

**Low-Energy Cobalt(III)–Catechol Electron Transfer. Subtle Coligand Bonding Effects for Co<sup>III</sup>(N-N)(3,6-DBSQ)(3,6-DBCat) (N-N = 1,10-Phenanthroline, 5-Nitro-1,10-phenanthroline; DBSQ = Di-*tert*-butylsemiquinonato; DBCat = Di-*tert*-butylcatecholato)**

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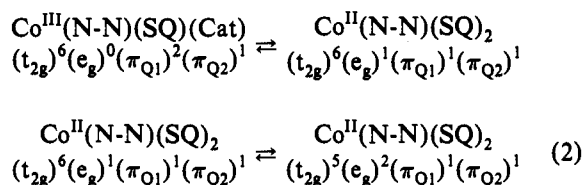
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Bistable molecules offer potential for use as sensors<sup>1</sup> and switches in molecular electronic devices.<sup>2</sup> Several years ago we reported that a complex of cobalt containing quinone ligands exhibited facile metal–quinone electron transfer in solution.<sup>3</sup> The complex was found to exist in a Co(III) form, Co<sup>III</sup>(bpy)(3,5-DBSQ)(3,5-DBCat), in the solid state at room temperature (DBSQ = di-*tert*-butylsemiquinonato; DBCat = di-*tert*-butylcatecholato). In toluene solution an equilibrium between Co(III) and Co(II) species (eq 1) was observed from changes in magnetism and magnetic resonance spectra. Tautomeric forms



of the complex are related by the transfer of an electron between the metal and a chelated quinone ligand, and magnetic measurements have been used to show that the electron-transfer process may be observed for Co(N-N)(SQ)(Cat) complexes in the solid state.<sup>4,5</sup> Since this initial report, quinone complexes containing other metals have been observed to show tautomeric equilibria.<sup>6</sup> In cases where electron transfer is accompanied by a structural change and complex units are linked in an extended crystal lattice, unique thermo- and photophysical properties have been observed.<sup>4,7</sup>

Tautomers shown in eq 1 are the products of a two-step process, electron transfer and Co(II) spin crossover (eq 2). Properties



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that influence either of these processes may be used to modulate the Co(III)/Co(II) transition temperature. We now describe experiments on complexes prepared with the 9,10-phenanthroline (phen) coligand that show the subtleties of coligand substituent effects.

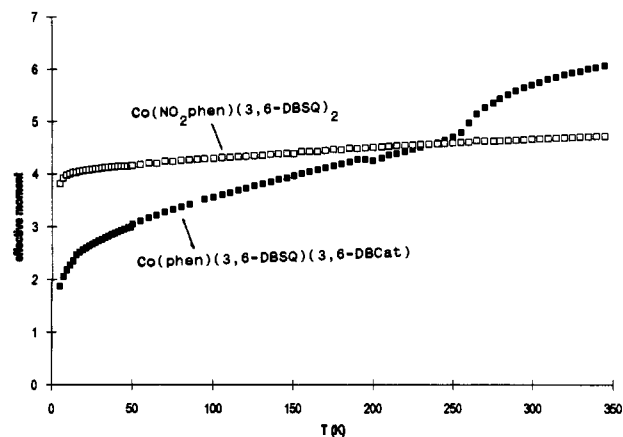
9,10-Phenanthroline has been used as a coligand in the synthesis of Co<sup>III</sup>(phen)(3,6-DBSQ)(3,6-DBCat).<sup>8</sup> Spectroscopic characterization of the complex in toluene solution has shown that the Co(III) form present at 180 K has visible transitions at 600 and 700 nm, while the Co(II) form present in solution at room temperature shows bands at 500, 560, and 850 nm. Spectral measurements over a range of temperatures have shown that the Co(III)/Co(II) transition temperature for Co(phen)(3,6-DBSQ)(3,6-DBCat) in toluene solution is 265 K, slightly below the transition temperature of Co(bpy)(3,6-DBSQ)(3,6-DBCat) ( $T_c = 275$  K).<sup>9</sup> Magnetic measurements on a solid sample of the complex (Figure 1) show the transition from  $S = 1/2$  Co<sup>III</sup>(phen)(3,6-DBSQ)(3,6-DBCat), present at low temperature, to high-spin Co<sup>II</sup>(phen)(3,6-DBSQ)<sub>2</sub>. Limiting values for the magnetic moment are 6.04  $\mu_B$  at 340 K and 1.78  $\mu_B$  at 5 K. The Co(III)/Co(II) transition in the solid state occurs over a broad temperature range, similar to Co(bpy)(4-MeO-3,6-DBSQ)(4-MeO-3,6-DBCat), and different from Co(bpy)(3,5-DBSQ)(3,5-DBCat), Co(bpy)(3,6-DBSQ)(3,6-DBCat), and Co(phen)(3,5-DBSQ)(3,5-DBCat), which undergo relatively sharp transitions.<sup>4,5</sup> Metal  $d\sigma$  and  $d\pi$  electrons interact differently with the unpaired SQ  $\pi$  spins of Co<sup>II</sup>(N-N)(SQ)<sub>2</sub>, and the resulting spin states may contribute to the complicated magnetic behavior of the Co(II) forms of these complexes at higher temperatures. Optical spectra recorded on a solid sample of Co<sup>III</sup>(phen)(3,6-DBSQ)(3,6-DBCat) in the infrared region show an intense transition at 2450 nm. Experiments have been carried out to show the temperature-dependent correlation between changes in the intensity of this band with changes in magnetism, and Figure 2 shows the reversible decrease in intensity with increasing temperature. This intense, low-energy transition, which has been tentatively assigned as a Cat → Co(III) charge-transfer band, has been observed for other Co(III) complexes of the Co<sup>III</sup>(N-N)(SQ)(Cat) series and appears as a general property for the cobalt complexes of this charge distribution.<sup>9</sup>

In striking contrast, Co(NO<sub>2</sub>-phen)(3,6-DBSQ)<sub>2</sub> shows no transition to the Co(III) form in the solid state. This is clear from its magnetic behavior, which remains nearly invariant at a high-spin value of 4.6  $\mu_B$  through the temperature range shown in Figure 1. It shows no low-energy charge-transfer band in the solid state, but does show an intense transition in the 800-nm region that appears characteristically for members of the Co<sup>II</sup>(N-N)(SQ)<sub>2</sub> series.<sup>9</sup> In toluene solution the 800-nm transition persists unchanged down to 200 K. At this temperature a band at 600 nm begins to develop, indicating the onset of the Co(III)/Co(II) transition. The solution transition temperature of Co(NO<sub>2</sub>-phen)(3,6-DBSQ)<sub>2</sub> is somewhat below 180 K.

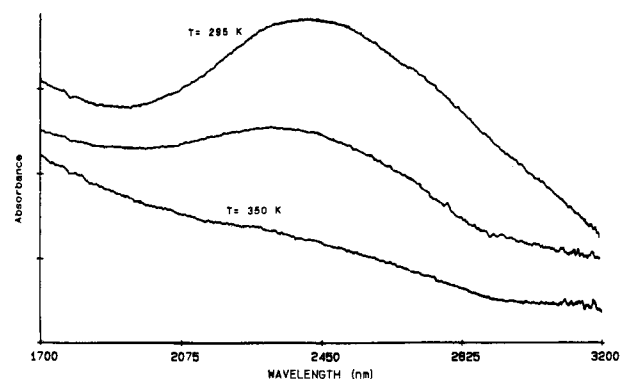
Structural characterization on Co(NO<sub>2</sub>-phen)(3,6-DBSQ)<sub>2</sub> has provided insight on its properties in the solid state.<sup>10</sup> The complex molecule is trigonal prismatic in structure (Figure 3) with a twist

(8) Co(phen)(3,6-DBSQ)(3,6-DBCat): Co<sub>2</sub>(CO)<sub>8</sub> (86 mg, 0.25 mmol) and 1,10-phenanthroline (90 mg, 0.52 mmol) were combined in 30 mL of toluene. The mixture was stirred for 5 min, and 3,6-DBSQ (220 mg, 1.0 mmol) in 30 mL of toluene was added. The mixture was stirred under Ar for 2 h at room temperature. Evaporation of the solvent produced a dark blue residue of the complex in 76% yield. Recrystallization from benzene gave large, dark blue crystals of the complex as the benzene solvate. Similar procedures were used to form the 3,4,7,8-tetramethyl-1,10-phenanthroline (Me<sub>4</sub>phen) and 5-nitro-1,10-phenanthroline (NO<sub>2</sub>-phen) analogs. Crystals of Co(NO<sub>2</sub>-phen)(3,6-DBSQ)<sub>2</sub> suitable for crystallographic characterization were grown by slow evaporation of a toluene solution, giving the complex as a toluene solvate.

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**Figure 1.** Temperature-dependent changes in magnetic moment ( $\mu_B$ ) for  $\text{Co}(\text{NO}_2\text{phen})(3,6\text{-DBSQ})_2$  and  $\text{Co}(\text{phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ .



**Figure 2.** Temperature-dependent changes in the low-energy  $\text{Cat} \rightarrow \text{Co}(\text{III})$  charge-transfer transition of  $\text{Co}(\text{III})(\text{phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  in the solid state (KBr pellet).

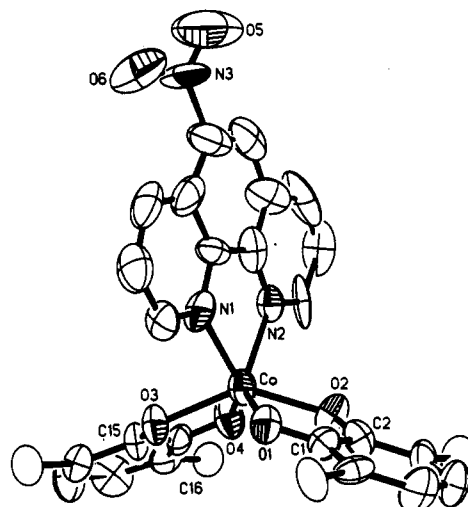
angle of  $3.7^\circ$ . Bond lengths to the metal are typical of  $\text{Co}(\text{II})$ , and the structural features of the 3,6-DBSQ ligands are those of semiquinonate ligands. In contrast,  $\text{Co}(\text{phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  likely has the octahedral  $\text{Co}(\text{III})$  structure of  $\text{Co}(\text{bpy})(3,5\text{-DBSQ})(3,5\text{-DBCat})$ ,  $\text{Co}(\text{phen})(3,5\text{-DBSQ})(3,5\text{-DBCat})$ , and  $\text{Co}(\text{bpy})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ .<sup>3-5</sup> The difference in charge distribution for  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$  and  $\text{Co}(\text{phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  is related to the change in donor strength of the phen and  $\text{NO}_2\text{-phen}$  ligands.<sup>11</sup> Ligand field effects allow high-spin  $\text{Co}(\text{II})$  to be either octahedral or trigonal prismatic, and a few examples of trigonal prismatic  $\text{Co}(\text{II})$  are known.<sup>12</sup> Low-spin  $\text{Co}(\text{III})$  would be expected to be rigidly octahedral.<sup>13</sup> Consequently,  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$  is locked in the  $\text{Co}(\text{II})$  form by its solid-state structure.

(10) X-ray analysis of  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2 \cdot \text{MeC}_6\text{H}_5$ : monoclinic, space group  $Pc$ ,  $a = 12.626(2) \text{ \AA}$ ,  $b = 11.297(2) \text{ \AA}$ ,  $c = 17.974(3) \text{ \AA}$ ,  $\beta = 105.55(1)^\circ$ ,  $V = 2469.9(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $R = 0.054$  for 4012 unique observed reflections. Details of the structure determination are given with the supplementary material.

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**Figure 3.** View of  $\text{Co}(\text{II})(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$ :  $\text{Co}-\text{O}_{\text{av}} = 2.066(6) \text{ \AA}$ ,  $\text{Co}-\text{N}_{\text{av}} = 2.165(7) \text{ \AA}$ ,  $\text{C}-\text{O}_{\text{av}} = 1.267(9) \text{ \AA}$ , twist angle =  $3.7^\circ$ .

The  $\text{Co}(\text{III})/\text{Co}(\text{II})$  transition may be observed by monitoring changes in either magnetic moment or optical spectrum, as techniques that probe different steps in the process described in eq 2. Transition temperatures have been estimated for a series of nitrogen-donor coligands, and the series includes complexes that range from species that remain in the  $\text{Co}(\text{III})$  form to complexes like  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$  that are exclusively  $\text{Co}(\text{II})$ .<sup>9</sup> All members of the series that exist in the  $\text{Co}(\text{III})$  form at any temperature show the characteristic 2500-nm transition, and the range of  $\text{Cat} \rightarrow \text{Co}(\text{III})$  optical charge transfer transition energies is narrow, 2200–2650 nm. Assuming that the range of thermal energies associated with electron transfer is similarly narrow and lower in energy, the differentiating step in eq 2 is the spin transition, rather than electron transfer. Understanding features that can be used to direct these steps separately may be key to the development of complex molecules that exhibit desirable switching properties.

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**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$  (13 pages); listing of observed and calculated structure factors for  $\text{Co}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2$  (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.