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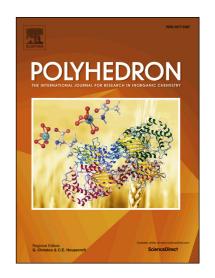
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High Spin Ground State Copper(II) and Nickel(II) Complexes Possessing the 3,5-di-*tert*-butyl-1,2-semiguinonate Radical Anion

Royce A. Davidson, a,b Jingjun Hao, Arnold L. Rheingold, Joel S. Miller A,*

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 $d_{x^2-v^2}/d_{z^2}$ 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 = -1 $JS_a \cdot S_b$] 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}(DPvA)(DTBSQ)(THF)₂]⁺ than [Cu^{II}(DPyA)(DTBSQ)]⁺ and is ascribed to greater orthogonality of the Cu^{II} d_{x2-y2}/d_{z2} 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_{DTBSO} distance, i.e. $[Cu(bipv)(DTBSQ)]^+ > [Cu^{II}(DPvA)(DTBSQ)(THF)_2]^+ > [Ni(DPvA)(DTBSQ)(THF)_2]^+$. 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-semiguinonate; triplet

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