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Intercluster Exchange Pathways in Polymer-Chain Molecular Magnets Cu(hfac)₂L^R Unveiled by Electron Paramagnetic Resonance

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Abstract: Polymer-chain complexes $Cu(hfac)_2L^R$ represent an interesting type of molecular magnets exhibiting thermally induced and light-induced magnetic switching, in many respects similar to a spin crossover. In the majority of these compounds the polymer chain consists of alternating one- and three-spin units composed of copper(II) ions and nitronyl nitroxides. The principal one-dimensional structure of the complexes has previously been assumed to play a key role in the observed magnetic anomalies. Using Q-band electron paramagnetic resonance (EPR) spectroscopy, we have reliably demonstrated that these complexes are indeed one-dimensional in the sense of the topology of their exchange channels; however, the magnetic chains spread across the structural polymer chains and consist solely of spin triads of nitroxide–copper(II)–nitroxide. Using four selected examples of complexes $Cu(hfac)_2L^R$, we have found the exchange coupling values between spin triads of neighboring polymer chains to range from <1 to ca. 10 cm⁻¹. This conclusion could only be reached due to the selective probing of one- and three-spin units by EPR and correlates perfectly with both previous magnetic susceptibility data and quantum chemical calculations performed in this work. These findings give new insights into the cooperativity effects and mechanisms of magnetic anomalies in the Cu(hfac)₂L^R family of molecular magnets.

Introduction

In recent decades, the design and synthesis of thermo- and photoswitchable molecular magnetic compounds have attracted significant attention due to both fundamental interest and potential applications in spintronics.^{1–7} A lot of studies have been devoted to the thermally induced and light-induced spin crossover and valence tautomerism observed for complexes of transition metal ions.^{1–34} Changes in the multiplicity of the

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ground state of a 3d-ion effected by temperature or light govern the changes in magnetization; therefore, such bi- or multistable systems can be considered as elementary magnetic switches.

A new family of polymer-chain complexes, $Cu(hfac)_2 L^R$ (later called "breathing crystals"), was found and studied extensively over the past several years.³⁵⁻⁴⁵ Polymer chains of breathing

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crystals are formed by bis(hexafluoroacetylacetonato)copper(II) and pyrazolyl-substituted nitronyl nitroxides (Chart 1).

In the majority of these compounds, the polymer chains have a "head-to-head" coordination motif and consist of alternating one- and three-spin units composed of copper(II) ions and nitronyl nitroxides. The compounds with butyl-substituted nitroxide (R = Bu) allow various solvent molecules (Solv) to be incorporated in the interchain space, forming the compounds Cu(hfac)₂L^{Bu}•0.5Solv.^{38,39} A key characteristic of breathing crystals is their ability to undergo reversible, thermally induced structural rearrangements, accompanied by changes in magnetic susceptibility, which are in many respects similar to a classical spin crossover. During these reversible rearrangements, the elongated (Jahn–Teller) axis of the octahedron CuO₆ is rotated, and the exchange interaction (J) between copper(II) and the

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nitroxide spins in a spin triad may change by up to 1-2 orders of magnitude.⁴³ This results in a change of the magnetic moment (i.e., spin transition), since at high temperatures the spins are weakly coupled $(|J| \ll kT)$, referred to as the weakly coupled spin (WS) state, whereas at low temperatures strong antiferromagnetic exchange effectively couples two of the three spins $(|J| \gg kT)$, and thus the spin triad converts to the strongly coupled spin (SS) state with a total spin S = 1/2. We have found that electron paramagnetic resonance (EPR) of breathing crystals allows one to monitor the spin transitions between WS and SS states and to measure the exchange interactions.^{40–45} We have also found recently that this magnetic switching can be induced by light.⁴⁶ In both cases of thermal and optical initiation, the switching of the magnetic properties is attributed to a significant change of the exchange interaction within the spin triads.⁴³ Note that similar magnetic anomalies have also been observed for other complexes of copper(II) with nitroxides.⁴⁷⁻⁵¹

In most cases, spin transitions in breathing crystals occur in a temperature range of 50-300 K and manifest themselves in changes of the magnetic moment and EPR spectra. Typical exchange interaction values in spin triads that govern these changes are about 100 cm⁻¹. However, in many compounds, an additional decrease of the magnetic moment at T < 20 K was experimentally observed.⁴² It was generally assigned to intercluster exchange interactions and assumed to play an insignificant role because its value is by 1-2 orders of magnitude smaller compared to intracluster exchange in spin triads. Magnetic susceptibility data could not give any insight into the nature of intercluster exchange in breathing crystals, as it reports the bulk magnetization contributed by both oneand three-spin units. However, understanding these relatively weak intercluster exchange interactions might give insights into the key properties of magnetic switching in breathing crystals. In particular, the character of spin transition (abrupt or gradual) and the mechanism that induces it should be correlated to the cooperativity introduced by intercluster exchange.

In this work we investigated the intercluster exchange pathways in breathing crystals using Q-band EPR (34 GHz) and quantum chemical calculations. Luckily, in these magnetically concentrated systems, the EPR signals of one- and three-

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spin units are well resolved. It is the selectivity of EPR to these two types of paramagnetic centers that allowed us to draw definite conclusions on the coupling scheme in the crystals and obtain several new insights. We have reliably shown that the magnetic "chains" do not coincide with the structural polymer chains but are instead formed by interconnected spin triads of neighboring polymer chains.

Experimental and Computational Details

Four compounds of the breathing crystals family, $Cu(hfac)_2 L^{Pr}$, $Cu(hfac)_2 L^{Bu} \cdot 0.5 C_7 H_{16} (C_7 H_{16} = heptane)$, $Cu(hfac)_2 L^{Bu} \cdot 0.5 C_8 H_{18}$ ($C_8 H_{18} = octane$), and $Cu(hfac)_2 L^{Bu} \cdot 0.5 C_8 H_{10} (C_8 H_{10} = o-xylene)$, have been synthesized according to previously developed procedures.^{35–37,39,42} Their structure and magnetic susceptibility behavior were also investigated previously.^{39,42}

EPR measurements were carried out in continuous-wave (CW) mode using a commercial Bruker Elexsys E580 X/Q-band EPR spectrometer equipped with an Oxford Instruments temperature control system (T = 4-300 K). In all cases, single crystals of the studied compounds were used. For each compound, the orientation of the crystal was adjusted experimentally, with the goal of achieving maximum spectral separation of the EPR lines of one-and three-spin clusters.

Our quantum chemistry study was focused on evaluation of exchange interactions between nitroxides of spin triads belonging to different polymer chains. Therefore, we used a simple model accounting for these dimeric exchange integrals only. The exchange integrals between selected pairs of radicals were calculated for the X-ray diffraction crystal structure of the above-mentioned compounds. The spin-unrestricted broken-symmetry approach⁵² at the $B3LYP^{53}$ and $PBE0^{54}$ levels of theory with $6-31+G(d)^{55}$ and SVP^{56} basis sets was used. It was demonstrated previously that the UB3LYP/6-31+G(d) method reproduces well the exchange interactions between nitronyl nitroxide radicals.⁵⁷ The values of exchange interaction were determined as $J_{\text{R-R}} = -(E_{\text{HS}} - E_{\text{BS}})/(\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}})$, where E_{HS} is the energy of the triplet state of the pair of radicals and E_{BS} is the energy of the open-shell singlet state within the broken-symmetry approach.⁵² This definition corresponds to the spin Hamiltonian of exchange coupling, written as $H_{\text{ex}} = -2J_{\text{R-R}}$. $S_{R1}S_{R2}$, and the singlet-triplet splitting, equal to ΔE_{S-T} = $2J_{\text{R-R}}$. In all cases, the $\langle S^2 \rangle$ value for the triplet states was ~ 2.1 , and that for the broken-symmetry singlet states was ~ 1.1 . The accuracy of the energy calculations was chosen to be 10^{-7} H, which provided calculations of J_{R-R} with an accuracy of 0.04 cm⁻¹. All calculations were performed using the Gaussian 03 suite of programs.58

Results and Discussion

We have selected four representative compounds of the family $Cu(hfac)_2L^R$ to study their intercluster exchange interactions.

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Figure 1. Left column: Temperature dependence of the effective magnetic moment for the four studied compounds (reference data measured previously). Right column: Corresponding temperature dependence of the ratio of second integrals $\gamma = I_{triad}/I_{one} \propto \chi_{triad}/\chi_{one}$ (in absolute units) measured by EPR. Red lines show the simulated functions $\gamma(T)$ in the low-temperature region.

The magnetic susceptibility data (Figure 1, left column) show different character of magnetic anomalies for each compound. The main spin transitions (changes in μ_{eff} from ca. 1.8 to 2.7 β at T > 50 K) were studied in detail in our previous works.^{37–45} They are associated with the SS↔WS state conversion in spin triads of nitroxide-copper(II)-nitroxide, where the estimated intracluster exchange couplings are $|J| \approx 100-150 \text{ cm}^{-1}$ in the SS state and |J| < 20 cm⁻¹ in the WS state.^{42,43} Typically, at T < 50 K, all spin triads are already in the SS state ($\mu_{\rm eff} \approx 1.8 \beta$), and the magnetic behavior at lower temperatures, which has not been addressed so far, is governed by intercluster exchange interactions. Two of the selected compounds, Cu(hfac)₂L^{Bu} \cdot 0.5C₇H₁₆ and Cu(hfac)₂L^{Bu} \cdot 0.5C₈H₁₈ (Figure 1a,b),



Figure 2. Representative EPR spectrum of $Cu(hfac)_2 L^{Bu} \cdot 0.5 C_8 H_{18}$ at T = 20 K at Q-band ($\nu_{mw} = 33.58$ GHz), single crystal, arbitrary orientation: (a) first integral and (b) the original spectrum. The signals of the one-spin unit >N-Cu-N< and the spin triad >N- $^{\circ}O$ -Cu- O° -N< are indicated on top.

display pronounced decreases in their magnetic susceptibility starting at T < 50 K, which implies relatively strong intercluster exchange interaction of about 10 cm⁻¹. The two other compounds, $Cu(hfac)_2 L^{Pr}$ and $Cu(hfac)_2 L^{Bu} \cdot 0.5C_8 H_{10}$ (Figure 1c,d), display nearly constant values of μ_{eff} at T from 50 to 4 K, and only at T < 4 K do they decrease, which implies relatively weak intercluster exchange on the order of a few cm⁻¹. However, in any case, the origin of this intercluster exchange interaction is not clear. At temperatures below the main spin transition, the polymer chain consists of two alternating types of paramagnetic centers, both in the S = 1/2 spin state. The first is the copper(II) ion in the CuO_4N_2 unit, and the second is the spin triad in the strongly coupled spin state in the CuO₆ unit. The decrease of $\mu_{\rm eff}$ at low temperatures might arise from antiferromagnetic coupling between neighboring centers of the same polymer chain. Alternatively, it might originate from copper(II)-copper(II) or triad-triad interactions between the polymer chains (or their combination). Magnetic susceptibility data do not allow one to distinguish between these possible exchange pathways, and exact quantum chemical computation of this complicated system is at the moment not feasible.

EPR is one of the key techniques to study exchange interactions,^{59–63} and EPR of breathing crystals has proved to be very informative.^{40–46} At low temperatures, the signal of spin triads in the SS state (with g < 2) and the signal of one-spin copper(II) ions (with g > 2) are spectrally well separated (Figure 2). It is well established that the second integral (*I*) over the EPR spectrum of paramagnetic species is proportional to its

magnetic susceptibility, $I \propto \chi \propto \mu_{\rm eff}^{2.64}$ Therefore, the ratio of the second integral over the spectrum of spin triads ($I_{\rm triad}$) to the second integral over the spectrum of one-spin copper(II) ions ($I_{\rm one}$), $\gamma = I_{\rm triad}/I_{\rm one} \propto \chi_{\rm triad}/\chi_{\rm one}$, can be measured experimentally. We have measured the ratio γ as a function of temperature for all four studied compounds (Figure 1, right column). At high temperatures (T > 200 K), the signals of oneand three-spin units begin to overlap due to the conversion of the spin triad to the WS state and line broadening; therefore, the $\gamma(T)$ dependence cannot be reliably measured. However, at the lower temperatures of our primary interest, the results are reliable and quantitative. Effects of saturation were ensured to be absent at any temperature (see Supporting Information).

It is evident that the shapes of the $\gamma(T)$ curves essentially reproduce the corresponding shapes of $\mu_{eff}(T)$ dependencies for each compound (Figure 1). The decrease of $\gamma(T)$ at T < 50 K is $Cu(hfac)_2L^{Bu} \cdot 0.5C_8H_{18}$ (Figure 1a,b), meaning that the magnetic susceptibility of spin triads decreases. This is unambiguous spectroscopic proof that the intercluster antiferromagnetic exchange responsible for the low-temperature magnetic behavior of the whole compound occurs between spin triads. In contrast, for breathing crystals Cu(hfac)₂L^{Pr} and Cu(hfac)₂L^{Bu}•0.5C₈H₁₀ (Figure 1c,d), no decrease of $\gamma(T)$ is observed down to 4 K (the lower limit for our EPR temperature setup). This again is in perfect agreement with the dependence of $\mu_{\text{eff}}(T)$, where the magnetic moment drops at T < 4 K. Thus, in two opposite cases of relatively strong and relatively weak intercluster exchange, the shapes of the $\mu_{eff}(T)$ and $\gamma(T)$ dependencies agree in the low-temperature region 4 < T < 50 K, meaning that all observed effects of intercluster antiferromagnetic exchange should be attributed to the coupling between spin triads. Though this kind of EPR experiment cannot be brought to a really quantitative level due to the baseline distortions and slight overlap of the line shoulders corresponding to the one- and three-spin units at high temperatures, there is no doubt about the qualitative conclusions drawn for the intercluster exchange coupling pathways in breathing crystals.

Quantum chemical calculations support the experimental conclusions drawn above. Table 1 shows that intercluster exchange interactions between nitronyl nitroxides (J_{R-R}) for breathing crystals Cu(hfac)₂L^{Pr} and Cu(hfac)₂L^{Bu}•0.5C₈H₁₀ are by a factor of 10 weaker than those for $Cu(hfac)_2L^{Bu} \cdot 0.5C_7H_{16}$ and $Cu(hfac)_2 L^{Bu} \cdot 0.5 C_8 H_{18}$. This is due to the different relative orientations of interacting radicals. For compounds with a strong intercluster exchange, the O and N atoms with significant positive spin density are situated against each other, encouraging the antiferromagnetic coupling (Figure 3a,b). For compounds with a weak intercluster exchange (Cu(hfac)₂L^{Pr} and $Cu(hfac)_2L^{Bu} \cdot 0.5C_8H_{10}$), the atoms with high spin density (N and O) of one radical are shifted from the corresponding atoms of the partner (Figure 3c,d). Thus, although the distance between oxygen atoms in Cu(hfac)₂L^{Bu} \cdot 0.5C₈H₁₀ is even shorter than that in $Cu(hfac)_2L^{Bu} \cdot 0.5C_7H_{16}$ and $Cu(hfac)_2L^{Bu} \cdot 0.5C_8H_{18}$, the overlap of corresponding orbitals and interaction of unpaired electrons is much lower. In addition, the O····O distance in the case of $Cu(hfac)_2L^{Pr}$ is much longer than in the other compounds, giving the weakest antiferromagnetic interaction (Figure 3c, Table 1). Thus, it is very significant that, in agreement with experiment, the 10-fold difference in intercluster exchange is found between two pairs of studied compounds.

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Table 1. Pair Exchange Parameters (*J*_{R-R}) for the Nearest Nitronyl Nitroxide Radicals Belonging to Different Polymer Chains, Calculated by the Spin-Unrestricted Broken-Symmetry Approach^a

		$J_{\mathrm{R},\mathrm{R}}/\mathrm{cm}^{-1}$				
compound	T/K	UBE0/SVP	UBE0/6-31+G*	UB3LYP/SVP	UB3LYP/6-31+G*	<i>d</i> (O-O)/pm
Cu(hfac) ₂ L ^{Bu} •0.5C ₇ H ₁₆ Cu(hfac) ₂ L ^{Bu} •0.5C ₈ H ₁₈ Cu(hfac) ₂ L ^{Pr} Cu(hfac) ₂ L ^{Pr}	120 100 50 60	-7.60 -7.57 -0.04 -1.32	-9.02 -8.71 -0.22 -0.81	-8.19 -8.32 -0.04 -1.71	-9.74 -9.55 -0.33 -0.94	392 400 526 330

^{*a*} The calculations were done for corresponding X-ray structures obtained at temperatures T. The values of d indicate the shortest distances O···O between interacting radicals.



Figure 3. Spin-density distribution in the high-spin state of the nearest nitronyl nitroxide radicals of $Cu(hfac)_2L^{Bu} \cdot 0.5C_7H_{16}$ (a), $Cu(hfac)_2L^{Bu} \cdot 0.5C_8H_{18}$ (b), $Cu(hfac)_2L^{Pr}$ (c), and $Cu(hfac)_2L^{Bu} \cdot 0.5C_8H_{10}$ (d) from the UB3LYP/6-31+G(d) calculations (color code: blue, >0.005; green, < -0.005). Hydrogen atoms are omitted.



Figure 4. Mulliken atomic spin densities of nitronyl nitroxide radical (a) and a fragment of nitroxide-copper(II)-nitroxide cluster (b), from UPBE0/SVP calculations.

As was mentioned above, we used a simple model accounting for pair exchange interactions only. At the same time, it is clear that spin-density distribution in the nitronyl nitroxide radical included in the spin triad would differ from that in a free radical, as demonstrated in Figure 4. For example, the value of Mulliken spin density on the uncoordinated oxygen atom is 0.46 in the radical incorporated in the cluster and only 0.37 in a free radical. Consequently, using our model, we slightly underestimate the exchange interactions between radicals incorporated in the clusters. Note that the pronounced increase of spin density on the end-standing NO groups of nitroxides incorporated in the clusters agrees with recently reported results.⁶⁵ Most probably, it is this localization of spin density that favors the intercluster exchange pathways between nitroxides of different polymer chains.

The calculated values of $J_{\text{R-R}}$ between nitroxides belonging to different chains are very reasonable. The broken-symmetry calculations at the B3LYP level usually overestimate the *J* values by about a factor of 2.^{66,67} Indeed, we can fit the lowtemperature decrease of $\gamma(T)$ dependencies for Cu(hfac)₂L^{Bu}•0.5C₇H₁₆ and Cu(hfac)₂L^{Bu}•0.5C₈H₁₈ using the value $\Delta E_{\text{S-T}} = 2J_{\text{R-R}} = -11 \text{ cm}^{-1}$ (Figure 1a,b). In this estimation, we modeled an infinite chain of coupled S = 1/2spins by a ring of eight spins S = 1/2, each interacting with its two neighbors. It was shown previously that, at $T > 0.5IJ_{\text{R-R}}/k$ ≈ 4 K, the susceptibility calculated in this way quickly approaches the asymptote for the infinite number of spins.⁶⁸

The EPR spectrum of spin triads at T < 50 K does not show any characteristics of the triplet-state spectrum that would arise from exchange-coupled pairs of two spins S = 1/2 (Figure 2).^{59,69} In fact, the spectrum of a triad at any temperature consists of a single EPR line, which implies exchange narrowing between more than two spins. The hyperfine structure from copper nuclei was never observed for spin triads, although it is nearly always observed for copper(II) ions in CuO₄N₂ units with typical splitting constant $A_{zz} \approx 14 \text{ mT} \approx 0.014 \text{ cm}^{-1}$.^{40–46} In the case of interaction between spin triads, this allows for estimation of $|J_{\text{triad-triad}}| \gg A_{zz} \approx 0.014 \text{ cm}^{-1}$, which, of course, agrees with the obtained values of $1-10 \text{ cm}^{-1}$. In the case of interaction between copper(II) ions and spin triads, this leads to an estimate of $|J_{\text{triad-one}}| \ll A_{zz} \approx 0.014 \text{ cm}^{-1}$. Again, both of these estimations support exchange coupling between triads and magnetic isolation of one-spin units. Therefore, in agreement with X-ray data, it is evident that spin triads form exchangecoupled infinite chains that spread across the structural polymer chains (Figure 5). Note that solvent molecules included in many breathing crystals do not occupy positions between NO groups of nitroxides belonging to different polymer chains but are instead located between the layers in the 3D structure. Solvent molecules strongly influence the character of magnetic anomaly (Figure 1) but do not have a direct impact on the magnitude of the intercluster exchange interaction.

As an outlook for future studies, we would like to mention the following observation. It is well known in classical spin crossover research that the abruptness of spin transitions is governed by cooperative interactions.³ Strong cooperativity leads to abrupt transitions, whereas weak cooperativity results in gradual transitions. It seems that, in breathing crystals, the

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Figure 5. Structure of polymer chains and exchange interaction pathways (highlighted in pink) in breathing crystals exemplified using $Cu(hfac)_2L^{Bu} \cdot 0.5C_7H_{16}$. Legend: green, Cu; red, O; blue, N; black, C. Note that, in the 3D structure, the solvent molecules (heptane) do not occupy positions between NO groups of neighboring chains as it appears in the

abruptness of the WS \leftrightarrow SS state transition correlates with the low-temperature behavior (T < 50 K) that is related to the intercluster exchange unveiled in this work. For example, Figure 1 demonstrates the cases of very (a) and moderately (b) abrupt spin transitions, and for these compounds we have found strong intercluster exchange of ca. 10 cm⁻¹ between spin triads of neighboring chains. On the other hand, Figure 1c,d shows very gradual WS \leftrightarrow SS state transitions, and for these compounds much weaker intercluster exchange (<1 cm⁻¹) is found. Understanding the exchange interaction pathways shown in Figure 5 gives sense to this magneto-structural correlation that seems to be consistent with all our observations made so far⁴⁰⁻⁴⁶ but must be addressed in more detail in the future.

Conclusions

picture.

In this paper we have studied the intercluster exchange interactions in polymer-chain molecular magnets of the family Cu(hfac)₂L^R. A rather simple approach of selectively probing the magnetic susceptibility using Q-band EPR allowed us to obtain key information on the intercluster exchange coupling pathways in these systems. We have reliably demonstrated that breathing crystals Cu(hfac)₂L^R are indeed 1D systems in the sense of their exchange channels' architecture. However, contrary to previous assumptions, the magnetic chains do not coincide with structural polymer chains but rather spread across them.

Apart from being generally a very interesting example of an unusual magneto-structural correlation, this finding is crucial for building models and proposing mechanisms of magnetic switching in breathing crystals. Unlike structural polymer chains, magnetic chains consist solely of spin triads of nitroxide–copper(II)–nitroxide without alternation with one-spin copper(II) ions, which is vital for theoretical consideration of spin-Peierls-like phenomena.^{70–72} We have also found that the abruptness of spin transitions in breathing crystals correlates with the magnitude of intercluster exchange. This reveals the connection of interchain exchange coupling between spin triads with the cooperativity and is possibly an important step toward the target of designing breathing crystals with desired character of magnetic anomalies.

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Supporting Information Available: Complete ref 58; crystallographic data in CIF format for the structures used in quantumchemical computations; description of EPR results proving the absence of saturation effects in all experiments presented in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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