

Synthesis and study of Cu^{II} complex with nitroxide, a jumping crystal analog

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We synthesized 1-ethylimidazolyl-substituted nitronyl nitroxides, *i.e.*, 2-(1-ethylimidazol-4-yl)- (L^{4Et}) and 2-(1-ethylimidazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide-1-oxyl (L^{5Et}). The stable radical L^{5Et} is an ethyl analog of 2-(1-methylimidazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide-1-oxyl (L^{5Me}) described earlier, the reaction of which with Cu(hfac)₂ (hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) leads to the formation of the [Cu(hfac)₂(L^{5Me})₂] jumping crystals. The reaction of Cu(hfac)₂ with L^{5Et} with reagent ratios 1 : 2 and 1 : 1 yields heterospin complexes [Cu(hfac)₂(L^{5Et})₂] and [Cu(hfac)₂L^{5Et}]₂, respectively. X-ray diffraction study of the mononuclear complex [Cu(hfac)₂(L^{5Et})₂] determined that the compound has a packing similar to that of jumping crystals studied earlier, with the only difference being that the O...O contacts between neighboring nitroxide groups were found to be 0.3–0.5 Å longer than in [Cu(hfac)₂(L^{5Me})₂]. As a result of the lengthening of these contacts, [Cu(hfac)₂(L^{5Et})₂] crystals lack chemomechanical activity. We found that when cooling crystals of binuclear complex [Cu(hfac)₂L^{5Et}]₂ below 50 K, the antiferromagnetic exchange between unpaired electrons of the >N–•O groups of neighboring molecules leads to the full spin-pairing of the nitroxides, with only the Cu²⁺ ions contributing to the residual paramagnetism of the compound.

Key words: Cu²⁺, nitroxide radicals, X-ray diffraction, magnetic properties.

Recently, transition metal hexafluoroacetylacetonate complexes with a nitronyl nitroxide radical, namely, 2-(1-methylimidazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide-1-oxyl (L^{5Me}), given by the general formula [M(hfac)₂(L^{5Me})₂], where M = Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺; hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, were described. A specific feature of the [M(hfac)₂(L^{5Me})₂] crystals is their ability to spontaneously move when excited with heat or light, owing to which they were named jumping.¹ In the solid phase of [M(hfac)₂(L^{5Me})₂], the deoxygenation reaction occurs, during which the starting complex with nitronyl nitroxide transforms into a complex with the corresponding imino nitroxide. These complexes (the complex with nitronyl nitroxide and the complex with imino nitroxide) form limited regions of solid solutions causing an increase of strain in the crystals over

the course of a gradually proceeding solid phase reaction and their subsequent destruction.^{2,3} In the study of the jumping crystal effect, both the metal-containing matrix and the paramagnetic ligand were modified.^{2,3} The crucial role of the heterospin crystal packing in the possibility of the appearance of chemomechanical activity was demonstrated. When varying the transition metal ion in the M(hfac)₂ matrix and replacing the methyl substituent in L^{5Me} with a CD₃ group (*i.e.*, going from L^{5Me} to L^{5CD3}), the chemomechanical activity of crystals remained the same. However, the substitution of the imidazole ring with a triazole one, *i.e.*, going from L^{5Me} to the topologically related, in terms of structure, 2-(1-methyl-1,2,3-triazol-5-yl)-4,4,5,5-tetramethyl-2-imidazoline 3-oxide-1-oxyl (L^{Tr}), quenches the chemomechanical activity of the crystals.^{2,3}