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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 [Cu(hfac)2LMe/Et] formed in the reaction of copper(II) hexafluoroacetylacetonate [Cu(hfac)2] with stable nitronyl nitroxide 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 [Cu(hfac)2LMe/Et2][[Cu(hfac)2]3LMe/Et2]. 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 μB. 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 μeff(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 [[Cu(hfac)2]3LBu/Et2] and [[Cu(hfac)2]5LBu/Et4] molecular complexes, which are models of the trinuclear fragment of the {[Cu(hfac)2]3LMe/Et2} pair cluster.

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