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TWO Cu(hfac)$_2$ COMPLEXES WITH THE IMIDAZOLINE NITROXIDE 4-AMIDO-2,2-DIMETHYL-5,5-DIMETHOXY-3-IMIDAZOLINE-1-OXYL. CONVERSION OF A DISCRETE MOLECULAR STRUCTURE TO A CHAIN STRUCTURE AS A RESULT OF STOICHIOMETRIC CHANGES

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Abstract—The reaction of copper hexafluoroacetylacetonate with the stable nitroxide 4-amido-2,2-dimethyl-5,5-dimethoxy-3-imidazoline-1-oxyl (L) in a ratio of 2:1 in hexane yielded the Cu(hfac)$_2$-saturated coordination chain polymer of composition [Cu(hfac)$_2$]$_2$L. In [Cu(hfac)$_2$]$_2$L, half of the Cu(hfac)$_2$ molecules coordinate L in bidentate fashion by the amide-group oxygen and the imine nitrogen of the heterocycle. The other Cu(hfac)$_2$ molecules arrange the above {Cu(hfac)$_2$L} fragments in polymer chains by alternate coordination of either the N$\stackrel{\cdot}{-}$O group, or the amide-group oxygens of two {Cu(hfac)$_2$L} fragments to axial positions. As a result [Cu(hfac)$_2$]$_2$L involves three copper ions with coordination number 6 and with different coordination environments. For metal complexes with nitroxides, this mode of chain formation was observed for the first time. The magnetic properties of the complex are described in terms of an exchange cluster model with ferromagnetic intracluster exchange interactions.

The complexes of metal hexafluoroacetylacetonates M(hfac)$_2$ (M = Mn, Co, Ni, Cu) with nitroxides have been the subject of much attention for some time, since they are convenient models for the investigation of exchange interactions in heterospin systems.[1] Recently, polyfunctional nitroxides and polynitroxides have been finding increasing use for the synthesis of such complexes.[2,3] The use of these ligands, together with variation of synthesis conditions and metal-containing matrices, offers considerable scope for the synthesis of complexes of

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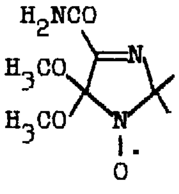
different stoichiometries and structures. These ligands are employed in studies aimed at developing approaches to the synthesis of two- and three-dimensional heterospin systems able to undergo the phase transition to the ferromagnetic state. They are also used on searching for fragments wherein effective exchange interactions between different paramagnetic centres can occur.

This work is concerned with the synthesis and structure of the polymer complex of copper hexafluoroacetylacetonate with the polyfunctional nitroxide 4-amido-2,2-dimethyl-5,5-dimethoxy-3-imidazoline-1-oxyl (L) of composition $[Cu(hfac)_2]_2L$. The structure and magnetic properties of $[Cu(hfac)_2]_2L$ are compared to those of the previously synthesized molecular complex $Cu(hfac)_2L$,[4] which may be regarded as the "precursor" of $[Cu(hfac)_2]_2L$. It is shown that the introduction of an additional amount of $Cu(hfac)_2$ in its reaction with $Cu(hfac)_2L$ leads to the transformation of the molecular complex to the polymer one.



L

EXPERIMENTAL

The nitroxide was prepared as described elsewhere.[5] Reagent grade solvents were used as purchased. Copper hexafluoroacetylacetonate was prepared by a literature method.[6]

Preparation of the complex

A mixture of 50 mg of L (0.24 mmol) and 240 mg of $Cu(hfac)_2 \cdot H_2O$ (0.48 mmol) was stirred in 20 cm^3 of boiling hexane until the reagents dissolved. The solution was filtered and kept for 4 h at ambient temperature. The green precipitate was collected and washed with hexane. Yield 140 mg (50%). M.p. 114–119°C. Found: Cu, 10.7; C, 27.7; H, 1.4; N, 3.7. Calc. for $Cu_2C_{28}H_{18}N_3F_{24}O_{12}$: Cu, 10.9; C, 28.6; H, 1.5; N, 3.6%.

Crystal structure solution and refinement

Crystals of the complex, suitable for X-ray diffraction study, were obtained on recrystallization of the material from pentane. The intensity data were obtained on an Enraf–Nonius CAD-4 diffractometer by standard techniques and corrected for Lorentz and polarization effects. The crystal data for $[Cu(hfac)_2]_2L$ and some experimental details are presented in Table 1. The structure was solved by direct methods and then refined using the SHELX-86 package (PC version).[7] Selected bond lengths and angles are given in Table 2.

Magnetic measurements

The magnetic susceptibility of the complex was measured by Faraday's method in the temperature range 4.2–300 K, the data being corrected for diamagnetic contributions estimated from Pascal constants and for temperature-independent copper(II) paramagnetism equal to 60×10^{-6} cm^3 mol^{-1}. The optimum exchange parameters were obtained by minimization of the function $\Sigma_i(\mu_{exp}(T_i) - \mu_{calc}(T_i))^2$ with the use of a program described in refs 8 and 9.

RESULTS AND DISCUSSION

The reaction of $Cu(hfac)_2 \cdot H_2O$ with the stable nitroxide 4-amido-2,2-dimethyl-5,5-dimethoxy-3-imidazoline-1-oxyl (L) in a molar ratio of 2:1 in hexane yielded a complex of formula $[Cu(hfac)_2]_2L$. As has been shown,[4] the interaction of these reagents at lower molar ratios (from 1.5:1 to 1:1) yielded the complex of 1:1 stoichiometry, $Cu(hfac)_2L$. Our efforts to isolate an adduct of intermediate composition between $[Cu(hfac)_2]_2L$ and $Cu(hfac)_2L$ failed. $[Cu(hfac)_2]_2L$ is stable under ordinary conditions and can be recrystallized from hexane or pentane. $[Cu(hfac)_2]_2L$ and $Cu(hfac)_2L$ can be transformed into each other by recrystallization with one equivalent of the nitroxide or the copper chelate, respectively:

$$Cu(hfac)_2L \underset{+L}{\overset{+Cu(hfac)_2}{\rightleftharpoons}} [Cu(hfac)_2]_2L.$$

The independent structural fragment of $[Cu(hfac)_2]_2L$ (Fig. 1) involves three crystallographically independent copper atoms, two of which, Cu(1) and Cu(3), lie on inversion centres [(0,0,0) and (0.5, 0.5, 0)], with one, Cu(2), being in a general position. The Cu(2) atom coordinates the nitroxide molecule in a bidentate mode by the imine nitrogen and the amide-group oxygen. At the same time the amide oxygen of L is bonded to Cu(3), it is bridging, and the nitroxide-group oxygen is coordinated by Cu(1). Thus, all three independent copper atoms are bonded by the same L molecule. The other coordination sites around copper atoms are occupied by the oxygens of hexa-

Table 1. Crystal data and structure refinement for [Cu(hfac)$_2$]$_2$L

Empirical formula	$C_{28}H_{18}Cu_2F_{24}N_3O_{12}$
Formula weight	1171.53
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit celll dimensions	$a = 12.577(3)$ Å, $\alpha = 90°$
	$b = 16.783(3)$ Å, $\beta = 98.65(1)°$
	$c = 20.697(4)$ Å, $\gamma = 90°$
Volume	4319(2) Å^3
Z	4
Density (calculated)	1.802 g cm^{-3}
Absorption coefficient	1.146 mm^{-1}
Crystal size	$0.3 \times 0.4 \times 0.6$ mm
θ range	1.57–24.84°
Index ranges	$0 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 19$, $-22 \leqslant l \leqslant 22$
Reflections collected	2905
Independent reflections	2745 $R_{\text{int}} = 0.0184$
Observed reflections	$1099 > 4\sigma$
Refinement method	block-diagonal least-squares on F
R index	0.036

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(hfac)$_2$]$_2$L

Cu(1)—O(1)	1.934(12)	Cu(2)—O(8)	2.189(11)
Cu(1)—O(2)	1.925(12)	Cu(2)—O(4)	2.417(10)
Cu(1)—O(3)	2.459(12)	Cu(3)—O(11)	1.913(13)
Cu(2)—O(9)	1.941(11)	Cu(3)—O(12)	1.947(13)
Cu(2)—O(7)	1.940(11)	Cu(3)—O(4)	2.474(13)
Cu(2)—O(10)	1.969(11)	N(3)—C(61)	1.33(2)
Cu(2)—N(2)	2.062(13)	O(4)—C(61)	1.18(2)
		O(3)—N(1)	1.243(14)
O(1)—Cu(1)—O(2)	92.3(5)	O(10)—Cu(2)—O(8)	89.7(3)
O(1)—Cu(1)—O(3)	85.7(5)	N(2)—Cu(2)—O(8)	98.3(4)
O(2)—Cu(1)—O(3)	87.8(5)	O(9)—Cu(2)—O(4)	89.3(3)
O(9)—Cu(2)—O(7)	176.5(3)	O(7)—Cu(2)—O(4)	87.7(3)
O(9)—Cu(2)—O(10)	90.8(5)	O(10)—Cu(2)—O(4)	98.3(3)
O(7)—Cu(2)—O(10)	91.4(4)	N(2)—Cu(2)—O(4)	73.9(5)
O(9)—Cu(2)—N(2)	84.8(3)	O(8)—Cu(2)—O(4)	171.3(3)
O(7)—Cu(2)—N(2)	92.6(3)	O(11)—Cu(3)—O(12)	93.2(5)
O(10)—Cu(2)—N(2)	171.1(4)	O(11)—Cu(3)—O(4)	85.9(5)
O(9)—Cu(2)—O(8)	93.9(3)	O(12)—Cu(3)—O(4)	97.0(5)
O(7)—Cu(2)—O(8)	88.8(4)	Cu(2)—O(4)—Cu(3)	123.1(5)

fluoroacetylacetonate anions. Since Cu(1) and Cu(3) occupy special positions, both Cu(1) and Cu(3) have tetragonally distorted octahedral coordination environments with four oxygen atoms of hfac anions in the equatorial planes of the octahedra (mean Cu—O = 1.93 Å) and, respectively, the nitroxide- or amide-group [bond lengths 2.46(2) and 2.47(1) Å] oxygens in the axial positions. The coordination number of the Cu(2) atom in the general position also equals 6. The coordination environment of this atom may be described as a strongly distorted octahedron consisting of three hfac oxygens [Cu—O 1.93(1)–1.97(1) Å] and the imine nitrogen of the nitroxide molecule [Cu—N 2.06(2) Å] in the equatorial plane. The axial positions are occupied by the remaining

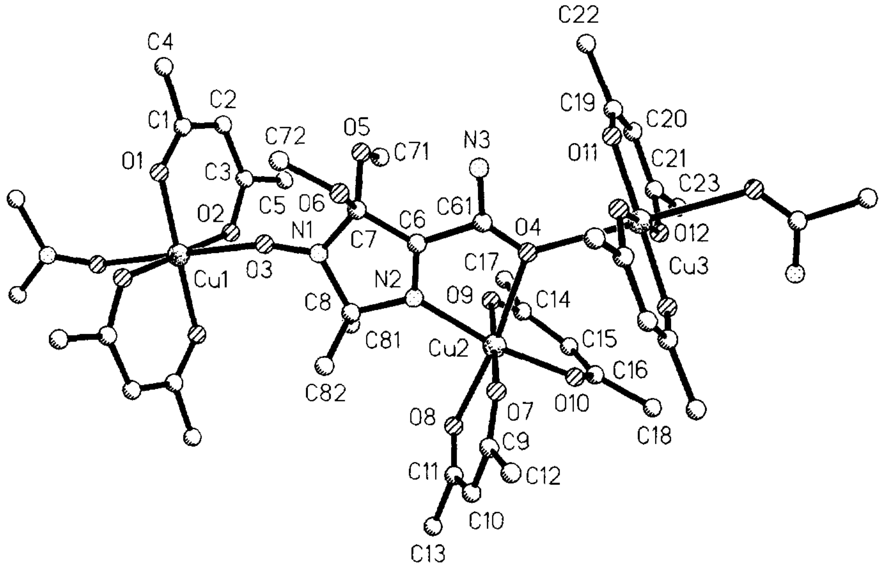


Fig. 1. A fragment of the chain in the structure of [Cu(hfac)$_2$]$_2$L. Fluorine and hydrogen atoms are omitted for clarity.

hfac-anion oxygen and the amide oxygen of the radical. The Cu—O bond lengths are 2.19(1) and 2.42(1) Å, respectively. The dihedral angle between hfac ligand planes is 69°. It should be noted that the structure of the fragment {Cu(2)(hfac)$_2$L} is very similar to the molecular structure of Cu(hfac)$_2$L (Figs 1 and 2).[4]

The geometric characteristics of the hfac anions and the imidazoline nitroxide molecules are ordinary.

The structure of the complex consists of zig-zag chains running along the [110] and [1$\bar{1}$0] directions, the chains being formed of L-bridged Cu(hfac)$_2$ fragments. It should be noted that the compound under discussion was the first one among M(hfac)$_2$–nitroxide complexes to exhibit the tridentate bridging-chelating coordination of the paramagnetic ligand.

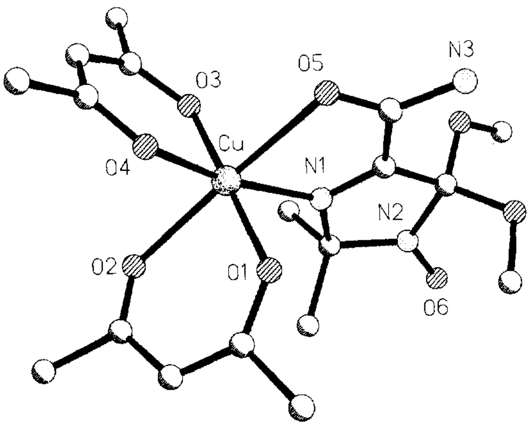


Fig. 2. A molecule of Cu(hfac)$_2$L. Fluorine and hydrogen atoms are omitted for clarity.

Comparison of Cu(hfac)$_2$L and [Cu(hfac)$_2$]$_2$L structures shows that the "excess" Cu(hfac)$_2$ in [Cu(hfac)$_2$]$_2$L links individual Cu(hfac)$_2$L molecules in an infinite chain, thus increasing the dimensionality of the complex. Such a transformation of the molecular complex to the chain polymer is possible due to the fact that L has three different donor groups capable of simultaneous coordination to different metal atoms. Thus, the pair Cu(hfac)$_2$L and [Cu(hfac)$_2$]$_2$L shows that variation of synthesis conditions can change not only the stoichiometry of the resulting complexes, but also their dimensionality. To the best of our knowledge it is the first example of such a transition for M(hfac)$_2$ complexes with nitroxides.

Figure 3 shows the temperature dependence of the effective magnetic moment and the reciprocal molar susceptibility of the complex (per {[Cu(hfac)$_2$]$_2$L}$_2$ fragment). The high-temperature value of magnetic moment (4.59 B.M.) shows good agreement with that expected for a molecular system with weakly interacting spins (4.24 B.M. provided $g = 2.00$). With decreasing temperature μ_{eff} gradually increases and at 4.25 K reaches 6.24 B.M. The dependence of $1/\chi_{\mathrm{m}}$ on T above 30 K is described in terms of the Curie–Weiss law, $\chi = C/(T-\theta)$, with $\theta = 8.69$ K and $C = 1.287$ cm^3 K mol^{-1}, which indicates that ferromagnetic exchange interactions prevail in the solid complex. Quantitative treatment of the cryomagnetic behaviour of [Cu(hfac)$_2$]$_2$L has been a problem. The structure of the complex is such that the elementary chain unit

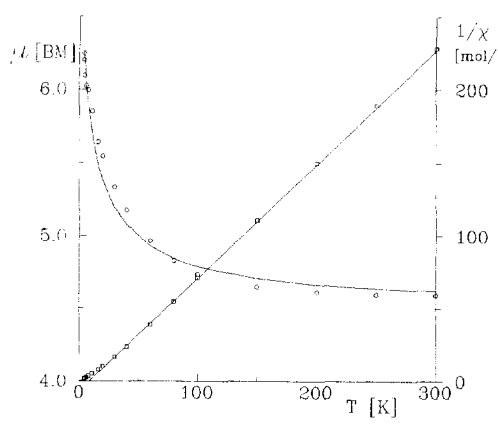


Fig. 3. Plots of $\mu_{eff}(T)$ and $1/\chi_m(T)$ dependences for $[Cu(hfac)_2]_2L$ (per $\{[Cu(hfac)_2]_2L\}_2$ fragment).

involves four Cu(hfac)$_2$ fragments and two L molecules (Fig. 4). Taking into account only the nearest neighbour interactions, one can distinguish four different exchange pathways: the direct exchange between Cu(1) and the radical (J_1), the exchange between Cu(2) and the radical through the imidazoline heterocycle (J_2), the exchange between Cu(2) and Cu(3) through the bridging amide oxygen (J_3), and the exchange between Cu(3) and the radical through the amide group (J_4). Thus, $[Cu(hfac)_2]_2L$ should be treated as a magnetic chain of a fairly complex structure. However, the model for the description of the magnetic properties of the complex can be simplified by using the magneto-structural correlations available for the copper–nitroxide system. It is well known that for the axial coordination of a nitroxide to Cu^{II} ion the exchange parameter (in this case J_1) is close to 10 cm^{-1} (for the spin-Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$).[1,2] It is also reasonable to assume J_2 to be about 25 cm^{-1}, as for the molecular complex Cu(hfac)$_2$L, whose structure is similar to that of the Cu(2)–nitroxide fragment (see above), the exchange parameter is equal to 24.9 cm^{-1}.[4] Estimating the value of J_4, one may refer to the investigation of the Cu(hfac)$_2$ complex with 2,2,5,5-tetramethyl-4-amide-3-imidazoline-1-oxyl:[4] for this complex it has been found that the exchange interactions between copper ion and nitroxide through the amide group in the fourth position of the heterocycle are no more than 1 cm^{-1}. Hence, it is reasonable to ignore J_4 as it is small compared with J_1 and J_2.

The indirect exchange between Cu(2) and Cu(3) (J_3) is difficult to estimate quantitatively. It should be remembered that both copper atoms have the 4+2-type coordination environment, the coordination polyhedra sharing the O(4) atom, which is axial for both Cu(2) and Cu(3). Having studied a substantial body of literature on magneto-structural correlations for copper dimers,[10,11] we found that this particular case of the axial–axial bridge had not been considered. However, some semi-quantitative conclusions can be made from the data available. It is common knowledge that as the bridge changes from equatorial–equatorial (so-called "in-plane" exchange) to equatorial–axial ("out-of-plane" exchange), the exchange energy essentially decreases (from 100–300 to less than 10 cm^{-1}).[12] The reason is that the axial ligand interacts with the d_{z^2} orbital, while the unpaired electron resides on the $d_{x^2-y^2}$ orbital directed towards equatorial ligands. Thus, it is reasonable to assume that with the bridging atom axial for both copper atoms, the energy of superexchange is even smaller and does not exceed 1 cm^{-1}. To verify this hypothesis, we retrieved data on copper complexes involving Cu^{II} ions with the 4+1 or 4+2 environment, bridged with an axial O—C fragment, from the Cambridge Structural Database (Jan. 1989 version). Only one compound was found to satisfy these requirements, with the environment of the two copper ions being square-pyramidal. The exchange energy between copper ions has been reported to be close to zero.[13] Thus, we have every reason to estimate the value of J_3 as <1 cm^{-1} and neglect it in the fitting of the magnetic susceptibility of $[Cu(hfac)_2]_2L$.

The assumption that J_3 and J_4 can be neglected essentially simplifies the situation: in this case the original magnetic chain splits into the separate fragments Cu(hfac)$_2$ and $[Cu(hfac)_2]_3L_2$. The contribution of the "isolated" fragments Cu(hfac)$_2$ to the product χT of the complex is constant, which reduces the problem of simulating the magnetic behaviour of $[Cu(hfac)_2]_2L$ to determining the parameters of the exchange cluster $S_{Cu(2)}$–S_R–$S_{Cu(1)}$–S_R–$S_{Cu(2)}$. To do this, we used the approach

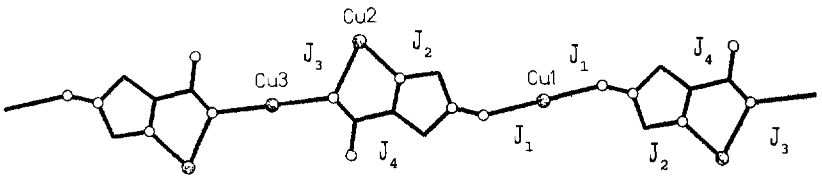


Fig. 4. The exchange pathways in $[Cu(hfac)_2]_2L$.

developed in ref. 9; the contribution of the "isolated" copper ion was estimated from the high-temperature data for $[Cu(hfac)_2]_2L$ assuming that the g-factors of all copper ions were equal ($\mu^2_{Cu2} = 3.59$ at $g_{Cu} = 2.20$). The parameters J_1, J_2, $g_{Cu(1)}$, $g_{Cu(2)}$ and $J'z$ (the effective parameter of intercluster interaction) were varied in the course of fitting, symmetry constraints being imposed. The following set of optimum spin-Hamiltonian parameters has been obtained: $J_1 = 7.5$ cm^{-1}, $J_2 = 20.2$ cm^{-1}, $g_{Cu(1)} = 2.21$, $g_{Cu(2)} = 2.19$, $J'z = 0.014$ cm^{-1}, and goodness-of-fit $\Sigma_i(\mu_{exp}(T_i) - \mu_{calc}(T_i))^2/(N-n) = 0.0129$. A $\mu_{eff}(T)$ curve calculated with the above values for $\{[Cu(hfac)_2]_2L\}_2$ is shown as a solid line in Fig. 3. It can be seen that the experimental data as a whole are quite well represented by the theoretical curve. An analysis of the spin-Hamiltonian parameters obtained shows that the optimum values of $g_{Cu(1)}$ and $g_{Cu(2)}$ practically coincide with the average g_{Cu} value given above. This suggests the estimate of the contribution of the "isolated" copper ion to the complex susceptibility to be correct. The values of the exchange parameters J_1 and J_2 are close to those expected. In terms of the model employed, the intercluster exchange parameter $J'z$ makes no particular physical sense and should be considered as a means of indirect account for the exchange pathways J_3 and J_4. The smallness of this parameter also supports the correctness of the model. However, it should be mentioned that equating $J'z$ to zero considerably misfits the theoretical and experimental values of μ_{eff} near 4 K.

A comparison between the magnetic properties of $Cu(hfac)_2L$ and $[Cu(hfac)_2]_2L$ shows that the transformation of the molecular complex to the chain polymer does not increase the magnetic dimensionality of the complex: the properties of both complexes are well described in terms of cluster models. When $Cu(hfac)_2L$ is transformed to $[Cu(hfac)_2]_2L$, the number of intracluster paramagnetic centres increases from two to five, with intracluster exchange interactions remaining ferromagnetic.

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