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Synthesis and Structure of a Complex Having a Quartet Ground State with Three Entirely Different Spin Carriers: Nitronyl Nitroxide, *o*-Semiquinone, and Cu^{II}

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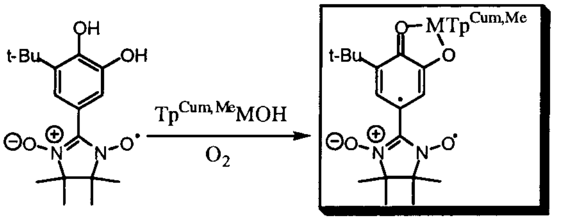
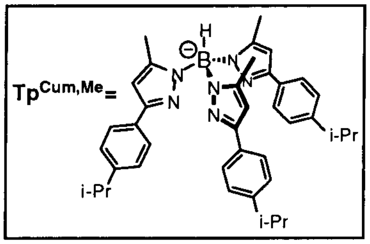
A “spin diverse” $S = 3/2$ ground-state complex, NN-SQCuTp^{Cum,Me}, has been prepared. The three $S = 1/2$ spin carriers are nitronyl nitroxide (NN), *o*-semiquinone (*o*-SQ), and cupric ion. The solid-state structure of the Zn^{II} derivative, NN-SQZnTp^{Cum,Me} ($C_{56}H_{69}BN_8O_4Zn$), was determined: monoclinic, $P2(1)/c$, $a = 12.5781(12)$ Å, $b = 17.7408(17)$ Å, $c = 24.440(2)$ Å, $\alpha = 90.00°$, $\beta = 98.240(2)°$, $\gamma = 90.00°$, $Z = 4$. The results of X-ray structural characterization of the Zn^{II} derivative suggest substantial interaction between the two spin carriers NN and *o*-SQ. Indeed, strong intramolecular exchange coupling has been determined by variable-temperature magnetic susceptibility studies. Intraligand ferromagnetic exchange is considerably greater than kT, such that only the triplet state is populated at 300 K, and Cu^{II}−ligand exchange is ferromagnetic, with $J = +75$ cm^{-1}.

An attractive feature of molecule-based magnetic materials[1−7] is that they can be comprised of multiple, entirely different spin carriers, including paramagnetic metal ions, coordinated and unbound organic radicals, and redox-active radical ions. This “spin diversity” allows the coexistence of physical properties associated with each constituent functionality, and opens the door for different properties due to synergistic relationships among organic and inorganic components.

These new materials and properties include magnetic conductors,[8] magnetic liquid crystals,[9,10] valence tautomerism,[11] photomagnetism,[12,13] and the photomechanical effect.[14] Certainly, even more new properties will emerge as additional molecules and materials are prepared through rational design and discovery. Herein, we report the preparation and properties of a spin diverse, ground-state $S = 3/2$ complex (NN-SQCuTp^{Cum,Me}) comprised of ferromagnetically coupled linear assembly of nitronyl nitroxide (NN), *o*-semiquinone (SQ), and cupric ion. In addition, the structure of the Zn^{II} derivative, NN-SQZnTp^{Cum,Me}, is reported.



NN-CatH$_2$ **NN-SQMTp^{Cum,Me}**



Other spin diverse species have been prepared. For example, Iwamura reported the preparation and magnetic properties of a triplet biradical ligand containing both NN and nitroxide functionality,[15] but to our knowledge, no complexes of this ligand have yet been reported. Iwamura also reported the synthesis and properties of triradicals composed of different nitroxides.[16] Rey and co-workers reported an $S = 7$ ground-state cluster with three different spin carriers: Ni^{II}, Fe^{III}, and an imino nitroxide.[17] Sugawara described the EPR spectral

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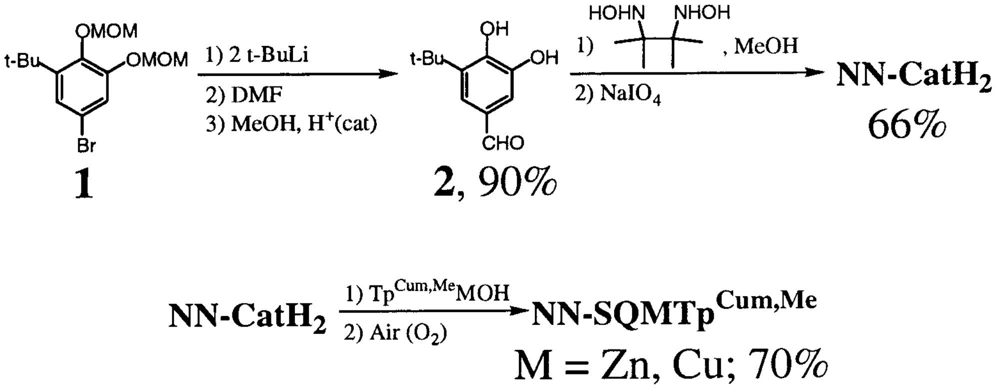
Scheme 1



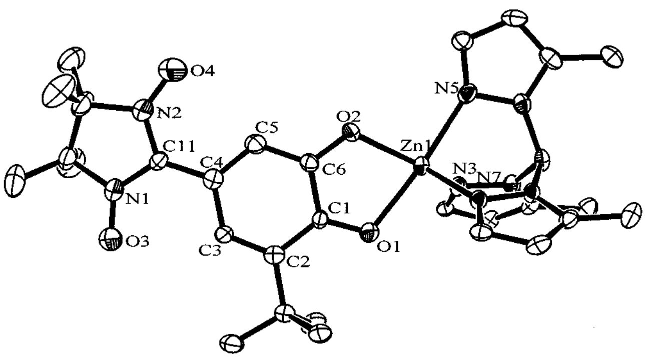


Figure 1. ORTEP of NN-SQZnTp$^{\mathrm{Cum,Me}}$. Cumenyl groups have been omitted for clarity.

characterization of a *p*-SQ-NN anion.[18] The *p*-SQ portion of the latter biradical was introduced by sodium metal reduction of the corresponding *p*-quinone-NN radical. Along these lines, we reported the EPR spectra of an *o*-SQ-nitroxide biradical,[19] but to our knowledge we are currently reporting the first example of a three-spin system composed of *o*-SQ, NN, and Cu$^{\mathrm{II}}$.

Our synthesis, shown in Scheme 1, begins with the preparation of a nitronyl nitroxide catechol, NN-CatH$_2$,[20] following an analogous procedure used by Veciana.[21] We added the *tert*-butyl group to the catechol ring to preclude bridging in metal complexes[22] and as steric protection of SQ spin density. We used Vahrenkamp's Tp$^{\mathrm{Cum,Me}}$ ancillary ligand[23] complexed to Zn$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$, following the work of Pierpont[24] and previous work in our group.[25] Thus, both NN-SQZnTp$^{\mathrm{Cum,Me}}$ and NN-SQCuTp$^{\mathrm{Cum,Me}}$ are obtained in good yield by reaction of Tp$^{\mathrm{Cum,Me}}$MOH with NN-CatH$_2$.

Ferromagnetic coupling within the biradical ligand of NN-SQMTp$^{\mathrm{Cum,Me}}$ is assured by covalently linking an SQ atom having positive spin density with an NN atom with negative spin density, in accord with principles of high-spin-molecule construction.[1,26] Ferromagnetic coupling between the SQ and Cu$^{\mathrm{II}}$ units is guaranteed by having orthogonal SQ and Cu$^{\mathrm{II}}$ magnetic orbitals,[6] as has been demonstrated for Ni$^{\mathrm{II}}$- and Cu$^{\mathrm{II}}$SQ species.[24,27–29] Thus, a linear, three-spin, ferromagnetically coupled complex is obtained.

Table 1. Crystallographic Data for NN-SQZnTp$^{\mathrm{Cum,Me}}$

chemical formula	$C_{56}H_{69}BN_8O_4Zn$
a/Å	12.5781(12)
b/Å	17.7408(17)
c/Å	24.440(2)
α/deg	90.00
β/deg	98.240(2)
γ/deg	90.00
V/Å^3	5397.3(9)
Z	4
formula weight	994.37
space group	monoclinic
T/°C	−115
λ/Å	0.710 73
ρ_{calcd}/g cm^{-3}	1.224
μ/cm^{-1}	5.07
R^a $[F^2 > 2\sigma(F^2)]$	0.0952
wR2^b (F^2)	0.1770

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR = 1/[\sigma^2(F_o^2) + (0.0470P)^2 + 23.7979P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Bond Lengths and Torsion Angle for NN-SQZnTp$^{\mathrm{Cum,Me}}$

bond	R (Å)
C1−O1	1.267(6)
C6−O2	1.286(6)
C1−C2	1.451(8)
C2−C3	1.350(7)
C3−C4	1.48(8)
C4−C5	1.389(8)
C5−C6	1.410(8)
C6−C1	1.481(8)
C4−C11	1.440(8)
C11−N1	1.359(7)
C11−N2	1.361(8)
N1−O3	1.276(7)
N2−O4	1.268(7)
Zn−O1	2.142(4)
Zn−O2	1.979(4)
Zn−N3	2.058(4)
Zn−N5	2.177(5)
Zn−N7	2.048(5)
atoms	**torsion angle**
C1−C6 N1−C11−N2	7.9(4)

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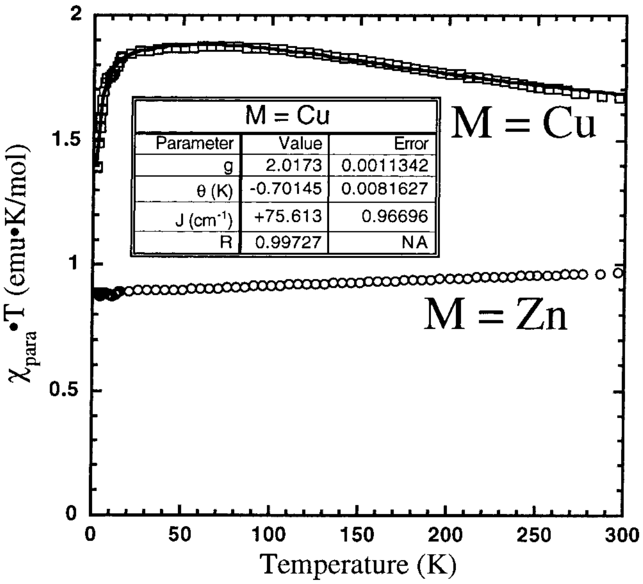

Figure 2. Temperature dependence of χT for NN-SQZnTp$^{\mathrm{Cum,Me}}$ and NN-SQCuTp$^{\mathrm{Cum,Me}}$.

Crystals of NN-SQZnTp$^{\mathrm{Cum,Me}}$ were obtained by diffusion of a methanol layer into a methylene chloride solution of the complex, and an ORTEP is shown in Figure 1. Crystallographic data and important bond lengths and angles are given in Tables 1 and 2, respectively. The *o*-SQ bond lengths deviate from typical values,[22,30] with a structural deviation parameter, $\sum|\Delta_i| = 0.19$.[25] In addition, the structural deviation from *o*-SQ is toward a quinoidal structure, suggesting substantial interaction of *o*-SQ with NN. Moreover, the NN bond lengths differ somewhat from those of the corresponding NN-CatH$_2$,[20] again suggesting substantial interaction between the *o*-SQ and NN groups.

Indeed, the interaction between the paramagnetic *o*-SQ and NN groups is substantial as indicated by the plot of $\chi_{\mathrm{para}}T$ vs T shown in Figure 2. The $\chi_{\mathrm{para}}T$ value decreases slightly from its room temperature value as the temperature is lowered; nonetheless, we contend that the intramolecular exchange coupling is so strong that only the triplet state of the biradical is populated. Therefore, only a lower limit of $\sim$310 cm^{-1} can be placed on the value of the exchange parameter, J. Consistent with the insulating properties of the ancillary Tp$^{\mathrm{Cum,Me}}$ ligand, the decrease in $\chi_{\mathrm{para}}T$ at very low temperatures due to intermolecular interactions is negligible.[31]

The plot of $\chi_{\mathrm{para}}T$ vs T for NN-SQCuTp$^{\mathrm{Cum,Me}}$ is also shown in Figure 2 and is consistent with the design principles described above. The room temperature $\chi_{\mathrm{para}}T$ value of 1.67 emu·K/mol is greater than both three uncorrelated spins ($\chi_{\mathrm{para}}T = 1.125$ emu·K/mol) and uncorrelated $S = 1$ and $S = 1/2$ species ($\chi_{\mathrm{para}}T = 1.375$ emu·K/mol), suggesting both strong intraligand ferromagnetic coupling and ferromagnetic metal–ligand coupling. In fact, the coupling within the organic ligand is so strongly ferromagnetic that the susceptibility data can be accounted for using the Heisenberg Hamiltonian:

$$H = -2J\hat{S}_1\hat{S}_2$$

with $\hat{S}_1$ representing the spin operator of an $S = 1$ ligand and $\hat{S}_2$ representing the spin operator of the $S = 1/2$ cupric ion. Using this Hamiltonian to solve for the spin state energies and determining the corresponding Weiss molecular field corrected Heisenberg–Dirac–Van Vleck expression[6,32] for the susceptibility permits a fit of the experimental data.

$$\chi_{\mathrm{para}}T = \frac{Ng^2\beta^2T}{6k(T-\theta)}\left[\frac{15 + 1.5\exp(-3J/kT)}{2 + \exp(-3J/kT)}\right]$$

The fit shown in Figure 2 was achieved with $g_{\mathrm{iso}} = 2.017$, $J_{\mathrm{SQ-Cu}} = +75.6$ cm^{-1}, and $\theta = -0.70$ K.

We prepared a biradical ligand having both a robust triplet ground state, and two quite different coordination sites. A full report of the magnetic properties of the NN-CatH$_2$ and paramagnetic metal complexes of *o*-SQ-NN will be reported in due course.

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Supporting Information Available: Synthetic details. X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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