

# Notes

## Ferromagnetically Coupled Bis(semiquinone) Ligand Enforces High-Spin Ground States in Bis-metal Complexes

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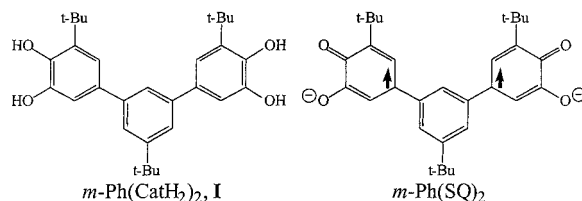
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### Introduction

One motif for preparing molecule-based magnetic materials is the so-called metal–radical approach, i.e., design of an extended lattice containing paramagnetic metal ions whose mutual magnetic interactions are determined by appropriate bridging radical ligands. This strategy has been applied successfully using nitronyl–nitroxide ligands,<sup>1,2</sup> di- and trinitroxide ligands,<sup>3,4</sup> and the TCNE<sup>•-</sup> ligand.<sup>5,6</sup>

Metal *o*-semiquinones are potential candidates for obtaining magnetic solids, provided that an appropriate criterion for designing poly-*o*-semiquinone ligands is used. The approach used by one of us, in agreement with the work developed in the design of high-spin organic molecules,<sup>7,8</sup> is to attach two *o*-semiquinone (SQ) units to a common linker fragment known to couple unpaired electrons in a ferromagnetic fashion.<sup>9–14</sup> The synthesis of the *m*-xylylene-type ligand 1,3-bis(3',4'-dihydroxy-

5'-*tert*-butylphenyl)-5-*tert*-butylbenzene (*m*-Ph(CatH<sub>2</sub>)<sub>2</sub>, **I**) has



been reported recently,<sup>10</sup> and EPR experiments suggest that the dianionic bis(semiquinone), *m*-Ph(SQ)<sub>2</sub>, is a triplet ground state.<sup>10,11,15</sup>

In the past some of us showed that Ni(CTH)(DBSQ)Y (CTH = D,L-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, DBSQ = 3,5-di-*tert*-butylsemiquinone, Y = ClO<sub>4</sub>, PF<sub>6</sub>) and Cu(Me<sub>3</sub>[12]N<sub>3</sub>)(DBSQ)Y (Me<sub>3</sub>[12]N<sub>3</sub> = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene) complexes are characterized by quartet and triplet ground-states, respectively, arising from the ferromagnetic coupling of the metal ions with the radical ligand.<sup>16,17</sup> In a similar fashion, the Cr(CTH)(DBSQ)Y<sub>2</sub> complex was shown to be a triplet ground state arising from the antiferromagnetic coupling of the two magnetic centers.<sup>18</sup> With these metal–radical interactions in mind, we prepared the dinuclear nickel(II), chromium(III), and copper(II) complexes using the above bis(semiquinone) ligand with the aim of exploring the possibility of obtaining complexes characterized by septet, quintet, and quintet electronic states, respectively.

### Results and Discussion

The reactions of **I** with basic solutions containing the above nickel and copper macrocycle acceptors under inert atmosphere were followed by aerial oxidation. This procedure yielded solutions containing the [Ni<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> and [Cu<sub>2</sub>(Me<sub>3</sub>[12]N<sub>3</sub>)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> complexes, which in turn were precipitated as the hexafluorophosphate salts. The same procedure using chromium(II)–CTH led to the isolation of Cr<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(Cat)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>) (Cat = catecholate), which was converted to the bis(semiquinone) derivative [Cr<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)](PF<sub>6</sub>)<sub>4</sub>·2H<sub>2</sub>O by treatment with cerium(IV). All attempts at obtaining crystals suitable for structural analysis were unsuccessful. However, the bis(semiquinone) character of the ligand in the isolated complexes is clearly supported by the magnetic, electrochemical, and spectral properties of the three isolated complexes, as will be discussed below. Therefore, it is postulated that these complexes contain dinuclear cations in which the metal ions are bridged by the bisbidentate *m*-Ph(SQ)<sub>2</sub>

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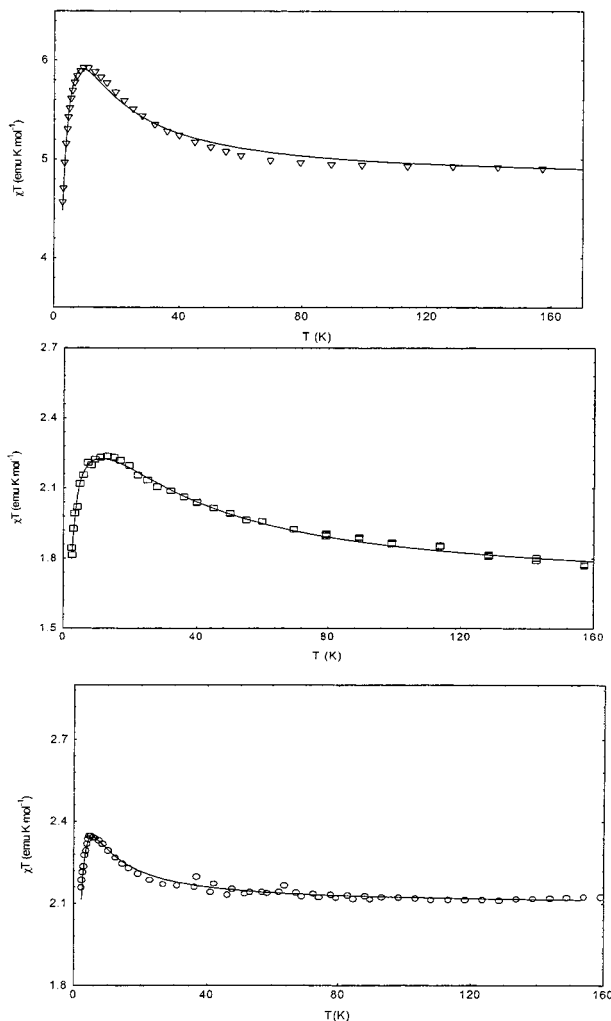
(15) A linear Curie plot was observed for [*m*-Ph(SQ)<sub>2</sub>][NBu<sub>4</sub>]<sub>2</sub>.<sup>10</sup> This observation is also consistent with *J* = 0, i.e., a singlet–triplet degeneracy. *The Chemistry of Quinonoid Compounds*; Berson, J. A., Ed.; John Wiley & Sons: New York, 1988; Vol. II, p 473.

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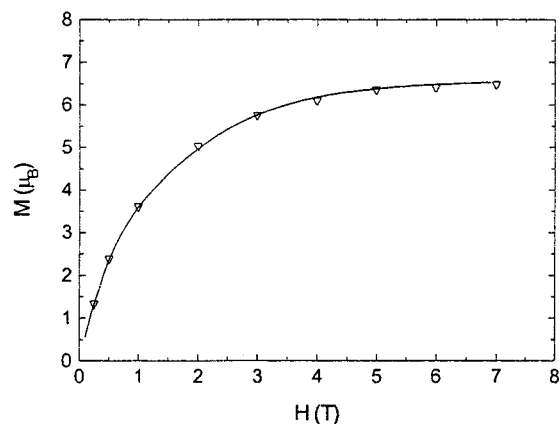




**Figure 3.** Temperature dependence of  $\chi_M T$  for Ni derivative (top), Cu derivative (center), and Cr derivative (bottom) and best-fit curves obtained with the parameters reported in the text.

different population of the  $M_s$  states due to zero-field splitting and saturation effects.

The temperature dependence of the magnetic susceptibility of  $[\text{Ni}_2(\text{CTH})_2(m\text{-Ph}(\text{SQ})_2)](\text{PF}_6)_2$  in the range 4–150 K is shown in Figure 3, top. The  $\chi_M T$  vs  $T$  curve is essentially flat in the range 100–150 K, the value being  $4.9 \text{ emu K mol}^{-1}$ , and increases with decreasing temperature, reaching a value of  $6.2 \text{ emu K mol}^{-1}$  at 11 K and 1.0 T. This behavior is consistent with an incompletely populated septet electronic ground state ( $S = 3$ ) arising from the ferromagnetic coupling of the four magnetic centers characterizing the complex. We point out that the mononuclear  $[\text{Ni}(\text{CTH})(\text{DBSQ})]\text{PF}_6$  complex shows a  $\chi_M T$  value of  $2.28 \text{ emu K mol}^{-1}$  in the temperature range 4–300 K as a result of a strong ferromagnetic interaction between the paramagnetic metal ion and the semiquinone radical ligand. Thus, a value equal to  $4.5\text{--}4.6 \text{ emu K mol}^{-1}$  ( $2 \times 2.28 \text{ emu K mol}^{-1}$ ) was expected for the present dinuclear derivative if the two paramagnetic nickel(II)–SQ moieties were uncorrelated. The observed experimental behavior, therefore, suggests that a further magnetic interaction occurs, leading to a ferromagnetic interaction among the four magnetic centers, and leads to a septet electronic ground-state. Following the guidelines discussed above, the experimental data were fitted with a Heisenberg–Dirac–van Vleck  $\chi_M T$  expression<sup>20</sup> valid for four interacting



**Figure 4.**  $M$  vs  $H$  for the nickel derivative at 2.3 K. The line is the theoretical curve obtained with the parameters reported in the text.

spins and a weak intermolecular interaction,  $\theta$ , yielding  $g = 2.22$ ,  $J_1 > 400 \text{ cm}^{-1}$ ,  $J_2 = +27 \text{ cm}^{-1}$ , and  $\theta = -0.33 \text{ K}$ . It should be noted that with these parameters, the  $S = 2$  state is lying only  $9 \text{ cm}^{-1}$  above the ground state and one  $S = 1$  and  $S = 0$  are lying only within  $18 \text{ cm}^{-1}$ . The low experimental value of the  $\chi_M T$  can then be attributed to the incomplete population of the ground spin-state.

To rule out any other possibility, we performed  $M$  vs  $H$  measurements at low  $T$  (Figure 4). At high field the magnetization is almost completely saturated, showing a value of  $6.5 \mu_B$  at 7 T and 2.1 K. This is in nice agreement with the expected saturation value of  $6.6 \mu_B$  for an  $S = 3$  with  $g = 2.2$ . The magnetization curve was satisfactorily reproduced by considering the relative populations of the ground and first excited states and a  $D$  value of  $0.6 \text{ cm}^{-1}$  for the ground state.

The temperature dependence of the magnetic susceptibility of the copper derivative is shown in Figure 3, center. The  $\chi_M T$  vs  $T$  curve increases with decreasing temperature, reaching a maximum at 13 K. Fitting of the data using the above four-spin Hamiltonian yields best-fit values of  $g = 2.106$ ,  $J_1 = +34.7 \text{ cm}^{-1}$ ,  $J_2 = +6.3 \text{ cm}^{-1}$ , and  $\theta = -0.55 \text{ K}$ , thus indicating a quintet electronic ground state with lower multiplicity levels that are still significantly populated at low  $T$ . As in the nickel(II) case, this result arises from the ferromagnetic coupling of the four magnetic centers in the molecule.

Finally, the magnetic properties of the chromium derivative (Figure 3, bottom) can be interpreted by assuming again a quintet ground-state of the molecule. The best-fit parameters were  $g = 1.99$ ,  $J_1 < -400 \text{ cm}^{-1}$ ,  $J_2 = +32 \text{ cm}^{-1}$ , and  $\theta = -0.25 \text{ K}$ . As expected,<sup>18,21,22</sup> a strong antiferromagnetic coupling characterizes the chromium(III)–SQ interaction, whereas the two SQ halves experience a weaker ferromagnetic interaction similar to the one observed in the nickel(II) complex.

It should be pointed out that for the nickel and chromium complexes the  $J_1$  values are the same as the corresponding values observed for mononuclear metal–semiquinone analogues. The  $J_1$  value observed for the copper complex is rather low when compared with the value of  $+104 \text{ cm}^{-1}$  observed for the mononuclear  $\text{Cu}(\text{DBSQ})$  analogue. This is most likely due either to poorer metal–semiquinone overlap or to the fact that the orthogonality between the magnetic orbitals of the paramagnetic centers is less rigorously maintained in this dinuclear complex.

The intraligand exchange coupling in  $m\text{-Ph}(\text{SQ})_2$  is ferromagnetic, in agreement with the connectivity of the spin coupler.

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Considering the spin densities of the semiquinone group<sup>23</sup> and the exchange parameter for *m*-xylylene,<sup>24</sup> the expected  $J_{\text{SQ-SQ}}$  ( $J_2$ ) value should be larger than those derived from the  $\chi_M T$  plots presented here. On the basis of the precedent for  $J$  modulation due to bond torsions in organic biradicals,<sup>8</sup> we propose that torsions between SQ and *m*-phenylene units in *m*-Ph(SQ)<sub>2</sub> could be responsible for the small ferromagnetic  $J$  values. If this hypothesis holds, this mechanism seems particularly efficient for offering an explanation of the small  $J_2$  value observed for the copper complex.

This finding is in agreement with the recently reported investigation on dioxolene-bridged dimolybdenum(V) derivatives.<sup>25</sup> These calculations confirm the role of the dihedral angle between the planes of the SQ rings in determining the value of the ferromagnetic coupling constant.<sup>8</sup> In agreement with these calculations it can also be suggested that in the present case the ferromagnetic coupling characterizing the *m*-Ph(SQ)<sub>2</sub> ligand results essentially from a spin polarization mechanism.

These data show how an appropriate strategy in designing semiquinone ligands (like nitroxides)<sup>3,4</sup> can be used to fix the magnetic properties of a collection of paramagnetic centers.

### Experimental Section

The nickel and copper complexes were prepared using the same procedure previously described for the DBSQ derivatives.<sup>16,17</sup> The reaction of Ni(CTH)(PF<sub>6</sub>)<sub>2</sub> and Cu<sub>2</sub>(Me<sub>3</sub>[12]N<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> with **I** in basic methanol under inert atmosphere was followed by aerial oxidation. The resulting suspension was filtered, and aqueous solutions of KPF<sub>6</sub> were added to the filtrates. The crude products were recrystallized from dichloromethane–hexane mixtures. The reaction of Cr(CTH)Cl<sub>2</sub> with **I** in basic methanol yielded the bis(catecholate) derivative Cr<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(Cat)<sub>2</sub>)(PF<sub>6</sub>)<sub>2</sub>. This compound was purified by chromatography on silica gel using dichloromethane–acetone as eluent and then isolated as bis(semiquinone) complex Cr<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)(PF<sub>6</sub>)<sub>4</sub>·2H<sub>2</sub>O after oxidation with cerium(IV). Anal. Calcd for Ni<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)(PF<sub>6</sub>)<sub>2</sub>: C<sub>62</sub>H<sub>106</sub>F<sub>12</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>4</sub>P<sub>2</sub> requires C, 51.93;

H, 7.46; N, 7.82. Found: C, 52.53; H, 7.86; N, 7.62. Anal. Calcd for Cu<sub>2</sub>(Me<sub>3</sub>[12]N<sub>3</sub>)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)·2H<sub>2</sub>O: C<sub>54</sub>H<sub>88</sub>Cu<sub>2</sub>F<sub>12</sub>N<sub>6</sub>O<sub>6</sub>P<sub>2</sub> requires C, 48.63; H, 6.60; N, 6.31. Found: C, 48.50; H, 6.42; N, 6.09. Anal. Calcd for Cr<sub>2</sub>(CTH)<sub>2</sub>(*m*-Ph(SQ)<sub>2</sub>)(PF<sub>6</sub>)<sub>4</sub>·2H<sub>2</sub>O: C<sub>62</sub>H<sub>110</sub>Cr<sub>2</sub>F<sub>24</sub>N<sub>8</sub>O<sub>6</sub>P<sub>4</sub> requires C, 42.62; H, 6.35; N, 6.41. Found: C, 42.91; H, 6.44; N, 6.29. The temperature dependence of the magnetic susceptibilities of the samples between 2.5 and 250 K was measured using a Metronique MS02 SQUID magnetometer with an applied field of 1.0 T. Data were corrected for sample holder contribution and diamagnetism of the sample using standard procedures. Magnetization measurements of nickel derivative were performed at 2.3 K with field up to 7 T using the same instrument.

Finally, the susceptibilities data were fit by minimizing the sum of the squares of the deviation of the computed  $\chi T$  values from the experimental values, using a simplex minimization procedure. The theoretical susceptibilities were calculated by employing CLUMAG.<sup>26</sup>

Electronic spectra were recorded in the range 5000–30000 cm<sup>-1</sup> on a Perkin-Elmer Lambda 9 spectrophotometer. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel model 553 potentiostat equipped with Amel 860, 560, and 568 elements) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). Before each experiment the acetonitrile solutions were carefully deaerated with an argon flow. All potentials are reported for cyclic voltammograms of 10<sup>-3</sup> M solutions of the complexes as referenced versus ferrocinium/ferrocene couple. Under the experimental conditions used (25 °C, 0.1 M NBu<sub>4</sub>PF<sub>6</sub>) this couple lies at +0.455 V vs SCE.

UV–vis, CH<sub>3</sub>CN, cm<sup>-1</sup> (ε): Ni: 10 900 sh, 12 100 (1100), 13 400 sh, 20 100 (4900), 26 450 (23 100). Cu: 10 500 sh, 11 800 sh, 13 200 (1250), 17 400 sh, 20 900 (7200), 26 500 (24 000). Cr: 9600 sh, 10 900 (750), 12 200 sh, 14 600 (5050), 15 000 sh, 15 900 sh, 18 800 (7900), 20 200 (7750), 27 400 (16 000).

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