

SUPPORTING INFORMATION

Intercluster exchange pathways in polymer-chain molecular magnets $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ unveiled by EPR

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(58) M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, *Gaussian 03 (Revision B.01)*, Gaussian, Inc., Pittsburg, 2003.

Absence of saturation effects in presented EPR experiments

The main conclusions of this work were made using the analysis of second integrals over EPR lines of spin triads and magnetically-isolated Cu(II) ions in polymer chains of molecular magnets $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$. In case of single crystals each spectrum consists of two well-separated signals corresponding to the spin triad and one-spin unit (Figures S1 and S2). We measured EPR spectra at variable temperature and calculated second integrals for spin triads (I_{triad}) and one-spin units (I_{one}) for each spectrum. Then the temperature dependence of ratio $\gamma = I_{\text{triad}}/I_{\text{one}} \propto \chi_{\text{triad}}/\chi_{\text{one}}$ was analyzed. We observed that the signal (and its second integral) of spin triads strongly decreases at low temperatures for two compounds ($\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}} \cdot 0.5\text{C}_7\text{H}_{16}$ and $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}} \cdot 0.5\text{C}_8\text{H}_{18}$) that also exhibit similar decrease of magnetic susceptibility.

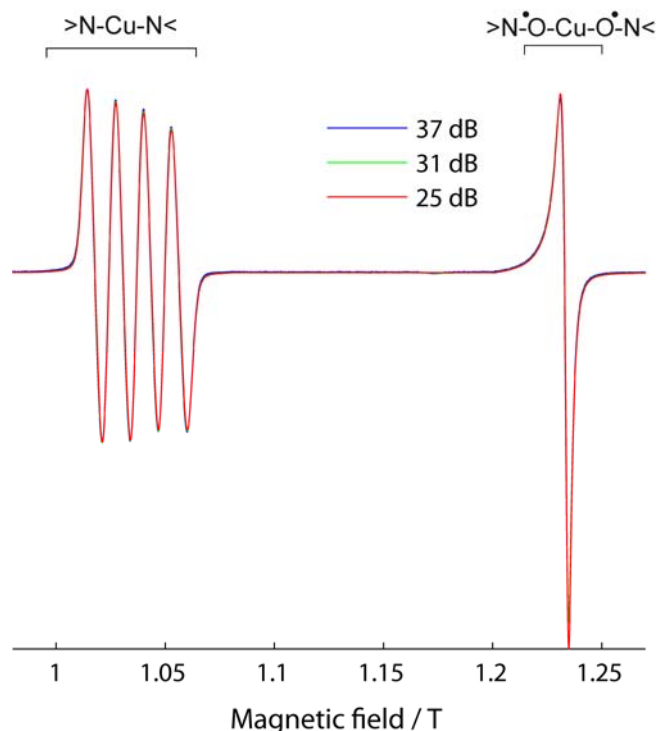


Figure S1. EPR spectra of $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_7\text{H}_{16}$ at different microwave power attenuation (indicated). $T=10$ K, $\nu_{\text{mw}}\approx 33.67$ GHz, single crystal, arbitrary orientation. The signals of one-spin unit $>\text{N-Cu-N}<$ and spin triad $>\text{N}\cdot\text{O-Cu-O}\cdot\text{N}<$ are indicated on top. All spectra are normalized.

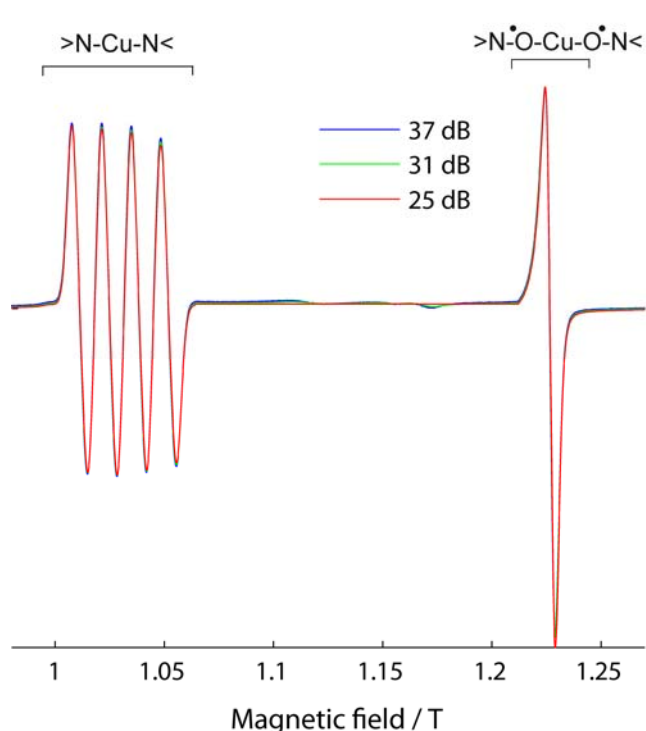


Figure S2. EPR spectra of $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ at different microwave power attenuation (indicated). $T=10$ K, $\nu_{\text{mw}}\approx 33.59$ GHz, single crystal, arbitrary orientation. The signals of one-spin unit $>\text{N-Cu-N}<$ and spin triad $>\text{N}\cdot\text{O-Cu-O}\cdot\text{N}<$ are indicated on top. All spectra are normalized.

However, it is critical to ensure that no saturation of spectral lines occurs in the low-temperature region. When the saturation is present, second integral may become not proportional to the magnetic susceptibility. In addition, if saturation occurs to a different extent in spin triads and one-spin units, experimentally measured ratio γ may also be wrong. Therefore we verified the absence of saturation conditions in compounds $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_7\text{H}_{16}$ and $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ at low temperatures.

Figures S1 and S2 show the results obtained at $T=10$ K. The microwave power attenuation was varied from 37 dB to 25 dB (around the value 30 dB used in experiments shown in Figure 1). One observes very good coincidence in signal shapes and unchanged ratios of signal amplitudes corresponding to spin triads and one-spin units. Figure S3 shows the dependences of signal intensity of spin triad on the amplitude of microwave field B_1 (calculated from power attenuation values). In the absence of saturation, signal intensity is proportional to the B_1 value. The experimental observations for both

compounds agree with this trend when the microwave power attenuation varies between 37 and 25 dB (indicated in Figure S3). This unambiguously proves the absence of saturation effects in our experiments and validity of $\gamma(T)$ functions presented in Figure 1.

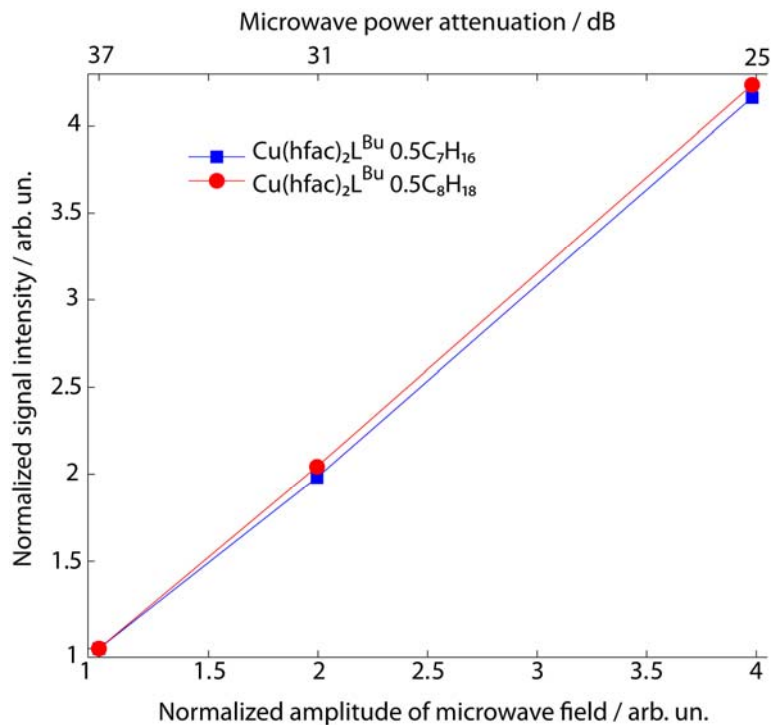


Figure S3. Signal intensity as a function of microwave field amplitude for $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_7\text{H}_{16}$ and $\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}\cdot 0.5\text{C}_8\text{H}_{18}$ at $T=10$ K. Actual scale of microwave power attenuation is shown on top.