

**Bistability of Co<sup>III</sup>(N-N)(3,6-DBSQ)(3,6-DBCat) : Subtle Diimine  
Ligand Effect (N-N=4,7-Dimethyl-1,10-phenanthroline, 5-Chloro-  
1,10-phenanthroline ; DBSQ = Di-*tert*-butylsemiquinonato ;  
DBCat = Di-*tert*-butylcatecholato)**

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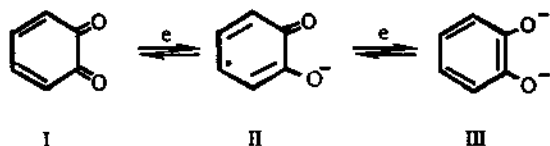
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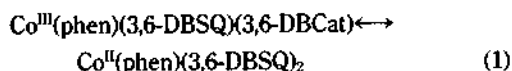
Studies of Co(N-N)(3,6-DBSQ)(3,6-DBCat)(N-N=4,7-dimethyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline; DBSQ = di-*tert*-butylsemiquinonato; DBCat = di-*tert*-butylcatecholato) have been carried out on the bistability by intramolecular cobalt-quinone electron transfer in solid state. The title complexes dominantly exist as Co<sup>III</sup>(N-N)(3,6-DBSQ)(3,6-DBCat) at room temperature and display a significant bistability on temperature variation. Subtle change in optical spectra and magnetic properties is observed when diimine ligands are changed.

### Introduction

The coordination chemistry of the *o*-quinone ligands in three different electronic forms of benzoquinone (BQ) (I), semiquinone (SQ) (II), and catecholate (Cat) (III) has been rich and unusual.<sup>1-3</sup> Many of the interesting and important features of transition metal complexes containing the *o*-qui-



none ligands are related to the similarity in energy between the *o*-quinone  $\pi^*$ -orbitals and the metal *d*-levels.<sup>4-7</sup> Recent papers reported that the electronic distribution between metal atom and the ligand is sensitive to temperature, light, or (solution or solid) state.<sup>8-15</sup> This property is responsible for intense, low-energy charge-transfer transitions that sometimes extend well into infrared region.<sup>8-11</sup> According to previous paper, Co(5-NO<sub>2</sub>-phen)(3,6-DBQ)<sub>2</sub> (3,6-DBQ = 3,6-di-*tert*-butylquinone)<sup>16</sup> exists as Co<sup>II</sup>(5-NO<sub>2</sub>-phen)(3,6-DBSQ)<sub>2</sub> form (5-NO<sub>2</sub>-phen = 5-nitro-1,10-phenanthroline) whereas phen analogue does as Co<sup>III</sup>(phen)(3,6-DBSQ)(3,6-DBCat) form (phen = 1,10-phenanthroline) in the solid state at room temperature.<sup>1</sup> Moreover, for the phen analogue, the bistability between Co<sup>III</sup> and Co<sup>II</sup> species was observed (eq. 1),<sup>1</sup> which was potential for use as sensors and switches in molecular electronic devices.<sup>17-21</sup> Another peculiar characteristic was that all members of the series that existed in the Co<sup>III</sup> form at any temperature showed the unusual low-energy charge-transfer band of approximate 2500 nm.<sup>22</sup>



Thus it appeared that there was a remarkable difference between phen and 5-NO<sub>2</sub>-phen complexes in their electronic distribution. In an effort to scrutinize the electronic effect

of diimine coligands for such a series of complexes, we now describe the solid state properties on complexes prepared with 5-chloro-1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline ligands.

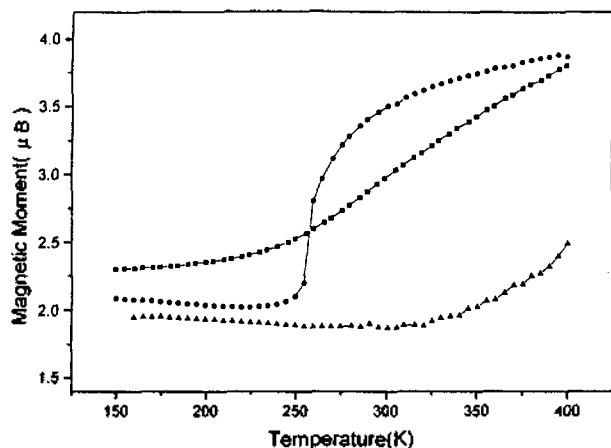
### Experimental

**Materials.** 3,6-Di-*tert*-butylbenzoquinone(3,6-DBBQ) was prepared according to a literature procedure.<sup>23</sup> 5-Chloro-1,10-phenanthroline (Cl-phen) and 4,7-dimethyl-1,10-phenanthroline (Me<sub>2</sub>-phen) were purchased from Aldrich, and dicobaltocarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>) from Alfa.

**Co<sup>III</sup>(Cl-phen)(3,6-DBSQ)(3,6-DBCat).** Co<sub>2</sub>(CO)<sub>8</sub> (86 mg, 0.25 mmol) and 5-chloro-1,10-phenanthroline (107 mg, 0.50 mmol) were combined in 30 mL of toluene. The mixture was stirred for 5 min, and 3,6-DBBQ (220 mg, 1.0 mmol) in 30 mL of toluene was further added. The mixture was then stirred under N<sub>2</sub> for 2 h at room temperature. Evaporation of the solvent produced a dark blue solid of the complex in 89% yield. Recrystallization from toluene gave dark blue crystals of the complex as the toluene solvate. Anal. found (calcd. for C<sub>40</sub>H<sub>47</sub>N<sub>2</sub>O<sub>4</sub>ClCo·2C<sub>7</sub>H<sub>8</sub>): C, 72.20 (72.18); H, 7.16 (7.06); N, 3.10 (3.12). IR (KBr, cm<sup>-1</sup>): 3733 (s), 3055 (s), 2948 (s), 1476 (s), 955 (s).

**Co<sup>III</sup>(Me<sub>2</sub>-phen)(3,6-DBSQ)(3,6-DBCat).** A similar procedure was used to prepare the 4,7-dimethyl-1,10-phenanthroline analog. Anal. found (calcd. for C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub>Co): C, 70.9 (71.27); H, 7.41 (7.40); N, 3.74 (3.96). IR (KBr, cm<sup>-1</sup>): 3937 (s), 3053 (s), 2944 (s), 1476 (s), 953 (s).

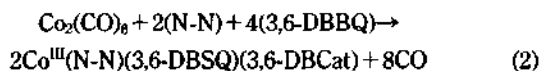
**Physical Measurement.** Elemental analysis (C, H, N) was carried out at the Advanced Analysis Center, KIST. Infrared spectra were obtained in 4400-400 cm<sup>-1</sup> range on a MIDAC 101025 FTIR spectrometer with samples prepared as KBr pellets. NIR spectra were recorded on a Bruker IFS 120 HR as KBr pellets in the range of 7000-2000 cm<sup>-1</sup>. Temperature-dependent magnetic measurements were made on a Quantum Design MPMS-5 SQUID magnetometer. Thermogravimetric analysis (TGA) was performed by using a Perkin Elmer System 4 Thermal Analysis.



**Figure 1.** Temperature-dependent changes in magnetic moment ( $\mu\text{B}$ ) for  $\text{Co}(\text{Cl-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  ( $\blacktriangle$ ) and  $\text{Co}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  ( $\blacksquare$ ) along with  $\text{Co}(\text{phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  ( $\bullet$ ).

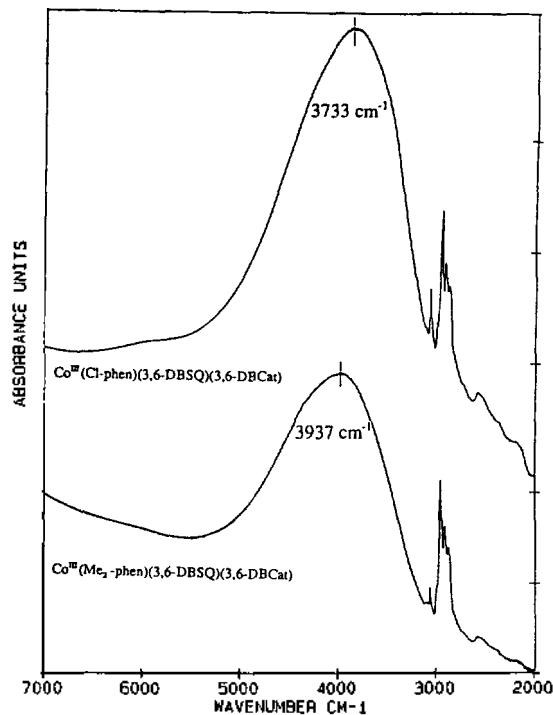
## Results and Discussion

The reaction between  $\text{Co}_2(\text{CO})_8$  and 3,6-di-*tert*-butyl-1,2-benzoquinone carried out in the presence of a stoichiometric equivalent of 5-chloro-1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline resulted in the formation of the present products, which are fairly stable at solid state (eq. 2).

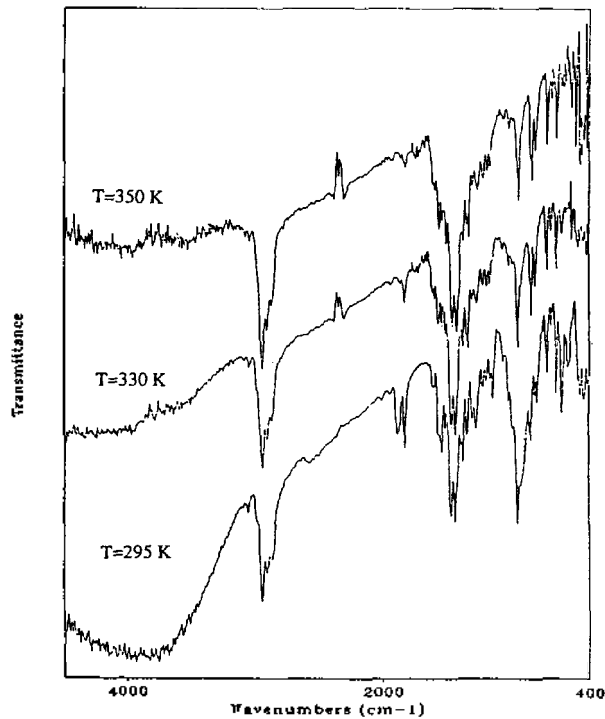


Magnetic measurements<sup>24</sup> measured in the range of 150 K–400 K for the present complexes along with that of phen analog were shown in Figure 1. The magnetic moment of  $\text{Me}_2\text{-phen}$  complex indicates that the  $\text{Co}^{\text{III}}$  charge distribution,  $\text{Co}^{\text{III}}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ , is the dominant form of the complexes in the solid state at temperature below 200 K. In this form, the complex has a single unpaired electron associated with the radical semiquinone ligand and its magnetic moment at 150 K are approximate 2.0  $\mu\text{B}$ . As the sample temperature is increased to above 200 K, magnetic moment changed toward the  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  equilibrium with the formation of  $\text{Co}^{\text{II}}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})_2$ . Coupling between the  $S=3/2$  metal ion and two radical ligands resulted in complicated magnetic behavior. The magnetic moment of 3.9  $\mu\text{B}$  at 400 K is due to weak antiferromagnetic exchange between the  $S=3/2$  metal center and the two  $S=1/2$  ligands. Magnetic moment of the Cl-phen analog is observed in a similar pattern. However, in striking contrast, the spin transition temperature of  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  for the Cl-phen complex was higher (340 K) and much more abrupt presumably owing to delicate electronic difference between the two ligands.

Figure 2 shows the near-IR (NIR) spectra (7000–2000  $\text{cm}^{-1}$ ) of the present complexes at room temperature. The intense low-energy transition, which has been tentatively assigned as a  $\text{Cat} \rightarrow \text{Co}$  atom charge-transfer band as a general property for the  $\text{Co}^{\text{III}}(\text{N-N})(\text{DBSQ})(\text{DBCat})$ ,<sup>1,11,22</sup> has been observed for the present complexes. Thus, for the present complexes, the charge distribution seems to be predominately  $\text{Co}^{\text{III}}(\text{N-N})(\text{DBSQ})(\text{DBCat})$  form at room temperature, which is consistent with the result obtained earlier from the magnetic mo-



**Figure 2.** NIR spectra of  $\text{Co}^{\text{III}}(\text{Cl-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  (top) and  $\text{Co}^{\text{III}}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  (bottom) in the range of 7000–2000  $\text{cm}^{-1}$  at room temperature.



**Figure 3.** Temperature-dependent changes in the intensity of  $\text{Cat} \rightarrow \text{Co}(\text{III})$  charge transfer band of  $\text{Co}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ .

ment measurements. The low-energy band of Cl-phen complex (3733  $\text{cm}^{-1}$ ) appeared to be red shifted by 204  $\text{cm}^{-1}$  compared with that of the  $\text{Me}_2\text{-phen}$  analog (3937  $\text{cm}^{-1}$ ). This

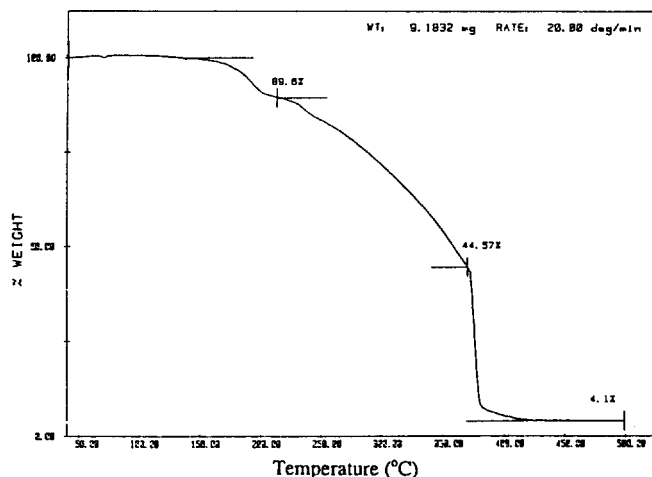


Figure 4. Thermogravimetric curve of  $\text{Co}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ .

shift indicates that the intense low-energy band is also very sensitive to an electronic property of the diimine ligands. In particular, the band of  $\text{Me}_2\text{-phen}$  complex is relatively weaker than that of  $\text{Cl-phen}$  analog owing probably to a bigger ratio of  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  as was seen in the magnetic moment data obtained at 298 K. Figure 3 shows the most prominent change of the optical spectrum with temperature: the intensity of the low-energy band for  $\text{Co}^{\text{III}}(\text{Me}_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$  showed reversible decrease with increasing temperature within the range of easily accessible temperature. Thus, shift in the  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  equilibrium may be monitored from the integration of the band. The temperature dependence of the band is also a conclusive evidence for the bistability of the present complexes.

A typical TGA curve of  $\text{Me}_2\text{-phen}$  complex is shown in Figure 4, indicating that the complex does not degrade up to  $170^\circ\text{C}$  at all ( $T_{10}=213^\circ\text{C}$ ). In addition, the higher degradation-temperature than evaporation-temperature of crystalline-water discloses that the intense low-energy band in optical spectra does not stem from the O-H stretching frequency which may be present as trace water in the sample or KBr. Another important fact from the TGA curve is that the transition between  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  is not accompanied by mass-loss.

In conclusion, the present complexes revealed bistable properties in contrast to the  $\text{NO}_2\text{-phen}$  analog investigated in ref. 1. The bistable properties for a series of the complexes significantly depend on the diimine ligand. It may be assumed that the electronegativity values of functional groups attached to diimine ligands be the key in the development of a molecule that exhibits desirable switching properties in the range of accessible temperature.

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## References

- Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 1127.
- Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.
- Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.
- Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907.
- Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2916.
- Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 1769.
- Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 1088.
- Haga, M.; Dodsworth, E. S.; Lever, A. B. P.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 7413.
- Lange, C. W.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 6582.
- Lange, C. W.; Foldeaki, M.; Nevodchikov, V. I.; Cherkasov, V. K.; Abakumov, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 4220.
- Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229.
- Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.
- Abakumov, G. A.; Nevodchikov, V. I.; Cherkasov *Dokl. Akad. Nauk SSSR* **1984**, *278*, 641.
- Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 880.
- Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221.
- The term *Quinone(Q)* is used for ligands derived from 1,2-di-oxobenzene; irrespective of their oxidation state, i.e., BQ, SQ, and Cat.
- Suski, J.; Largeau, D.; Steyer, A.; Van de Pol, F. C. M.; Blom, F. R. *Sens. Actuators A* **1990**, *A24*, 221.
- Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4192.
- Kahn, O.; Krobert, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718.
- Gourdon, A. *New J. Chem.* **1992**, *16*, 953.
- Krober, J.; Codjovi, E.; Kahn, O.; Groliere, F.; Jay, C. *J. Am. Chem. Soc.* **1993**, *115*, 9810.
- Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.
- Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, E. V.; Ershov, V. V. *Izv. Akad. Nauk SSSR* **1972**, 1594.
- For magnetism studies of benzoquinone complexes, see Dei, A.; Gatteschi, D. *Inorg. Chim. Acta* **1992**, *198-200*, 813.