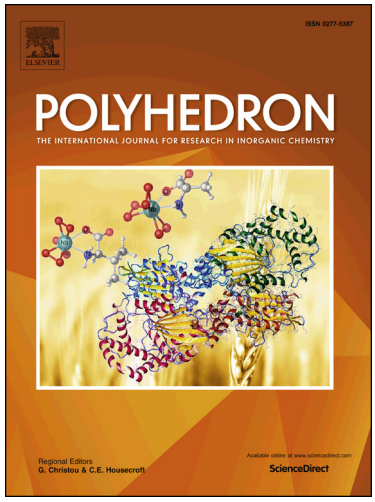

High Spin Ground State Copper(II) and Nickel(II) Complexes Possessing the 3,5-di-*tert*-butyl-1,2-semiquinonate Radical Anion

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

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

[a] Material Research Science and Engineering Center, University of Utah, Salt Lake City, UT 84112, USA
[b] Department of Chemistry, 315 S. 1400 E. RM 2124, University of Utah, Salt Lake City UT 84112-0850, USA
[c] Department of Chemistry and Biochemistry University of California, San Diego, La Jolla, CA 92093-0358

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, $[DTBSQ]^{\bullet-}$, as they possess unpaired electron spins in orthogonal d_{x2-y2}/d_{z2} and π* orbitals, are described. $[Cu^{II}(DPyA)(DTBSQ)](ClO_4)$ (DPyA = 2,2'-dipyridylamine) was reinvestigated and its singlet excited state is 282 cm^{-1} [0.035 eV; J/k_B = 406 K ($H = -JS_a \bullet S_b$)] above the triplet ground state. $[Cu^{II}(bipy)(DBCat)MeOH)]$ (bipy = 2,2-bipyridine; DBCat = 3,5-di-*tert*-butylcatecholate), $[Cu^{II}(bipy)(DTBSQ)](BF_4)$, $[Cu^{II}(DPyA)(DTBSQ)(THF)_2](BF_4)$ and $[Ni^{II}(DPyA)(DTBSQ)(THF)_2](BF_4)$ 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_{x2-y2}/d_{z2} and $[DTBSQ]^{\bullet-}$ 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 $M\text{-}O_{DTBSQ}$ 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 $[DTBSQ]^{\bullet-}$ sites.

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