

# A Copper-Nitroxide Adduct Exhibiting Separate Single Crystal-to-Single Crystal Polymerization-Depolymerization and Spin Crossover Transitions

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## Abstract

© 2016 American Chemical Society. A complex cascade of solid-state processes initiated by variation of temperature was found for the heterospin complex  $[\text{Cu}(\text{hfac})_2\text{LMe}/\text{Et}]$  formed in the reaction of copper(II) hexafluoroacetylacetonate  $[\text{Cu}(\text{hfac})_2]$  with stable nitronyl nitroxide 2-(2-methyl-3-ethyl-1H-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (LMe/Et). The cooling of the compound below 260 K initiated a solid-state chemical reaction, which led to a depolymerization of chains and formation of a pair heterospin complex  $[\text{Cu}(\text{hfac})_2\text{LMe}/\text{Et}_2][[\text{Cu}(\text{hfac})_2]_3\text{LMe}/\text{Et}_2]$ . Further decrease in temperature below 144 K led to a spin transition accompanied by a drastic decrease in the effective magnetic moment from 2.52 to 2.24  $\mu\text{B}$ . When the compound was heated, the order of effects was reversed: at first, the magnetic moment abruptly increased, and then the molecular fragments of the pair cluster united into polymer chains. Two hysteresis loops correspond to this cascade of temperature-induced structural transformations on the experimental dependence  $\mu_{\text{eff}}(T)$ : one at high ( $T' = 283$  K and  $T'' = 260$  K) and the other at low ( $T = 161$  K,  $T = 144$  K) temperature. The spin transitions were also recorded for the  $[[\text{Cu}(\text{hfac})_2]_3\text{Lbu}/\text{Et}_2]$  and  $[[\text{Cu}(\text{hfac})_2]_5\text{Lbu}/\text{Et}_4]$  molecular complexes, which are models of the trinuclear fragment of the  $\{[\text{Cu}(\text{hfac})_2]_3\text{LMe}/\text{Et}_2\}$  pair cluster.

<http://dx.doi.org/10.1021/acs.inorgchem.6b00140>

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