

## Magnetic Properties and Redox Isomerism for 4,4'-Bis(semiquinone) Complexes of Copper

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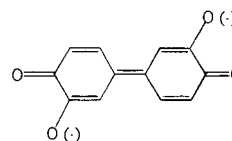
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### Introduction

Studies on cooperative effects that might result in unusual bulk molecular magnetic properties have been directed at understanding exchange coupling in simple one-dimensional polymers. Linear polymers containing multispin subunits may serve as simple models for higher order two- and three-dimensional arrays.<sup>1</sup> Their magnetic properties may provide insight on competing intra- and intersubunit interactions that contribute to complicated temperature-dependent magnetic behavior for more extended polymers. In an effort to design multispin subunits with well-defined spin components, we have turned to linear chains consisting of radical semiquinone (SQ) ligands chelated with paramagnetic transition metal ions. Radical spin is localized in an orbital of  $\pi$  symmetry, directed perpendicular to the ring plane. Paramagnetic metal ions may be chosen with spin in d orbitals of defined symmetry. The design of ferromagnetically coupled chains becomes a matter of coupling radical SQ ligands with metal ions containing orthogonal magnetic orbitals, in sufficient contact to permit strong interaction. Within monomeric complexes, the best illustration for this paradigm is found for the semiquinone complexes of Cu(II).<sup>2</sup> The  $d^9$  metal ion shows preference for square planar and square pyramidal coordination geometries with spin concentrated in the in-plane  $d\sigma$  ( $d_{x^2-y^2}$ ) orbital, orthogonal to the  $\pi$  spin of a chelated SQ ligand. The interaction between

spins can be strong, because of the proximity of spin centers, and ferromagnetic, because of their respective orientation. Examples of copper–SQ complexes that exhibit ferromagnetic coupling are few and are molecular complexes rather than polymers.<sup>3</sup> The extension to polymeric materials may be made with the design and syntheses of bridging bis(semiquinone) (SQ–SQ) ligands.<sup>4</sup>

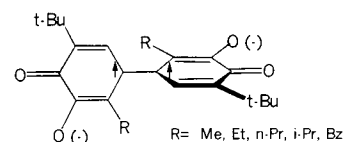
Bis(semiquinones) may be formed by the partial reduction of a bis(benzoquinone). Conjugation between rings results in coplanar alignment



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and a singlet ground-state electronic structure.<sup>5</sup> Dinuclear complexes of Ru have been prepared with bis(semiquinone)<sup>6</sup> and bis(benzoquinonedimine)<sup>7</sup> bridging ligands in studies on metal ion communication through an extended redox-active bridge. Steric interactions that result from bulky functionalization at the ring carbon atoms adjacent to the bridge between rings may result in orthogonal alignment of ring planes and a triplet, high-spin ground state.<sup>8</sup>

Abakumov and co-workers recently published a report on the syntheses of bis(benzoquinones) containing methyl and other alkyl substituents at the 3 and 3' ring positions of a 4,4'-bis(1,2-benzoquinone) (BQ–BQ).<sup>9</sup>



These compounds may serve as precursors to high-spin diradical bis(semiquinone) (SQ–SQ) subunits of a linear coordination polymer.<sup>10</sup> Ring functionalization has been used to constrain the angle between rings to a value close to 90°. Structural characterization of 4,4'-di(3-methyl-6-tert-butyl-1,2-benzoquinone) (BQ<sup>Me</sup>–BQ<sup>Me</sup>) has shown that rings of the unreduced bis(benzoquinone) are nearly orthogonal with a dihedral angle of 82.9° between planes.<sup>9</sup> The linear polymer {[TiMe<sub>2</sub>(thf)]<sub>2</sub>–(SQ<sup>Me</sup>–SQ<sup>Me</sup>)}<sub>n</sub> prepared by a metathetic BQ/SQ exchange between TiMe<sub>2</sub>(3,6-DBSQ) and BQ<sup>Me</sup>–BQ<sup>Me</sup> was found to have a dihedral angle of 51.5° between planes of the semiquinone rings.<sup>10</sup> Even though the linking C–C bond between rings was found to have the length of a single bond, indicating little direct conjugation between SQ rings, the polymer was diamagnetic.

Concurrent with this investigation, polymers of copper were prepared as materials that contain metal–radical interactions in addition to intra- and interligand radical–radical coupling. Prior research had shown that *o*-benzoquinones react directly with copper metal in the presence of a coordinating ligand (L) to give either L<sub>2</sub>Cu<sup>I</sup>(SQ) or L<sub>2</sub>Cu<sup>II</sup>(Cat) species, with charge distribution directed by the donating properties of the ancillary ligands.<sup>11</sup> Similarly, the reaction between BQ<sup>Me</sup>–BQ<sup>Me</sup> and

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**Table 1.** Crystallographic Data for (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>)

formula	C <sub>32</sub> H <sub>34</sub> CuN <sub>2</sub> O <sub>4</sub>
fw	574.2
space group	$P\bar{1}$
<i>a</i> (Å)	14.1735(2)
<i>b</i> (Å)	16.5827(1)
<i>c</i> (Å)	16.5985(2)
α (deg)	71.100(1)
β (deg)	75.844(1)
γ (deg)	68.908(1)
vol (Å <sup>3</sup> )	3407.29(7)
Z	4
<i>T</i> (K)	176
λ(Mo Kα) (Å)	0.710 73
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.119
μ(mm <sup>-1</sup> )	0.674
<i>R</i> , <sup>a</sup> <i>R</i> <sub>w</sub> <sup>b</sup>	0.061, 0.114

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

copper metal in THF has been observed to give a microcrystalline dark blue-green solid that is insoluble in noncoordinating organic solvents. Analytical data are consistent with a 1:1 Cu to BQ<sup>Me</sup>-BQ<sup>Me</sup> formulation.

### Experimental Section

**Li<sub>2</sub>(SQ<sup>Me</sup>-SQ<sup>Me</sup>).** 4-(2-Methyl-3,4-dihydroxy-5-*tert*-butylphenyl)-3-methyl-6-*tert*-butyl-1,2-benzoquinone (H<sub>2</sub>Cat<sup>Me</sup>-BQ<sup>Me</sup>) (356 mg, 1.0 mmol) was dissolved in 10 mL of methanol and slowly added to an aqueous solution of Li(OH) (48 mg, 2 mmol). The solvent was evaporated and the dark-blue powder was dried in a vacuum. Li<sub>2</sub>(SQ<sup>Me</sup>-SQ<sup>Me</sup>) was obtained in 80% yield (293 mg).

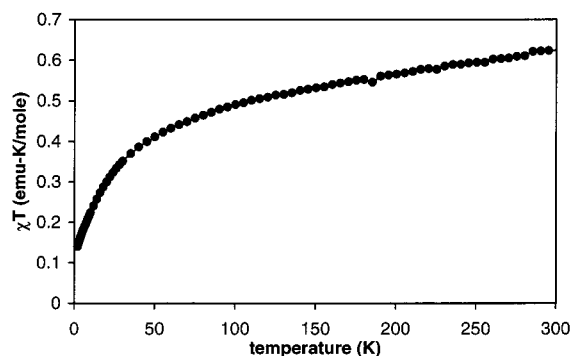
**[Cu(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>].** Li<sub>2</sub>(SQ<sup>Me</sup>-SQ<sup>Me</sup>) (368 mg, 1.0 mmol) dissolved in 10 mL of methanol was slowly added to an aqueous solution of CuCl<sub>2</sub>·2H<sub>2</sub>O. A dark blue-green microcrystalline precipitate of [Cu(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>] (398 mg, 95%) was obtained by filtration, washed with methanol and ether, and air-dried. The product is air-stable and insoluble in organic solvents and water. Anal. Calcd: C, 63.2; H, 6.2. Found: C, 63.8; H, 6.5.

**(bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>).** 4,4'-Di-(3-methyl-6-*tert*-butyl-1,2-benzoquinone) (BQ<sup>Me</sup>-BQ<sup>Me</sup>) (0.354 g, 1.0 mmol) and 2,2'-bipyridine (0.156 g, 1.0 mmol) were dissolved in 50 mL of degassed THF. Excess copper metal (shavings) was added to the solution, and the reaction was allowed to proceed at room temperature over a period of 7 days. Dark-green crystals of (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>) were obtained (0.384 g, 67%), washed with THF, and air-dried. Anal. Calcd: C, 63.2; H, 6.2; Cu, 11.1. Found: C, 63.8; H, 6.5; Cu, 11.0.

**Crystallographic Characterization of (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>).** Crystals of (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>) were obtained by slow evaporation of a dichloromethane solution of the complex. They form in the triclinic space group  $P\bar{1}$  in a unit cell of the dimensions given in Table 1. Data were collected using a Brüker SMART CCD diffractometer at 176(2) K. The structure was solved using direct methods. Refinement converged with *R*(*F*) = 0.061 and *R*<sub>w</sub>(*F*<sup>2</sup>) = 0.114.

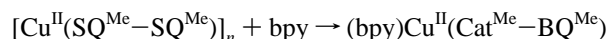
### Results and Discussion

The direct reaction between metallic Cu and BQ<sup>Me</sup>-BQ<sup>Me</sup> occurs slowly; an alternative synthesis is described in the Experimental Section. In this procedure the dilithium salt of the doubly reduced dibenzoquinone is added to an aqueous solution of CuCl<sub>2</sub> to give a microcrystalline product that is identical to the polymer formed by the direct reaction between Cu and BQ<sup>Me</sup>-BQ<sup>Me</sup>. The results of magnetic characterization on the polymer are shown in Figure 1. From room temperature to approximately 50 K,  $\chi T$  decreases almost linearly from a value of 0.7 to 0.4 emu K mol<sup>-1</sup>. Below 50 K the rate of decrease becomes sharper to a value of 0.14 at 2 K. The value for the magnetic moment at 300 K is close the value for two unpaired electrons, and the value at 2 K is less than the value

**Figure 1.** Plot of  $\chi T$  vs temperature (K) for the [Cu<sup>II</sup>(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>] polymer.

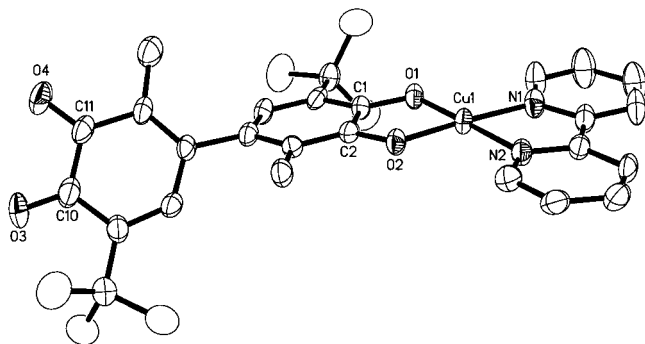
for one unpaired electron per Cu(BQ<sup>Me</sup>-BQ<sup>Me</sup>) subunit. It has not been possible to grow single crystals of the polymer that are of sufficient size for crystallographic characterization. However, the features of Cu(3,6-DBSQ)<sub>2</sub> and {[TiMe<sub>2</sub>(thf)<sub>2</sub>-(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>} provide insight on structure.<sup>10,12</sup> The square planar geometry of Cu(3,6-DBSQ)<sub>2</sub> is the most probable structure for the -(SQ)Cu<sup>II</sup>(SQ)- unit of the [Cu(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>] polymer. The twist between SQ<sup>Me</sup>-SQ<sup>Me</sup> ring planes results in a linear chain of noncoplanar Cu(SQ)<sub>2</sub> units rotated by the dihedral angle between rings of the SQ<sup>Me</sup>-SQ<sup>Me</sup> ligand. Magnetic interactions within subunits of the polymer include exchange between the metal ion and the radical ligands [Cu-SQ], coupling between radical ligands through the metal [SQ-SQ<sub>inter</sub>], and coupling between SQ radicals of the same bridging ligand [SQ-SQ<sub>intra</sub>]. From observations on Cu(3,6-DBSQ)<sub>2</sub> and {[TiMe<sub>2</sub>(thf)<sub>2</sub>-(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>} all three interactions are expected to be strong and collectively responsible for the temperature dependence of the magnetic moment. Competing ferromagnetic [Cu-SQ] and antiferromagnetic [SQ-SQ] interactions make precise quantitative interpretation of the magnetic data impossible. A similarity to the temperature-dependent magnetic properties of Cu(3,6-DBSQ)<sub>2</sub> points strongly to a planar structure for the -(SQ)Cu<sup>II</sup>(SQ)- subunits of the polymer.

The insoluble [Cu(SQ<sup>Me</sup>-SQ<sup>Me</sup>)<sub>n</sub>] polymer slowly dissolves in a dichloromethane solution containing 2,2'-bipyridine to give dark-green crystals of the monomeric bpy addition product.



An alternative synthetic procedure involving the direct reaction of BQ<sup>Me</sup>-BQ<sup>Me</sup>, bpy, and metallic copper is described in the Experimental Section. Crystallographic characterization has indicated that bipyridine coordination to Cu(SQ<sup>Me</sup>-SQ<sup>Me</sup>) subunits of the polymer gives the (bpy)Cu<sup>II</sup>(Cat<sup>Me</sup>-BQ<sup>Me</sup>) monomer shown in Figure 2. Structural features contained in Table 2 show that the bis(quinone) ligand is chelated to copper through catecholate oxygens that result from the unsymmetrical shift in charge distribution upon bipyridine coordination. Carbonyl vibrations for the uncoordinated BQ region of the ligand appear at 1660 and 1685 cm<sup>-1</sup> in the infrared, and the EPR spectrum is typical of d<sup>9</sup> Cu(II).<sup>13</sup> Solution and glass EPR spectra

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- (13) EPR spectra of (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>): powder; *g*<sub>||</sub> = 2.186, *g*<sub>⊥</sub> = 2.044, *A*<sub>||</sub> = 92 G (seven lines, two equivalent Cu nuclei), Δ*M*<sub>s</sub> = two transition (seven lines, two equivalent Cu nuclei); chloroform (solution, *T* = 293 K), *g*<sub>iso</sub> = 2.099, *A*<sub>iso</sub>(<sup>63,65</sup>Cu) = 92.7 G, *A*<sub>iso</sub>(<sup>14</sup>N) = 11.4 G; chloroform/toluene (glass, *T* = 140 K), *g*<sub>||</sub> = 2.198, *g*<sub>⊥</sub> = 2.049, *A*<sub>||</sub>(<sup>63,65</sup>Cu) = 207 G, *A*<sub>⊥</sub>(<sup>63,65</sup>Cu) = 36 G, *A*<sub>||</sub>(<sup>14</sup>N) = 10.5 G, *A*<sub>⊥</sub>(<sup>14</sup>N) = 12 G.

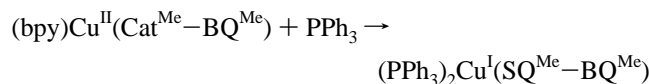


**Figure 2.** View of one (bpy)Cu<sup>II</sup>(Cat<sup>Me</sup>-BQ<sup>Me</sup>) complex molecule.

**Table 2.** Selected Averaged Bond Lengths (Å) for (bpy)Cu(Cat<sup>Me</sup>-BQ<sup>Me</sup>)

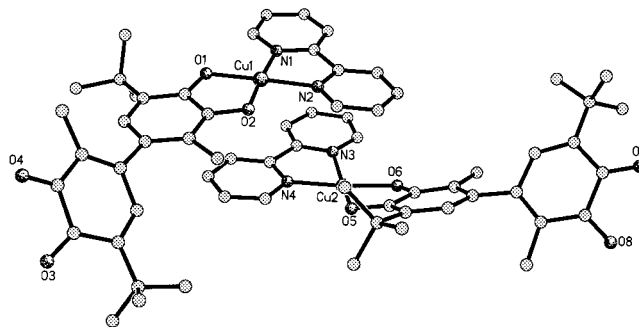
Cu-N	1.966(4)
Cu-O	1.884(3)
C-O <sub>Cat</sub>	1.358(7)
C-O <sub>BQ</sub>	1.220(6)
C1-C2 <sub>Cat</sub>	1.421(7)
C10-C11 <sub>BQ</sub>	1.531(7)
C-C <sub>bridge</sub>	1.470(6)
ring <sub>Cat</sub> -ring <sub>BQ</sub> dihedral angle	49.5°

show the anisotropy and hyperfine coupling of a monomeric complex, but powder spectra contain a weak half-field signal split into seven hyperfine lines associated with a weakly coupled copper dimer. The crystal structure consists of two independent complex molecules paired through their Cu(bpy) regions (Figure 3). Separation between planes is 3.2 Å, a distance that is apparently sufficient to promote weak exchange. Toluene solutions of (bpy)Cu<sup>II</sup>(Cat<sup>Me</sup>-BQ<sup>Me</sup>) react with triphenylphosphine or 2,6-dimethylphenylisonitrile to give species that exhibit radical semiquinone EPR spectra.<sup>14</sup> The product obtained with PPh<sub>3</sub>,



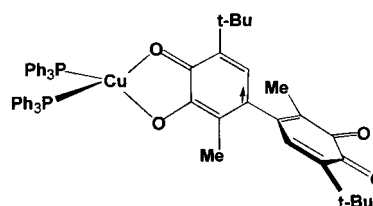
shows a hyperfine coupling pattern consisting of contributions from the copper, two equivalent phosphorus nuclei, and a single ring proton. On the basis of related coligand-dependent shifts

(14) EPR spectrum of (PPh<sub>3</sub>)<sub>2</sub>Cu(SQ<sup>Me</sup>-BQ<sup>Me</sup>): toluene,  $g_{\text{iso}} = 2.0072$ ,  $A(^{63,65}\text{Cu}) = 10.5$  G,  $A(^{31}\text{P}) = 17.5$  G,  $A(^1\text{H}) = 3.1$  G.



**Figure 3.** View of the pairing interaction between bpy ligands of adjacent (bpy)Cu<sup>II</sup>(Cat<sup>Me</sup>-BQ<sup>Me</sup>) complex molecules leading to Cu-Cu coupling in the solid-state EPR spectrum.

in charge distribution observed previously for copper complexes containing quinone ligands, we formulate these products as L<sub>2</sub>-Cu<sup>I</sup>(SQ<sup>Me</sup>-BQ<sup>Me</sup>) species.<sup>11</sup>



The quinone ligands are unique in their ability to reversibly exchange charge with a chelated transition metal ion.<sup>15</sup> In the form of radical semiquinones they exhibit M-SQ and SQ-SQ magnetic interactions.<sup>2</sup> Observations obtained with the bis-(quinone) ligand show that these properties may carry over to the complexes of polyquinone ligands.

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**Supporting Information Available:** X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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