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# MAGNETIC RESONANCE IN Cu(hfac)$_2$L$^R$ HETEROSPIN CHAIN POLYMER COMPLEXES

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Cu(hfac)$_2$ chain polymer heterospin complexes with pyrazole-substituted nitronylnitroxides (L$^R$, where R = Me, Et) with a composition Cu(hfac)$_2$L$^R$, exhibiting structural rearrangements with magnetic effects in the solid state at reduced temperatures, were studied by magnetic resonance. The magnetic resonance spectrum changes substantially for substituents of different types. The results of this study are discussed in the context of the cluster approach in view of the specific crystal structure of the compounds.

**Keywords:** magnetic resonance, magnetic clusters, anisotropy.

## INTRODUCTION

Magnetic studies have recently experienced revival due to the design of molecular magnets (MMs). The building materials for these compounds are organic paramagnetic molecules (stable radicals and polyradicals, carbene high-spin molecules) or paramagnetic complexes in which metal ions as magnetic carriers are surrounded by a ligand shell of organic molecules.

Due to a number of their advantages, molecular magnets are promising materials for studies. These are light, transparent, flexible materials characterized by photoinduced magnetism and compatibility with polymers for composite materials, as well as inexpensive low-temperature (e.g., room-temperature) synthesis and easy treatment. Magnetic ordering at room temperature makes it possible to use MMs in microelectronics and data recording, magnetic visualization and protection from low-frequency magnetic fields, as well as in various electronic and magnetic devices, etc.

For design of molecular magnet systems, the organic, organometal, or inorganic (metal coordination centers) paramagnetic components found for this purpose should be arranged in a crystal structure in such a way that exchange interactions between spins led to ordering of these components throughout the system.

This work was stimulated by previously obtained data about the structure and magnetic properties of a family of Cu(hfac)$_2$ heterospin chain polymer complexes with pyrazole-substituted nitronylnitroxides (L$^R$, where R = Me–(CH$_3$), Et–(C$_2$H$_5$)) with a composition Cu(hfac)$_2$L$^R$, exhibiting structural rearrangements with magnetic effects in the solid state at reduced temperatures. It was shown [1] that the magnetic properties of the systems are determined by the exchange-coupled clusters; due to a crystal structure rearrangement, the magnitude and even the sign of intracluster exchange change drastically when the temperature is lowered. Therefore it was interesting to study these compounds by magnetic resonance and to trace

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how changes in exchange interactions affect the resonance spectra.

## SAMPLES AND EXPERIMENTAL PROCEDURE

Magnetic resonance studies were carried out with $Cu(hfac)_2L^R$ polycrystalline samples in the *X* range of frequencies (9.4 GHz) at temperatures $4.2 < T < 300$ K. For these measurements we employed a standard RADIOPAN *X*-band spectrometer (Poland) with a cylindrical resonator and with linear polarization of a field SHF-modulated at a frequency of 100 MHz. When the sample was cooled, the resonator stayed at room temperature. The line intensity was determined as the product of the square of the half-width of the derivative of the absorption line and its amplitude.

The synthetic procedure, details of crystal structure solution, and changes in the structural parameters at reduced temperatures are found in [1].

Polymer chains with a "head-to-head" ($Cu(hfac)_2L^{Et}$) or "head-to-tail" ($Cu(hfac)_2L^{Me}$) motif are formed as a result of the bridging coordination of $L^R$ via the imine N atom of pyrazole and one of the O atoms of the nitronylnitroxide fragment [1]. Figure 1 shows the molecular structures of $Cu(hfac)_2L^{Et,Me}$ complexes and their "head-to-head" ($Cu(hfac)_2L^{Et}$) and "head-to-tail" ($Cu(hfac)_2L^{Me}$) motifs.

The structure of $Cu(hfac)_2L^{Et}$ does not change its symmetry at reduced temperatures (space group *C*/2*c*). The most important structural features of $Cu(hfac)_2L^{Et}$ at 293 K are short Cu–O and Cu–N axial distances (2.237(4) Å and 2.375(5) Å) found in the centrosymmetric crystallographically independent $CuO_6$ and $CuO_4N_2$ units, respectively. As the temperature decreases, the axial Cu–$O_L$ distances in the $CuO_6$ octahedra gradually increase to 2.260(3) Å at 188 K and to 2.281(3) Å at 115 K. The Cu–$O_{hfac}$ distances in the $CuO_6$ units also change. When the axial distances along the $O_L$–Cu–$O_L$ "axis" increase, each of the Cu–$O_{hfac}$ distances along one of the $O_{hfac}$–Cu–$O_{hfac}$ directions concurrently decreases by a comparable value (~0.043(9) Å). When Cu–$O_{hfac}$ distances are shortened from 2.028(5) Å to 1.985(4) Å, all Cu–$O_{hfac}$ bond lengths in $CuO_6$ units become equal at reduced temperatures.

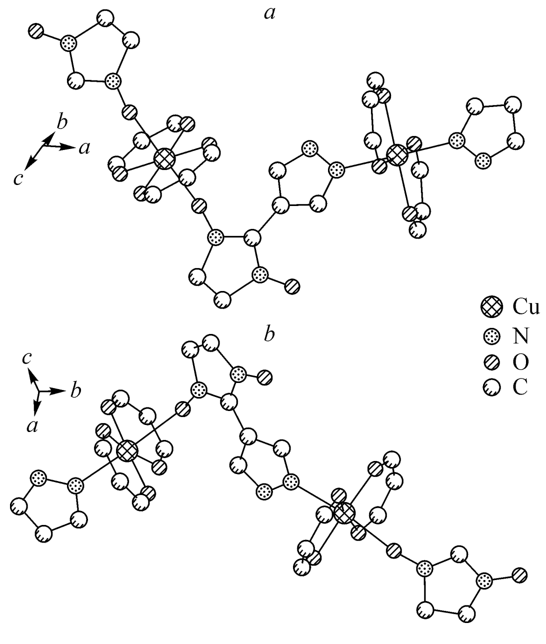

**Fig. 1**. Molecular structures of $Cu(hfac)_2L^{Et}$ (*a*) and $Cu(hfac)_2L^{Me}$ (*b*) complexes and their "head-to-head" and "head-to-tail" motifs. Trifluoromethyl groups, hydrogen atoms, and some nitrogen atoms are omitted for clarity.

In the $CuO_4N_2$ units, the long axis of the Cu bipyramid is actually displaced at 188 K. The coordinated N atoms of the pyrazole heterocycles pass to the equatorial positions ($d_{Cu–N}$ 2.375(5) Å → 2.079(4) Å), removing two $O_{hfac}$ atoms to the axial positions ($d_{Cu–O}$ 1.996(4) → 2.269(3) Å). Below 188 K, the Cu–$N_L$ distances in the $CuO_4N_2$ units continue to decrease, while the Cu–$O_L$ distances in the $CuO_6$ units continue to increase. The structural changes observed in solid $Cu(hfac)_2L^{Et}$ at reduced temperatures are generally localized inside $CuO_6$ and $CuO_4N_2$ coordination units since the angles and distances in coordinated hfac anions and $L^{Et}$ do not change within the experimental error.

Investigation of the structure of $Cu(hfac)_2L^{Me}$ at 293 K [1] revealed that the compound has a chain polymer structure. However, the chain motif differs radically from that for $Cu(hfac)_2L^{Et}$. In $Cu(hfac)_2L^{Me}$, the chains have a "head-to-tail" motif. The copper atom is surrounded by two hfac ligands with short Cu–$O_{hfac}$ distances in the equatorial plane and by the NO oxygen and pyrazole nitrogen atoms from different bridging $L^{Me}$ ligands in the axial plane. The Cu–$O_L$ distance to the axial oxygen of the nitroxyl group is 2.484 Å. At room temperature, all $CuO_5N$ coordination units are identical (space group $P2_1/n$). At lower temperatures, however, the character of changes in the crystal structure of $Cu(hfac)_2L^{Me}$ was shown [1] to be radically different from that of $Cu(hfac)_2L^{Et}$. At 141-146 K, in *half* of all $CuO_5N$ units, the coordinated $O_1$ atoms of nitroxyl groups pass from axial to equatorial position, forming two structurally nonequivalent $CuO_5N$ coordination units. The symmetry of the unit cell decreases to triclinic.

## RESULTS OF EXPERIMENT

The temperature evolution of the magnetic resonance spectrum in $Cu(hfac)_2L^{Et}$ is shown in Fig. 2. At room temperature the spectrum is a single line. The line width is $\Delta H_{pp}(300\ K) \cong 245$ Oe; the resonance field is $H_{res}(300\ K) \cong 3111$ Oe. At $T < 50$ K, the low-field shoulder of the absorption line is asymmetric probably because of the anisotropic $g$ factor of the copper ion. The line intensity of the magnetic resonance spectrum increases at reduced temperatures.

The line width decreases at $T = 220$ K, showing anomalous behavior (Fig. 3). In contrast to $Cu(hfac)_2L^{Et}$, the magnetic resonance spectrum of $Cu(hfac)_2L^{Me}$ is less trivial (Fig. 4).

The low-field line with the parameters $\Delta H_{pp}(300\ K) \cong 108$ Oe, $H_{res}(300\ K) \cong 1710$ Oe and the line with the parameters $\Delta H_{pp}(300\ K) \cong 256$ Oe, $H_{res}(300\ K) \cong 3170$ Oe are the most pronounced features of the spectrum. The temperature dependences of the line width and low-field line intensity are presented in Fig. 5.

At reduced temperatures, the low-field line shifts downfield, and its width increases monotonously; at temperatures of the order of 160 K the line intensity reaches maximum and then decreases to zero. At ambient temperatures, the low-field line has a pronounced "fine" structure and line intensity obviously exceeds the spectrometer noise (Fig. 4).

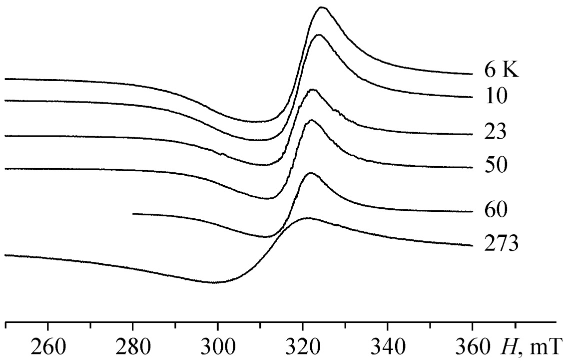

**Fig. 2**. Temperature evolution of the magnetic resonance spectrum in $Cu(hfac)_2L^{Et}$.

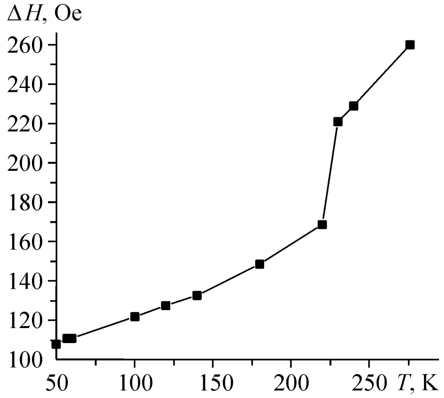

**Fig. 3**. Temperature behavior of the magnetic resonance line width in $Cu(hfac)_2L^{Et}$.

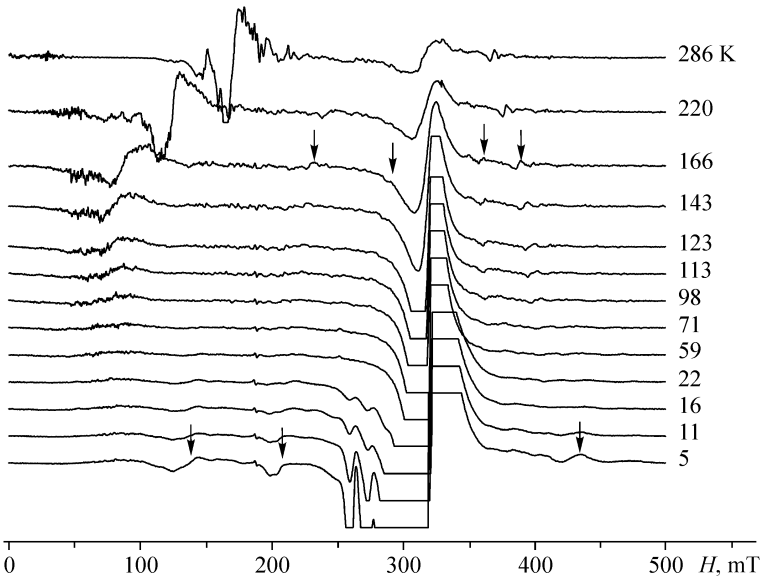

**Fig. 4**. Temperature evolution of the magnetic resonance spectrum in $Cu(hfac)_2L^{Me}$.

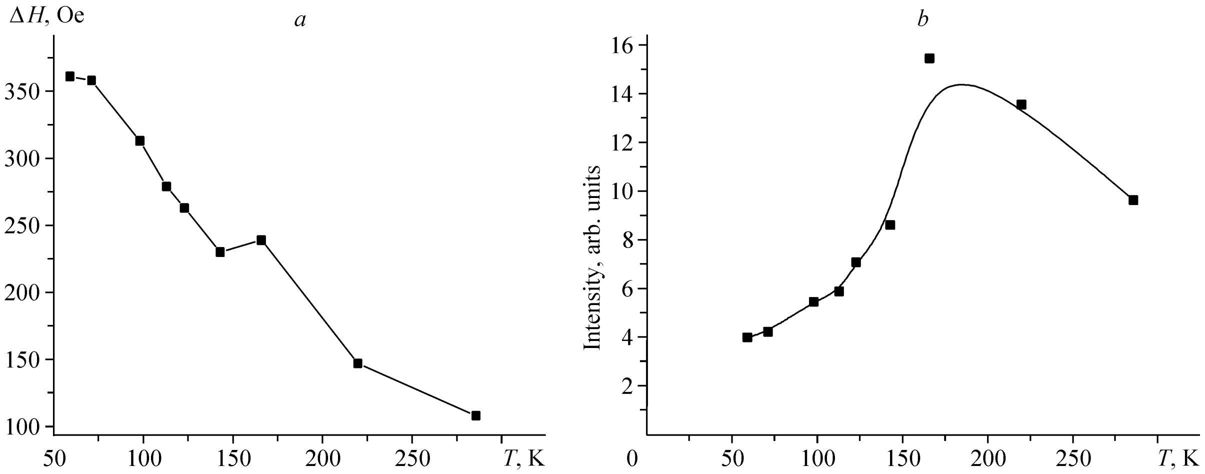

**Fig. 5**. Temperature dependences of the line width (*a*) and intensity (*b*) of the low-field line.

The width $\Delta H_{pp}$ of the second resonance line ($g = 2.086$) decreases monotonously with temperature; its resonance field is practically independent of temperature, and the intensity increases (the spectra in Fig. 4 are recorded with identical amplification so that the line amplitudes are cut out). Below 30 K the left wing of the line contains four equally intense resolved lines with a hyperfine structure (hfs) and with an $A_{hfs}$ constant of 135 Oe characteristic of a single copper ion. Moreover, the spectra have additional weak lines marked with arrows (Fig. 4).

## DISCUSSION OF RESULTS

As mentioned above, in solid $Cu(hfac)_2L^{Et}$, structural changes at reduced temperatures mostly take place in $CuO_6$ and $CuO_4N_2$ coordination units. In view of the "head-to-head" motif of polymer chains in this structure, the discussion of the resonance properties may be limited to consideration of an exchange-coupled cluster >N–•O–Cu(II)–O•–N<, consisting of the magnetic moment of the $C^{2+}$ ion ($S = 1/2$) and two magnetic moments of nitroxyl O•–N with spin $S = 1/2$ for each.

Because of the specifics of the crystal structure, these clusters may be regarded as noninteracting as they are separated from each other by an extended bridge of diamagnetic ions. The net spin of this cluster is $S_\Sigma = 3/2$. This cluster will have either spin 1/2 (antiferromagnetic exchange) or 3/2 (ferromagnetic exchange) depending on the sign of exchange interaction in the ground state. The magnitude of splitting between the ground and excited states is determined by the value of exchange interaction in the cluster. It was established [1] that because of the distortion of the octahedral environment of the copper ion at reduced temperatures as described above, the exchange interaction in the >N–•O–Cu(II)–O•–N< cluster changes abruptly from weak antiferromagnetic at $T = 225$-300 K to ferromagnetic at $T < 220$ K. This shows itself as an abrupt decease in the resonance line width at $T = 220$ K (Fig. 3) and may be explained by exchange-induced narrowing of the resonance line. The absence of fine structure from the transitions $\Delta M_S = \pm 1$ at pivot points of the field suggests that the fine structure parameter $D$ of the clusters is small compared to the natural line width (less than 100 Oe).

The "head-to-tail" motif of the structure of Cu(hfac)$_2$L$^{\mathrm{Me}}$ permits us to regard this molecule as an exchange-coupled cluster Cu(II)–O•–N< with net spin $S_\Sigma = 1$. In this case, the cluster will have $S = 0$ (antiferromagnetic exchange) or $S = 1$ (ferromagnetic exchange) depending on the sign of exchange interaction in the ground state. It was shown [1[ that in the temperature range 4.2-300 K ferromagnetic exchange interaction is dominant in the cluster. At the same time, at $T \sim 145$ K, the effective magnetic moment of the Cu(hfac)$_2$L$^{\mathrm{Me}}$ molecule decreased by a factor of $\sqrt{2}$ (half of all spins vanished). Analysis of changes in the crystal lattice of Cu(hfac)$_2$L$^{\mathrm{Me}}$ indicated that at reduced temperatures there are two types of structurally nonequivalent CuO$_5$N coordination units with different (anti- and ferromagnetic) exchange interactions in Cu(II)–O•–N< exchange clusters.

Analysis of magnetic resonance spectra makes it possible to draw the following conclusions. The low-field resonance line seems to be due to so-called "forbidden" transitions $\Delta M_S = \pm 2$ in the region $g \approx 4$ of the Cu(II)–O•–N< cluster with antiferromagnetic exchange interactions. These transitions are often observed in disordered media [2-4] with certain relationships between the isotropic and anisotropic exchange interactions and the external magnetic field. The relatively large amplitude of the $\Delta M_S = \pm 2$ line is due to the weak angular dependence of its resonance field [4]. The decreased intensity of the low-field line at reduced temperature (Fig. 5) unambiguously shows that these CuO$_5$N coordination units have antiferromagnetic exchange interactions. At temperatures at which the low-field line is observed, the magnetic resonance spectrum has weaker lines (marked with arrows in Fig. 4) characteristic of the fine structure lines of clusters with spin $S_\Sigma = 1$. They vanish together with the low-field line. In polycrystalline samples, these lines appear at pivot points of the field. Judging from the temperature dependence of line intensity, they may be regarded as belonging to the Cu(II)–O•–N< antiferromagnetic cluster. The distance between the extreme components of these lines corresponds to the doubled fine structure parameter $D$ of the cluster, determined by the anisotropy of exchange and dipole-dipole interaction of spins in the cluster. The parameter $D$ ($T = 166$ K) estimated in this way is of the order of 800 Oe and is temperature-dependent, as can be seen from the spectra.

The second line is due to the conventional transitions $\Delta M_S = \pm 1$. Judging from the temperature behavior of the line intensity, this line belongs to the single paramagnetic copper ions. This is supported by four hfs lines of the single copper nucleus that appear on the left wing of the line at low temperatures. The sample evidently contains these ions due to defects of the crystal structure.

In the temperature range 5-20 K, the spectra also contain weak lines. The intensity of these lines increases, while the distance between the extreme components remains unaltered at reduced temperatures, due to which they may be identified as the fine structure lines of a ferromagnetic cluster. The line width increases at elevated temperatures, and the lines become hardly observable. The fine structure parameter $D$ ($T = 5$ K) of this ferromagnetic cluster is of the order of 2230 Oe.

Thus analysis of the magnetic resonance spectra indicates that two types of structurally nonequivalent CuO$_5$N coordination units coexist in Cu(hfac)$_2$L$^{\mathrm{Me}}$ over a wide range of temperatures.

## CONCLUSIONS

Heterospin chain polymer complexes of $Cu(hfac)_2$ with pyrazole-substituted nitronylnitroxides ($L^R$, where R = Me, Et) with a composition $Cu(hfac)_2L^R$, which undergo structural rearrangements with magnetic effects in the solid state at reduced temperatures, have been studied by magnetic resonance. The magnetic properties of the compounds are determined by exchange interactions in Cu(II)–nitroxide clusters. The structural dynamics of the complexes differ significantly depending on the type of the R substituent in the lateral chain of the ligand; this leads to the formation and coexistence of ferro- and antiferromagnetic clusters. The fine structure parameters were estimated for the ferro- and antiferromagnetic clusters.

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