A new Cu/Zn carboxylato-bridged 1D polymer: direct synthesis, X-ray structure and magnetic properties.

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Streszczenie

A new complex [Cu2Zn(O2CMe)6(NH3)2]n was isolated as an unexpected product in an open-air synthesis of a mixed-metal compound using zero-valent copper, zinc oxide and ammonium acetate in the presence of 2-diethylaminoethanol in acetonitrile solution. Its structure consists of Cu2(O2CMe)4 units situated on crystallographic inversion centres and Zn(NH3)2(O2CMe)2 units on crystallographic 2-fold axes. One O atom of each of the O2CMe groups is attached via Zn bridges to the Cu atoms of the dimeric Cu2(O2CMe)4 unit forming a 1D polymer in the bc direction. The polymer is not linear, with the dihedral angles between successive Cu–Cu vectors being 48.9°. Within the Cu2(O2CMe)4 units the Cu···Cu distance is 2.675(2) Å and the angles between the O2CMe planes are 88.8(5)°. The magnetic properties have been analyzed using the Hamiltonian Ĥ = JŜ1Ŝ2 with J = 286 cm−1 and g = 2.13. High-field EPR spectra showed both the exchange-coupled copper pair and non-interacting copper(II) ions. The presence of the latter species was explained as an effect of zinc atoms occupying a fraction of the copper sites.Graphical abstractA high fraction of uncoupled copper(II) ions observed both in the EPR spectra and in magnetic susceptibility of the new polymer [Cu2Zn(O2CMe)6(NH3)2]n was explained by postulating that zinc(II) can substitute one of the copper(II) ions in the ‘paddlewheel’ dimeric units, thereby freeing another Cu(II) ion from the exchange interactions.Highlights► A new Cu/Zn complex with acetate and ammonia was isolated. ► ‘Paddlewheel’ copper acetate dimers and monomeric zinc complex units alternate forming a 1D polymer. ► High-field EPR spectra showed both the exchange-coupled copper pair and non-interacting copper(II) ions. ► The presence of the latter species was explained as an effect of zinc atoms occupying a fraction of the copper sites.

Słowa kluczowe

1 D polymer, Exchange interactions, High-field EPR, crystal structure, Zero-valent copper

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