

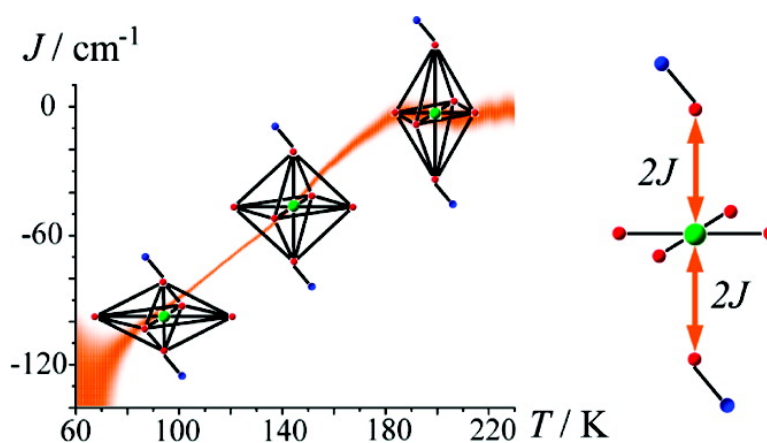
Communication

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J. Am. Chem. Soc., **2008**, 130 (8), 2444-2445 • DOI: 10.1021/ja710773u

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High-Field EPR Reveals the Strongly Temperature-Dependent Exchange Interaction in “Breathing” Crystals $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$

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The research on molecule-based magnetism is a dynamically evolving field of modern chemistry focused on the design of novel materials with relevant magnetic properties and development of molecular spin devices.¹ The key role of exchange interactions in molecular magnetic compounds is well-established and is being actively investigated.¹ Electron paramagnetic resonance (EPR) spectroscopy is one of the most informative techniques for studying the interactions between paramagnetic species, which is used extensively in the field of molecule-based magnets.²

Recently, we reported EPR studies of novel compounds based on copper(II) hexafluoroacetylacetonates and pyrazole-substituted nitronyl nitroxides (Figure 1).³ These $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ compounds undergo reversible structural rearrangements with temperature accompanied by magnetic phenomena, similar to a spin-crossover, manifested by the dependence of the effective magnetic moment $\mu_{\text{eff}}(T)$.⁴ The reversible change of the elementary cell volume during rearrangements reaches ca. 15% for some $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ crystals; therefore, we call them “breathing”. This complete reversibility of structural and magnetic properties in breathing crystals makes them highly perspective as the bases for various molecular spin and magneto-mechanical devices. The EPR spectra of these compounds were found to be very specific and rich, providing direct information on exchange interactions. All magnetic anomalies are attributed to the structural changes in strongly exchange-coupled spin triads nitroxide–copper(II)–nitroxide in the polymer chains of $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$. In previous works, we studied the basic trends and magnetic effects in these systems and their spectroscopic manifestations.³

In this work, we focus on very unusual and highly important characteristics observed in $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ breathing crystals by means of W-band EPR (95 GHz). In the overwhelming majority of the exchange-coupled clusters investigated in the field of molecular magnetism, the exchange interaction is constant on temperature. However, in $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ breathing crystals, it is strongly temperature-dependent. It has been suggested that this temperature dependence is a consequence of the structural rearrangements in spin triads.^{3c} However, unambiguous experimental evidence for this and the explicit dependence $J(T)$ could not be obtained. In this Communication, we provide the missing experimental evidence by using the high-field EPR on single crystals of $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$.

The complex $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$, where C_8H_{18} is octane, is suitable to exemplify the temperature dependence of the exchange interaction in the whole $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ family. The polymer chains of $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ contain the alternating one- and three-spin units. The intercluster exchange coupling (within a spin triad) is smaller than the intracluster exchange (between one- and three-

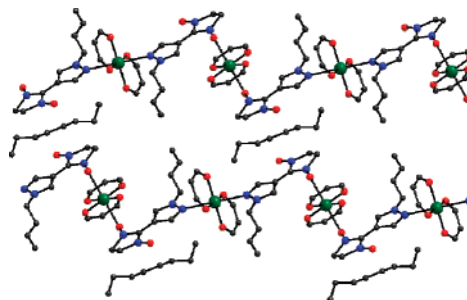


Figure 1. Polymer chain structure of the complex $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$. Cu: green ball; O: red ball; C: black ball; N: blue ball. The H atoms and CH_3 and CF_3 groups are omitted for clarity.

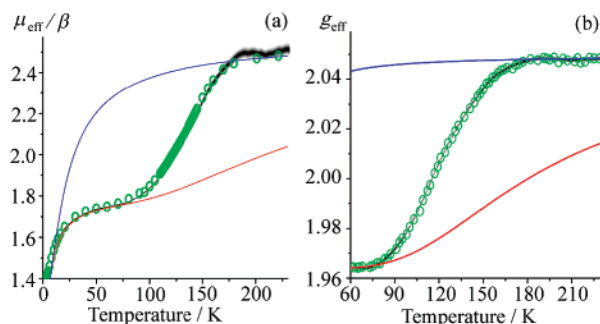


Figure 2. Experimental (green) $\mu_{\text{eff}}(T)$ (a) and $g_{\text{eff}}(T)$ (b) dependence of a single crystal of $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ and related calculations (black) using $J(T)$ dependence. Solid lines show the result obtained for the constant $J = -10 \text{ cm}^{-1}$ (blue) and -120 cm^{-1} (red).

spin units) by at least an order of magnitude. Spin triad is symmetric with respect to the copper atom; it has a closely linear geometry and thus can be described by the following spin-Hamiltonian of exchange interaction: $\hat{H}_{\text{ex}} = -2JS^{\text{Cu}}(S^{\text{R}1} + S^{\text{R}2})$, where superscripts refer to the spins of copper and two nitroxides. The temperature dependence of the effective magnetic moment $\mu_{\text{eff}}(T)$ shows the strong decrease between 200 and 50 K corresponding to the effective coupling of two spins of three within a spin triad (Figure 2a).^{3c}

The $\mu_{\text{eff}}(T)$ dependence cannot be satisfactorily described in a model of constant exchange interaction using the above-mentioned spin-Hamiltonian, which is clearly demonstrated in Figure 2a by attempts at achieving agreement separately in the high- and low-temperature regions of the dependence. However, this discrepancy alone cannot prove the temperature dependence of the exchange interaction in the spin triad since the bulk property of the compound containing different paramagnetic centers is measured leaving a space for alternative interpretations. The high-field EPR is selective with respect to spin triads and one-spin units, and spectral resolution at W-band is sufficient to resolve these signals and to draw definite

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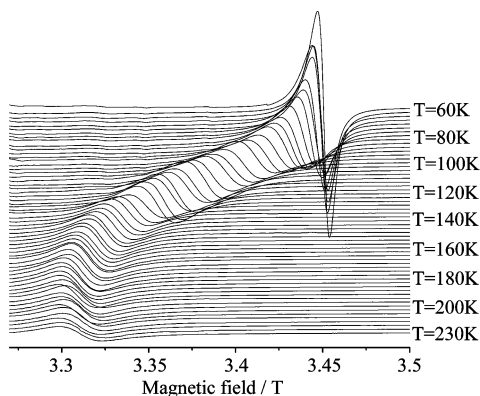


Figure 3. The W-band EPR spectra of single-crystal $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ versus temperature; $\nu_{\text{mw}} = 94.9$ GHz.

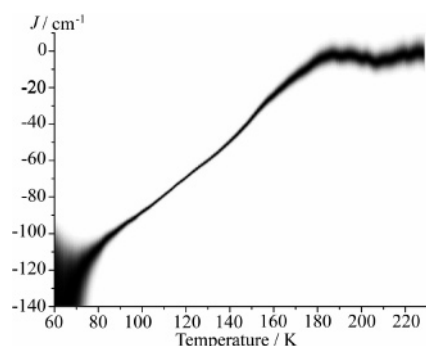


Figure 4. Temperature dependence of the exchange interaction $J(T)$ calculated using experimental function $g_{\text{eff}}(T)$ and eq 1.

conclusions. We have shown previously^{3c} that the effective g -factor of the spin triad can be described by the equation

$$g_{\text{eff}}(T) = \frac{(4\mathbf{g}^{\text{R}} - \mathbf{g}^{\text{Cu}}) + 3\mathbf{g}^{\text{Cu}} \times e^{2J/kT} + 10(2\mathbf{g}^{\text{R}} + \mathbf{g}^{\text{Cu}}) \times e^{3J/kT}}{3(1 + e^{2J/kT} + 10e^{3J/kT})} \quad (1)$$

where \mathbf{g}^{R} and \mathbf{g}^{Cu} are individual g -tensors of nitroxides and copper, respectively, and kT is the thermal energy. This equation links the dependence $g_{\text{eff}}(T)$, which can be obtained experimentally using EPR, with the dependence $J(T)$. Figure 2b shows the experimental dependence $g_{\text{eff}}(T)$ of a single-crystal $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ that was obtained from the temperature-dependent W-band spectra shown in Figure 3 (spectroscopic details in Supporting Information).

Similar to the temperature dependence of $\mu_{\text{eff}}(T)$ in Figure 2a, it is obvious that $g_{\text{eff}}(T)$ cannot be simulated in a model of constant exchange interaction: the experimental slope is much steeper than the theoretical ones attempting to achieve agreement at the high- or low-temperature regions. Numerical fitting of the dependence $g_{\text{eff}}(T)$ using eq 1 allows one to obtain the distribution of functions $J(T)$ shown in Figure 4 (calculation details in Supporting Information).

The width of the distribution characterizes the ambiguity of $J(T)$ determination. The broad distributions at high- and low-temperature regions correspond to the plateaus of the dependence $g_{\text{eff}}(T)$, where the EPR spectrum does not depend on temperature anymore. However, in the middle region of temperatures, the precision of $J(T)$ measurement is high, and overall, it is remarkable that the exchange interaction is changed by about an order of magnitude during the reversible structural rearrangements. The reason for this “switching” of exchange interaction is the significant change of

inter-spin Cu–O distances with temperature (X-ray data in Supporting Information).

Note that the function $J(T)$ shown in Figure 4 allows one also to fit perfectly the dependence of the effective magnetic moment $\mu_{\text{eff}}(T)$ shown in Figure 2a (intercluster exchange $z'J' = -10$ cm^{-1} was taken into account;⁵ see Supporting Information). This is an additional and independent confirmation of the validity of the $J(T)$ function obtained using a high-field EPR.

Thus, we have determined the strong temperature dependence of the exchange interaction between copper(II) ion and nitroxide ligands within a three-spin system in a compound of composition $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$. Similar effects have also been found in other compounds of a family of $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ breathing crystals. The strong dependence $J(T)$ makes them interesting and promising compounds in the research toward creation of molecular-magnetic switches and related spin devices, and we have demonstrated that the high-field EPR is a very convenient tool to study this dependence. We believe that these results will be demanded in future basic and applied studies.

Acknowledgment. This work was supported by INTAS (YSF 06-1000014-5915), RFBR (Nos. 05-03-32264, 06-03-32157, 06-03-04000), Lavrentiev grant of SB RAS (No. 79), grants of RF president (MK-6673.2006.3), FASI state contract No. 02.513.11.3044, and RAS.

Supporting Information Available: Spectroscopic and calculation details, crystallographic data, and a sketch of reversible structural rearrangements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA710773U