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High Spin Ground State Copper(II) and Nickel(II) Complexes Possessing the 3,5-di-*tert*-butyl-1,2-semiquinonate Radical Anion

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Abstract

Several high spin ground-state compounds based upon ferromagnetic coupling between a metal ion and the chelating 3,5-di-*tert*-butyl-1,2-semiquinonate radical anion, [DTBSQ]^{•-}, as they possess unpaired electron spins in orthogonal $d_{x^2-y^2}/d_{z^2}$ and π^* orbitals, are described. [Cu^{II}(DPyA)(DTBSQ)](ClO₄) (DPyA = 2,2'-dipyridylamine) was reinvestigated and its singlet excited state is 282 cm⁻¹ [0.035 eV; $J/k_B = 406$ K ($H = -JS_a \cdot S_b$)] above the triplet ground state. [Cu^{II}(bipy)(DBCat)MeOH] (bipy = 2,2-bipyridine; DBCat = 3,5-di-*tert*-butylcatecholate), [Cu^{II}(bipy)(DTBSQ)](BF₄), [Cu^{II}(DPyA)(DTBSQ)-(THF)₂](BF₄) and [Ni^{II}(DPyA)(DTBSQ)(THF)₂](BF₄) have been structurally characterized and have high spin ground states whose low spin excited states lie 28 cm⁻¹ (0.0034 eV), 382 cm⁻¹ (0.047 eV), 335 cm⁻¹ (0.042 eV), and 108 cm⁻¹ (0.013 eV) higher, respectively. The triplet-singlet separation is 18% greater for [Cu^{II}(DPyA)(DTBSQ)(THF)₂]⁺ than [Cu^{II}(DPyA)(DTBSQ)]⁺ and is ascribed to greater orthogonality of the Cu^{II} $d_{x^2-y^2}/d_{z^2}$ and [DTBSQ]^{•-} π^* orbitals for octahedral [Cu(DPyA)(DTBSQ)(THF)₂]⁺ with respect to distorted square pyramidal structure of [Cu(DPyA)(DTBSQ)]⁺. This greater energy of the excited state correlates with the shorter than average M-O_{DTBSQ} distance, i.e. [Cu(bipy)(DTBSQ)]⁺ > [Cu^{II}(DPyA)(DTBSQ)(THF)₂]⁺ > [Ni(DPyA)(DTBSQ)(THF)₂]⁺. The order of magnitude lower value for [Cu^{II}(bipy)(DBCat)MeOH] arises from a weak intradimer $S = 1/2$ Cu(II) interaction, not via ferromagnetic coupling between the $S = 1/2$ Cu(II) and [DTBSQ]^{•-} sites.

Keywords: Copper(II); Nickel(II); Magnetic properties; 1,2-semiquinonate; triplet

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