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Letters to the Editor

New metal-containing matrix in the design of heterospin systems: bis(1,1,1,5,5,5-hexafluoro-4-iminopent-2-en-2-olato)copper(II) complex with nitroxide*

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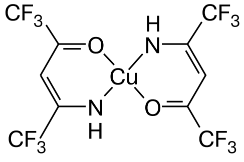
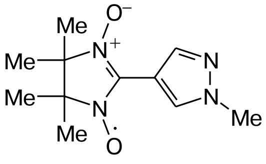
In the design of heterospin systems, metal-containing fluorinated matrices in which the central atom has strong electron-withdrawing properties (which is favorable for coordination of weak donors, such as >N—O groups of nitroxides) have attracted considerable attention.[1—3] However, these matrices are few in number. In the present study, we established the structures of bis(1,1,1,5,5,5-hexafluoro-4-iminopent-2-en-2-olato)copper(II) (**CuL$_2$**) and its first heterospin complex with 2-(1-methyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**R$_{NO}$**) of composition **CuL$_2$R$_{NO}$**.

The **CuL$_2$** compound has a molecular structure. In the solid phase, there are three crystallographically independent molecules of bis-chelate **CuL$_2$**. In each molecule, the central atom is in a nearly square-planar environment with a *trans* arrangement of the ligands **L** existing in the imino enol form (Fig. 1, *a*). In the coordination units, the Cu—O and Cu—N distances are in the ranges of 1.926(3)—1.936(3) Å and 1.919(4)—1.939(4) Å, respectively. In the crystal, the **CuL$_2$** molecules are stacked, and the shortest Cu...Cu distances in the stacks are 4.922(2) Å.



CuL$_2$



R$_{NO}$

The **CuL$_2$R$_{NO}$** compound also has a molecular structure. The coordination environment of the copper atom is a square pyramid (Fig. 1, *b*), whose apex is occupied by the O atom of the >N—O group of the paramagnetic ligand ($d_{\text{Cu—O}_\text{R}}$ = 2.403(7) Å, $d_{\text{Cu—O}_\text{L}}$ = 1.949(5) and 1.954(5) Å, $d_{\text{Cu—N}_\text{L}}$ = 1.933(6) and 1.937(7) Å). The

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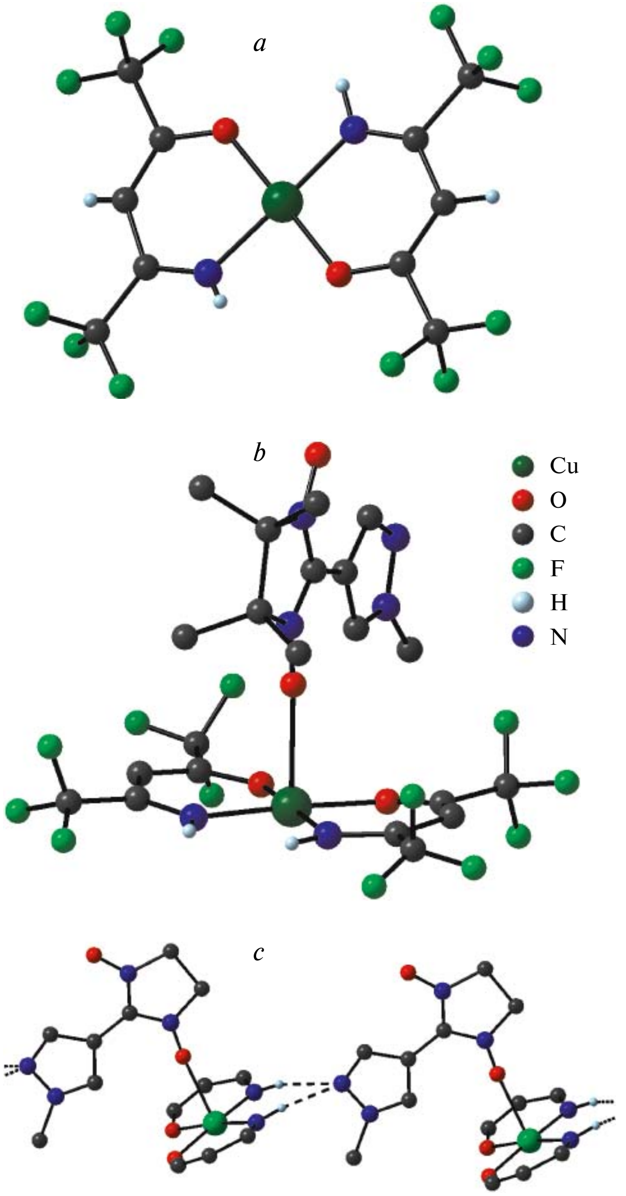

Fig. 1. Molecular structures of **CuL$_2$** (*a*) and **CuL$_2$R$_{NO}$** (*b*) and the fragment of the chain of **CuL$_2$R$_{NO}$** (*c*).
Note. Fig. 1 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

distinguishing feature of the structure of **CuL$_2$R$_{NO}$** is that both NH groups in the bis-chelate fragment are oriented in the same direction due to the *cis* arrangement of the ligands **L** and, consequently, the NH groups are involved in hydrogen bonding with the imine N atom of the pyrazole ring of the adjacent molecule ($d_{\mathrm{N}_{\mathbf{R}}\ldots\mathrm{N}'_{\mathbf{L}}}$ = 3.100(13) and 3.118(14) Å), resulting in the formation of chains (Fig. 1, *c*). Along with the fact that the formation of **CuL$_2$R$_{NO}$** is accompanied by a nontrivial transformation of the NH fragments in the CuN$_2$O$_2$ coordination unit from *trans* to *cis* positions, the unique fact is that the >N—O group is coordinated by the copper ion (Fig. 1, *b*, *c*) in spite of the presence of the imine N atom in nitroxide **R$_{NO}$**. In all bis(hexafluoroacateylacetonate)copper(II) complexes with nitronyl nitroxides bearing a nitrogen-containing (including pyrazole) heterocycle at position 2 of the 2-imidazoline ring, which have been studied earlier, coordination occurs primarily through the donor N atom of the heterocycle of the side chain.[1—4]

Nitroxide **R$_{NO}$** was prepared according to a known procedure.[5]

Complex CuL$_2$. Ammonium acetate (1.54 g, 0.02 mol) was added to a solution of hexafluoroacetylacetone (3.8 g, 0.018 mol) in anhydrous methanol. The reaction mixture was stirred at room temperature until hexafluoroacetylacetone was completely consumed and the corresponding β-aminovinyl ketone (**HL**) was formed.[6] The course of the reaction was monitored by TLC (Silufol UV-254; CHCl$_3$, C$_6$H$_6$, and acetone as eluents). The spots on the plates were visualized with the use of aqueous solutions of copper acetate and KMnO$_4$. Then copper(II) acetate (1.8 g, 0.009 mol) was added. The reaction mixture was stirred until **HL** was completely consumed and then concentrated. The residue was chromatographed on a column (silica gel L 100/250, hexane as the eluent). The product was recrystallized from hexane. The yield of **CuL$_2$** was 2.6 g (61%).

Complex CuL$_2$R$_{NO}$. The **CuL$_2$** compound (0.1002 g, 0.21 mmol) and nitroxide **R$_{NO}$** (0.0500 g, 0.21 mmol) were dissolved in acetone (2 mL), and heptane (4 mL) was added to the resulting solution. The mixture was kept in an open flask at room temperature. After 5 h, the volume of the solution decreased by approximately one-third, and dark-blue crystals were obtained. The crystals were filtered off, washed with heptane, and dried in air. The product contained predominantly the start-

Table 1. Crystallographic data for the **CuL$_2$** and **CuL$_2$R$_{NO}$** compounds

Parameter	**CuL$_2$**	**CuL$_2$R$_{NO}$**
Molecular formula	C$_{10}$H$_4$CuF$_{12}$N$_2$O$_2$	C$_{21}$H$_{21}$CuF$_{12}$N$_6$O$_4$
M	475.67	712.98
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a/Å	17.460(6)	12.3297(14)
b/Å	9.844(3)	9.7157(11)
c/Å	17.463(6)	12.3301(14)
β/deg	90.073(5)	97.479(2)
Z	8	2
V/Å	3001(2)	1464.5(3)
μ/mm^{-1}	1.604	0.860
Number of measured reflections	23263	11357
θ Angle range/deg	1.68—26.43	1.67—23.33
Number of reflections with $I > 2\sigma(I)$	6144	4177
R_1	0.0590	0.0646
wR_2	0.1237	0.1723
ρ_{calc}/g cm^{-3}	2.105	1.617

ing nitroxide $\mathbf{R_{NO}}$, from which single crystals of $\mathbf{CuL_2R_{NO}}$ were mechanically separated. Since the crystals of the complex are similar in color, size, and shape to the crystals of the starting nitroxide $\mathbf{R_{NO}}$, the crystals of the complex $\mathbf{CuL_2R_{NO}}$ were chosen based on X-ray diffraction data. When benzene, toluene, diethyl ether, or their mixtures with heptane or hexane were used as the solvent, the solid phase contained only the starting $\mathbf{CuL_2}$ and $\mathbf{R_{NO}}$ compounds.

X-ray diffraction study. X-ray diffraction data sets were collected on a SMART APEX CCD Bruker AXS diffractometer (Mo-Kα, λ = 0.71073 Å, T = 295 K). Absorption corrections were applied using the Bruker SADABS software (Version 2.10). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms. In most cases, the positions of H atoms were calculated theoretically. The H atoms of the methyl groups were refined isotropically in the rigid-body approximation. All calculations associated with the structure solution and refinement were carried out with the use of the Bruker SHELXTL program package (Version 6.14). The crystallographic data are given in Table 1.

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