C ($S = 1/2$, $\mathbf{g}^{\mathrm{B}} > 2$, and $S = 3/2$, $\mathbf{g}^{\mathrm{C}} > 2$) has a negligible influence on the EPR spectrum. However, if all the states have comparable populations at $kT > |J|$, the fast spin exchange process leads to an averaging effect and appearance of a single line in the "center of mass" of the spectrum. Consequently, due to the redistribution of spin state populations with increasing temperature, the center of mass should shift toward higher g values, as is observed in experiment.

Figure 3 shows the W-band study of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ (disordered sample), which fully supports the Q-band results. Note, that the values of $\mathbf{g}^{\mathrm{Cu}}$ obtained from simulations[13] coincide at Q- and W-bands at $T = 90$ K. The effective g-values of the shifting line also agree well at Q- and W-bands for the same T within an experimental accuracy. Figure 4a shows the temperature dependence of the oriented polycrystalline powder sample spectra at the W-band. In the case of the oriented sample, the spectrum of the spin triad consists of the single line corresponding to one crystal orientation. Similarly to the EPR spectra of the disordered sample, this line becomes broadened and shifts toward higher g-values upon increasing the temperature.

We have found that the other compounds of a family Cu(hfac)$_2$L$^{\mathrm{R}}$ exhibit similar characteristics. As an example, Figure 5a shows the temperature-dependent Q-band EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Bu}}$/orthoxylene, from which the trends are like those in Figure 2a. The W-band EPR spectra of the oriented sample manifest one additional feature relevant for the spin exchange process between multiplets of a spin triad (Figure 5b). For this compound, the gradual transformation of the EPR line of a state A into the EPR line of a state C is observed. At $70 < T < 130$ K one observes the shift and simultaneous broadening of the "g < 2 line". At $T \sim 130$ K, another broadened line with $g > 2$ appears, and two lines are observed simultaneously. At $T > 130$ K, the "g > 2 line" becomes dominant, while the other one disappears. This behavior can be understood by assuming an intermediate rate of spin exchange process between the "g < 2 line" and "g > 2 lines", i.e. when the rate of exchange process is comparable to the frequency difference between the lines. Consequently, Cu(hfac)$_2$L$^{\mathrm{Pr}}$ and Cu(hfac)$_2$L$^{\mathrm{Bu}}$/orthoxylene

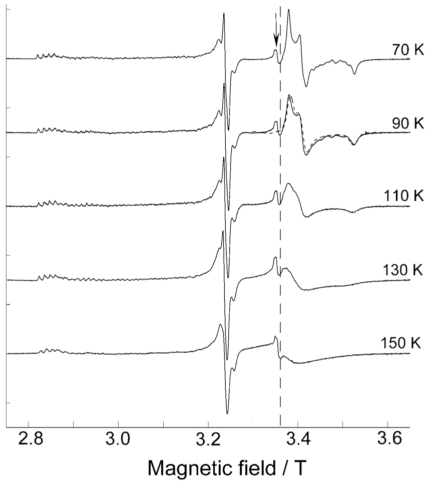

Figure 3. Experimental polycrystalline powder EPR spectra of Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at W-band ($\nu_{\mathrm{mw}} = 94.2$ GHz); $g_{\mathrm{eff}} = 2$ corresponds to $B \sim 3.36$ T (dashed line). The temperatures are indicated on the right; the arrow on the top trace indicates the undesired signals of nitroxides arising as a result of polycrystalline powder crushing. The dashed line shows the simulation of the spectrum at 90 K using the same parameters as in ref 7: 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}.

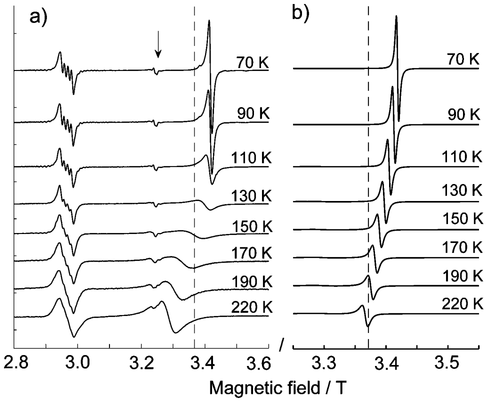

Figure 4. (a) Experimental EPR spectra of oriented polycrystalline powder Cu(hfac)$_2$L$^{\mathrm{Pr}}$ at W-band ($\nu_{\mathrm{mw}} = 94.3$ GHz); $g_{\mathrm{eff}} = 2$ corresponds to $B \sim 3.37$ T (dashed line). The arrow on top indicates the signal of the >N−Cu−N< unit remaining from the disordered powder. (b) Model calculations of EPR spectra of the spin triad including electron spin exchange process, oriented sample (one single-crystal position). The parameters used are: $g^{\mathrm{Cu}} = 2.12$, $J = -100$ cm^{-1}, $\omega_1 = 0.01$ MHz, $\nu_{\mathrm{mw}} = 94.3$ GHz, $T_2^{\mathrm{A}} = T_2^{\mathrm{B}} = 2$ ns, $T_2^{\mathrm{C}} = 0.5$ ns, $K = 5 \times 10^{11}$ s^{-1}, $\Delta J/J = 5 \times 10^{-2}$. The values of temperature are indicated on the right.

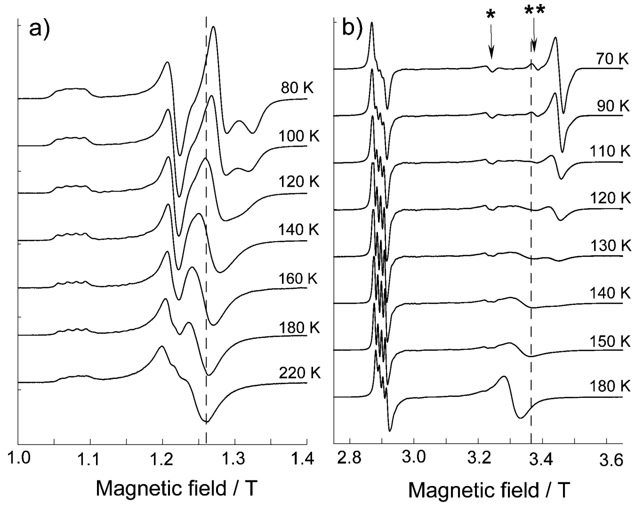

Figure 5. (a) Experimental polycrystalline powder EPR spectra of Cu(hfac)$_2$L$^{\rm Bu}$/orthoxylene at Q-band ($\nu_{\rm mw}$ = 35.33 GHz); $g_{\rm eff} = 2$ corresponds to $B \sim 1.26$ T (dashed line). (b) Experimental EPR spectra of oriented polycrystalline powder Cu(hfac)$_2$L$^{\rm Bu}$/orthoxylene at W-band ($\nu_{\rm mw}$ = 94.28 GHz); $g_{\rm eff} = 2$ corresponds to $B \sim 3.37$ T (dashed line). The arrows indicate the signals of copper in >N−Cu−N< unit (∗) and of three-spin cluster (∗∗) remaining from the disordered powder. The values of temperature are indicated on the right.

represent cases of fast and intermediate rate of spin exchange processes, respectively.

Similar effects have been observed for several other compounds Cu(hfac)$_2$L$^{\rm R}$, therefore, the manifestation of the spin exchange process appears to be a general characteristic of the strongly coupled triads. In cases where $\mathbf{g}^{\rm A}$, $\mathbf{g}^{\rm B}$, and $\mathbf{g}^{\rm C}$ are sufficiently different, these effects will be most pronounced. Otherwise, they may be barely visible although present. The indications of these averaging processes have been also found by Gatteschi et al.,[8−10] who have observed a slight temperature-dependent shift of the *g*-factor in spin triads and proposed similar explanations to the one given above; however, their experimental data did not allow for the definite conclusions and detailed investigations. Therefore, below we address the electron spin exchange process in strongly coupled triads theoretically and compare the obtained trends with experiments.

3. Mechanism of Spin Exchange Process and Theoretical Modeling. Any allowed spin transitions between different multiplets of a spin triad A, B, and C may cause a spin exchange process manifested in EPR spectra. Each given spin triad can be found in any of states A, B, or C, with the corresponding probability described by Boltzman equilibrium distribution. The effective *g*-factors of multiplets A, B, and C are different, and thus the EPR transitions within each individual multiplet have different frequencies. Assume now that each triad continuously undergoes the stochastic transitions between different multiplet states. In other words, the spin finds itself jumping at random from one environment within a triad (one particular multiplet) to another one. During this process, the Larmor frequency of electron spin changes at random between corresponding frequencies of multiplets A, B, and C. Note that this process is similar to the case where the molecule undergoes fast geometry changes, leading to the changes in magnetic parameters (e.g., *g*-factor or chemical shift): in this case, the exchange processes between different spectral lines are well-known in EPR and NMR. In our case, fast transitions between different multiplets of each given triad can be viewed as spin jumps from the current multiplet to another one. If this exchange process is fast enough compared to the detection frequency of an EPR spectrometer, the coalescence of corresponding EPR lines will occur, and one narrow line will be observed in the center of mass of the spectrum.

The most obvious mechanism that may induce the transitions between multiplets A, B, and C is the modulation of exchange interaction *J* by lattice vibrations (phonons). Using the language of relaxation mechanisms, each of these transitions is analogous to the direct one-phonon process but occurring at high frequency $\hbar\omega \sim kT$, where the density of phonons resonant with a transition is close to its maximum. This is why in this case such a direct process might be more efficient than the two-phonon Orbach−Aminov and Raman processes.[14−16] In addition, the large value of *J* in Cu(hfac)$_2$L$^{\rm R}$ might be the other factor leading to a high efficiency of this mechanism, which is the subject of the following consideration, and thus to its dominance over all other mechanisms.

It is known that the modulation of isotropic exchange interaction does not cause the transitions between triplet and singlet states in strongly coupled two-spin systems ($S_1 = 1/2$, $S_2 = 1/2$). However, for clusters of three or more spins, the transitions between different multiplets with the same value of total spin can be induced.[17] If the modulated part of the isotropic exchange interaction is described by the spin-Hamiltonian

$$\hat{H}_1^{\rm iso}(t) = J_1(t)\mathbf{S}^{\rm R1}\mathbf{S}^{\rm Cu} + J_2(t)\mathbf{S}^{\rm R2}\mathbf{S}^{\rm Cu} \qquad (4)$$

one obtains that two transitions $|5\rangle \leftrightarrow |7\rangle$ and $|6\rangle \leftrightarrow |8\rangle$ are induced (Figure 1) with the matrix elements between these states $\langle 5|\hat{H}_1^{\rm iso}(t)|7\rangle = -\langle 6|\hat{H}_1^{\rm iso}(t)|8\rangle = (\sqrt{3}/4)[J_1(t) - J_2(t)]$. The matrix elements between all other states are zeroes, leading to zero transition amplitudes. However, the matrix elements connecting the states of multiplet C with two other multiplets will be different from zero if the anisotropic part of the exchange interaction is taken into account. In this case, the transitions C $\leftrightarrow$ A,B become weakly allowed, but still they might be quite efficient for the large *J*. Assume that the modulated part of the exchange interaction has the form

$$\hat{H}_1^{\rm an}(t) = J_1^{||}(t)S_z^{\rm R1}S_z^{\rm Cu} + J_1^{\perp}(t)[S_x^{\rm R1}S_x^{\rm Cu} + S_y^{\rm R1}S_y^{\rm Cu}] + J_2^{||}(t)S_z^{\rm R2}S_z^{\rm Cu} + J_2^{\perp}(t)[S_x^{\rm R2}S_x^{\rm Cu} + S_y^{\rm R2}S_y^{\rm Cu}] \qquad (5)$$

corresponding to the axially symmetric $J_{1,2} = [J_{1,2}^{\perp}, J_{1,2}^{\perp}, J_{1,2}^{||}]$. Then one obtains the following nonzero matrix elements

$$\langle 2|\hat{H}_1^{\rm an}|5\rangle = -\langle 3|\hat{H}_1^{\rm an}|6\rangle = [(J_1^{||}(t) - J_1^{\perp}(t)) - (J_2^{||}(t) - J_2^{\perp}(t))]/(2\sqrt{6})$$
$$\langle 2|\hat{H}_1^{\rm an}|7\rangle = \langle 3|\hat{H}_1^{\rm an}|8\rangle = [(J_1^{||}(t) - J_1^{\perp}(t)) + (J_2^{||}(t) - J_2^{\perp}(t))]/(6\sqrt{2})$$
$$\langle 5|\hat{H}_1^{\rm an}|7\rangle = -\langle 6|\hat{H}_1^{\rm an}|8\rangle = [(J_1^{||}(t) + 2J_1^{\perp}(t)) - (J_2^{||}(t) + 2J_2^{\perp}(t))]/(4\sqrt{3}) \qquad (6)$$

From these expressions, one concludes that the matrix elements of transitions C $\leftrightarrow$ A,B are smaller than the ones of transitions A $\leftrightarrow$ B by an approximate factor of $\sim (J^{||} - J^{\perp})/(J^{||} + 2J^{\perp}) \equiv \Delta J/J$.

Another reason should be mentioned why the transitions between multiplets C $\leftrightarrow$ A may become weakly allowed even for isotropic exchange interaction. The eigenstates $|2\rangle$, $|3\rangle$, $|7\rangle$, and $|8\rangle$ are magnetic field dependent. In the presence of a magnetic field, these states change compared to eqs 2 by factors of the order B^2/J^2. For the systems studied in this work, $J \sim 100$ cm^{-1} ~ 100 T and $B \sim 0.3-3$ T, and thus we expect that $\Delta J/J \gg B^2/J^2$. Thus, the anisotropy of the exchange interaction is expected to be more important for making the transitions between quartet and doublet states allowed.

We now estimate the rate of the spin exchange process due to the modulation of the isotropic exchange interaction. We will follow the approach of ref 16 to make estimation by an order of magnitude. Suppose that the lattice vibration leads to an oscillation of distance between copper and one of the radicals (e.g., R1) described as $r = r_0(1 + \epsilon \cos \omega t)$, where $\epsilon \ll 1$. Assuming the exponential decay of the exchange interaction on radical−copper distance, one obtains

$$J(r) = J_0\, e^{-r/\lambda} = J_0\, e^{-r_0(1+\epsilon \cos \omega t)/\lambda} \approx J(r_0)\left(1 - \frac{\epsilon r_0}{\lambda}\cos \omega t\right) \equiv J + J_m(t) \quad (7)$$

where λ is the characteristic distance of the exchange interaction decay and is usually on the order of Angstroms, $\epsilon r_0 \ll \lambda$ and $J_m(t) \equiv -J(\epsilon r_0/\lambda) \cos \omega t$. Then, the time-average square of the modulated part of $J(r)$ can be found as

$$\langle J_m{}^2(t)\rangle = \frac{r_0{}^2J^2}{2\lambda^2}\epsilon^2 = \frac{r_0{}^2J^2}{2\lambda^2}\frac{\rho_{\text{ph}}\, \mathrm{d}\omega}{2\rho\upsilon^2} = \frac{3}{8}\left(\frac{r_0J}{\lambda}\right)^2 \frac{\hbar\omega^3}{\pi^2\rho\upsilon^5}\frac{\mathrm{d}\omega}{e^{\hbar\omega/kT} - 1} \quad (8)$$

where υ is the speed of sound, ρ is the density of a crystal, ρ_{ph} dω is the phonon density in the frequency range dω, and the relations

$$2\rho\upsilon^2\epsilon^2 = \rho_{\text{ph}}\, \mathrm{d}\omega = \frac{3\hbar\omega^3}{2\pi^2\upsilon^3}\frac{\mathrm{d}\omega}{e^{\hbar\omega/kT} - 1} \quad (9)$$

are used.[16] The probability of the induced transition can be calculated as

$$w_\uparrow = \frac{2\pi}{\hbar^2}\,|\langle i| - 2J_m(t)S^{\text{Cu}}S^{\text{R1}}|j\rangle|^2 f(\omega) = \frac{2\pi}{\hbar^2}\, m_{ij}{}^2\langle J_m{}^2(t)\rangle f(\omega) \quad (10)$$

where m_{ij} is the dimensionless matrix element of spin operator $-2S^{\text{Cu}}S^{\text{R1}}$, and $f(\omega)$ is the line shape function fulfilling $\int f(\omega)\, \mathrm{d}\omega = 1$. Assuming that the phonon density does not change within the line (i.e., $f(\omega) = \delta(\omega)$), we finally arrive at

$$w_\uparrow = \frac{3}{4}\, m_{ij}{}^2\left(\frac{r_0J}{\lambda}\right)^2 \frac{\omega^3}{\pi\hbar\rho\upsilon^5}\frac{1}{e^{\hbar\omega/kT} - 1} \quad (11)$$

The probability of spontaneous transition is known to be $w_\downarrow = w_\uparrow e^{\hbar\omega/kT}$, then we obtain for the characteristic time of exchange process

$$\frac{1}{T_{\text{ex}}} = w_\uparrow + w_\downarrow = \frac{3}{4}\, m_{ij}{}^2\left(\frac{r_0J}{\lambda}\right)^2 \frac{\omega^3}{\pi\hbar\rho\upsilon^5}\, \text{cth}\left(\frac{\hbar\omega}{2kT}\right) \equiv K\cdot\text{cth}\left(\frac{\hbar\omega}{2kT}\right) \quad (12)$$

Assuming $r_0 \sim 2$ Å,[6] $\lambda \sim 1$ Å (typical order of the bond length), $\rho \sim 2$ g/cm^3, $\upsilon = 3 \times 10^5$ cm/s, $J \sim 100$ cm^{-1}, $\hbar\omega \sim kT \sim J$, and $m_{ij} \sim 1$ for A $\leftrightarrow$ B transitions, we obtain $K \sim 5 \times 10^{11}$ s^{-1} and thus $1/T_{\text{ex}}^{\text{A}\leftrightarrow\text{B}} \sim 10^{12}$ s^{-1} at $kT \sim \hbar\omega$. Taking into account the interaction with the second radical R2 will even double this estimate. The value obtained for $1/T_{\text{ex}}^{\text{A}\leftrightarrow\text{B}}$ agrees reasonable well with the experiment, because the frequency difference between lines of multiplets A and B is $\Delta\omega_{A,B} < 10^{11}$ s^{-1} even at W-band, and thus the spin exchange process will be fast enough to average the individual lines into a single one in the center of mass. It is less straightforward to make a similar estimate for the transitions C $\leftrightarrow$ A,B induced by the modulation of anisotropic exchange interaction. The value of J anisotropy is not known and its estimation using, e.g., the anisotropy of g-tensor is problematic.[18] If $\Delta J/J \sim 10^{-2} - 10^{-1}$, we obtain $m_{ij}^2 \sim (\Delta J/J)^2 \sim 10^{-4}-10^{-2}$ and $1/T_{\text{ex}}^{\text{C}\leftrightarrow\text{A,B}} \sim 10^8-10^{10}$ s^{-1}. This value still agrees with experiment quite reasonably because: (i) the frequency difference between lines C $\leftrightarrow$ A,B at W-band is $\Delta\omega_{\text{C}\leftrightarrow\text{A,B}} < 5 \times 10^{10}$ s^{-1}, and (ii) the multiplet C is the upper one and thus significantly contributes only at higher temperatures where the factor cth$(\hbar\omega/2kT) \gg 1$ and spin exchange process become even faster. In addition, we can hypothesize that the modulation of parallel and perpendicular components of J is not equivalent because one of the axes of octahedrons is more flexible, resulting in shortening or lengthening with temperature. This would mean that the difference $|J^{\|}(t) - J^{\perp}(t)|$ in expression 6 might be larger than the difference between the corresponding static components, leading to a higher rate of spin exchange process.

Thus, we have found that the modulation of exchange interaction induces rapid transitions between multiplets of a strongly coupled spin triad. Of course, for the system with smaller J, the case of intermediate rate of spin exchange process can be realized. As was discussed above, the experimental data supposes that indeed the fast exchange process takes place for Cu(hfac)$_2$L$^{\text{Pr}}$ and the intermediate exchange process takes place for Cu(hfac)$_2$L$^{\text{Bu}}$ with orthoxylene. On the basis of the frequency separation of the exchanged lines in Cu(hfac)$_2$L$^{\text{Bu}}$ with orthoxylene at 130 K, we can roughly estimate $1/T_{\text{ex}}^{\text{C}\leftrightarrow\text{A,B}} \sim 10^{10}$ s^{-1} for this system, which is in good agreement with the theoretical estimations above.

Finally, to confirm the expected manifestations of spin exchange processes in EPR spectra of strongly coupled spin triads, we present the results of numerical simulations. The spin exchange processes in EPR are usually modeled using the Bloch equations modified to include these processes.[19,20] Basically, it is assumed that two EPR transitions involved in the spin exchange process arise from two different species, which transform one into another in reversible monomolecular reaction. Then, writing the differential Bloch equations one simply should include the terms accounting for these transformations in the same way as it is done in chemical kinetics (it is assumed that the magnetization is proportional to the concentration of each species). The rate of transformation corresponds to the rate of exchange process. In our case, we will consider the spin exchange process between different multiplets A, B, and C of a spin triad in a similar way.

Let $M_{x,y,z}^{\text{A,B,C}}$ be the corresponding components of the magnetization vectors for the effective spins corresponding to multiplets A, B, and C. Assume that the saturation is negligible, and thus $M_z^{\text{A,B,C}} \approx M_0^{\text{A,B,C}}$. Then the modified Bloch equations for the complex variables $G^{\text{A,B,C}} = M_x^{\text{A,B,C}} - iM_y^{\text{A,B,C}}$ can be written as[19]

$$\frac{\mathrm{d}G^{\mathrm{A}}}{\mathrm{d}t} = -\frac{G^{\mathrm{A}}}{T_2^{\mathrm{A}}} + i\Delta\omega^{\mathrm{A}}G^{\mathrm{A}} - i\omega_1 M_0^{\mathrm{A}} - \frac{G^{\mathrm{A}}}{\tau_{\mathrm{AB}}} - \frac{G^{\mathrm{A}}}{\tau_{\mathrm{AC}}} + \frac{G^{\mathrm{B}}}{\tau_{\mathrm{BA}}} + \frac{G^{\mathrm{C}}}{\tau_{\mathrm{CA}}}$$

$$\frac{\mathrm{d}G^{\mathrm{B}}}{\mathrm{d}t} = -\frac{G^{\mathrm{B}}}{T_2^{\mathrm{B}}} + i\Delta\omega^{\mathrm{B}}G^{\mathrm{B}} - i\omega_1 M_0^{\mathrm{B}} - \frac{G^{\mathrm{B}}}{\tau_{\mathrm{BA}}} - \frac{G^{\mathrm{B}}}{\tau_{\mathrm{BC}}} + \frac{G^{\mathrm{A}}}{\tau_{\mathrm{AB}}} + \frac{G^{\mathrm{C}}}{\tau_{\mathrm{CB}}} \quad (13)$$

$$\frac{\mathrm{d}G^{\mathrm{C}}}{\mathrm{d}t} = -\frac{G^{\mathrm{C}}}{T_2^{\mathrm{C}}} + i\Delta\omega^{\mathrm{C}}G^{\mathrm{C}} - i\omega_1 M_0^{\mathrm{C}} - \frac{G^{\mathrm{C}}}{\tau_{\mathrm{CA}}} - \frac{G^{\mathrm{C}}}{\tau_{\mathrm{CB}}} + \frac{G^{\mathrm{A}}}{\tau_{\mathrm{AC}}} + \frac{G^{\mathrm{B}}}{\tau_{\mathrm{BC}}}$$

where $T_2^{\mathrm{A,B,C}}$ are the corresponding transverse relaxation times in the absence of the spin exchange process, $\Delta\omega^{\mathrm{A,B,C}}$ are the corresponding resonance offsets, ω_1 is the microwave field amplitude, $1/\tau_{MN} = w_{\uparrow,\downarrow}$ are the corresponding transition rates from multiplet M to a multiplet N, and the relation $1/\tau_{MN} = (1/\tau_{NM}) \exp((E_M - E_N)/kT)$ takes place. Because we are looking for a stationary solution of this system, $\mathrm{d}G^{\mathrm{A,B,C}}/\mathrm{d}t = 0$, and then the absorption line shape is obtained as usual by taking $M_y = -\mathrm{Im}(G^{\mathrm{A}} + G^{\mathrm{B}} + G^{\mathrm{C}})$.

In addition, because we model three multiplets by three interacting species with corresponding effective spins, the different amplitudes of EPR lines corresponding to A, B, and C must be introduced into $M_0^{\mathrm{A,B,C}}$. One contribution to the line amplitude comes from the Boltzman population differences, and another one is due to the different number of transitions and different transition amplitudes within each multiplet. By calculating the corresponding matrix elements and introducing the Boltzman factors one obtains

$$\begin{aligned} M_0^{\mathrm{A}} &= M_0 \\ M_0^{\mathrm{B}} &= e^{2J/kT} M_0 \\ M_0^{\mathrm{C}} &= e^{3J/kT}\, 10 M_0 \end{aligned} \quad (14)$$

The analytical solution of the system (eq 13) is too cumbersome to prove useful, therefore, we present only the results of numerical calculation. The anisotropy of the g-tensor of copper was taken into account by convolution of spectra corresponding to different orientations.[13] As was discussed above, the distances between copper and nitroxides in $\mathrm{Cu(hfac)_2L^R}$ decrease on lowering the temperature,[5,6] and thus the exchange interaction itself is expected to be temperature-dependent and increase at low temperature, which complicates the situation and is a separate topic of investigation. Therefore, here we focus on reproducing the general trends rather than on fitting actual temperature-dependent EPR spectra, and demonstrate the effect of the fast spin exchange process for the case of constant exchange interaction.

Figure 2b shows the calculated EPR spectra of the disordered sample using the g-tensor of $\mathrm{Cu(hfac)_2L^{Pr}}$. The calculations essentially reproduce the trends in experimentally obtained spectra of spin triads in Figure 2a. The powder-pattern EPR line transforms into a single line with an increase of the temperature, which moves toward the higher g-factors. The shift of the simulated line is slightly smaller than the experimental one because the exchange interaction ($J = -100$ cm^{-1}) is considered to be constant. The use of a temperature-dependent exchange interaction (e.g., $J = -150-50$ cm^{-1} at $T = 50-200$ K) would lead to more significant shift due to a stronger change of a factor J/kT. Figure 4b shows the result of similar calculations for the oriented sample. Again, the broadening and the shift of the EPR line are clearly observed. The values $T_2^{\mathrm{A,B,C}}$ used in simulations are quite realistic for the magnetically concentrated samples. $T_2^{\mathrm{C}} < T_2^{\mathrm{A,B}}$ is taken to account for the dipole−dipole interaction induced relaxation within a quartet state, which is expected to be an additional relaxation pathway. Thus, we conclude that the experimental trends are well modeled by the calculations and the observed phenomena are well explained in terms of electron spin exchange processes between different multiplets of a spin triad.

Conclusions

In this work we have reported the experimental observation of electron spin exchange processes in strongly coupled spin triads. These processes manifest themselves in the significant shift of the EPR line position with temperature ($\Delta g \sim 0.1$ at $T = 70-220$ K) found for the compounds of family $\mathrm{Cu(hfac)_2L^R}$. This occurs due to the redistribution of populations between different multiplets of the exchange-coupled system with temperature. The modulation of the exchange interaction between copper and nitroxide was proposed as a mechanism inducing the spin exchange process, and the theoretical estimations agree with the rates expected from experimental data analysis.

The rate of these exchange processes increases rapidly with the increase of exchange coupling, therefore they become very efficient in strongly coupled triads and cannot be neglected. We have found that the basic spectral characteristics such as the line position and shape are strongly influenced by spin exchange processes. It was supposed earlier that the spin exchange processes are efficient in spin triads and larger clusters and might be responsible for the observation of only one EPR line and its temperature shift[8−10] Our high-field EPR results on $\mathrm{Cu(hfac)_2L^R}$ provide clear evidence for the exchange processes in strongly coupled spin triads, which are also expected to be ubiquitous in other various strongly coupled heterospin systems.

As an outlook, we note that in case of fast exchange process the position of the EPR line corresponds to the effective g-factor of spin triad, which, in turn, is a function of temperature and intracluster exchange coupling J. Therefore, the temperature dependence of the effective g-factor allows one to determine the value of J and its temperature dependence, which will be the topic of our next publication.

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