Bistability of Co^{III}(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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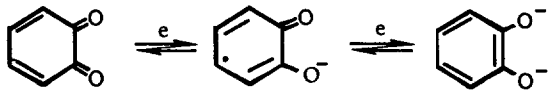
Studies of Co(N-N)(3,6-DBSQ)(3,6-DBCat)(N-N=4,7-dimethyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline; DBSQ=di-*tert*-butylsemiquinonato; DBCat=di-*tert*-butylcatecholato) have been carried out on the bistability by intramolecular cobalt-quinone electron transfer in solid state. The title complexes dominantly exist as Co^{III}(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.[1-3] Many of the interesting and important features of transition metal complexes containing the *o*-qui-



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none ligands are related to the similarity in energy between the *o*-quinone π^*-orbitals and the metal *d*-levels.[4-7] Recent papers reported that the electronic distribution between metal atom and the ligand is sensitive to temperature, light, or (solution or solid) state.[8-15] This property is responsible for intense, low-energy charge-transfer transitions that sometimes extend well into infrared region.[8-11] According to previous paper, Co(5-NO_2-phen)(3,6-DBQ)$_2$ (3,6-DBQ=3,6-di-*tert*-butylquinone)[16] exists as Co^{II}(5-NO_2-phen)(3,6-DBSQ)$_2$ form (5-NO_2-phen=5-nitro-1,10-phenanthroline) whereas phen analogue does as Co^{III}(phen)(3,6-DBSQ)(3,6-DBCat) form (phen=1,10-phenanthroline) in the solid state at room temperature.[1] Moreover, for the phen analogue, the bistability between Co^{III} and Co^{II} species was observed (eq. 1),[1] which was potential for use as sensors and switches in molecular electronic devices.[17-21] Another peculiar characteristic was that all members of the series that existed in the Co^{III} form at any temperature showed the unusual low-energy charge-transfer band of approximate 2500 nm.[22]

$$Co^{III}(phen)(3,6\text{-}DBSQ)(3,6\text{-}DBCat) \longleftrightarrow Co^{II}(phen)(3,6\text{-}DBSQ)_2 \quad (1)$$

Thus it appeared that there was a remarkable difference between phen and 5-NO_2-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.[23] 5-Chloro-1,10-phenanthroline (Cl-phen) and 4,7-dimethyl-1,10-phenanthroline (Me_2-phen) were purchased from Aldrich, and dicobaltoctacarbonyl ($Co_2(CO)_8$) from Alfa.

Co^{III}(Cl-phen)(3,6-DBSQ)(3,6-DBCat). $Co_2(CO)_8$ (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_2 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 $C_{40}H_{47}N_2O_4ClCo \cdot 2C_7H_8$): C, 72.20 (72.18); H, 7.16 (7.06); N, 3.10 (3.12). IR (KBr, cm^{-1}): 3733 (s), 3055 (s), 2948 (s), 1476 (s), 955 (s).

Co^{III}(Me_2-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 $C_{42}H_{52}N_2O_4Co$): C, 70.9 (71.27); H, 7.41 (7.40); N, 3.74 (3.96). IR (KBr, cm^{-1}): 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^{-1} 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^{-1}. 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.

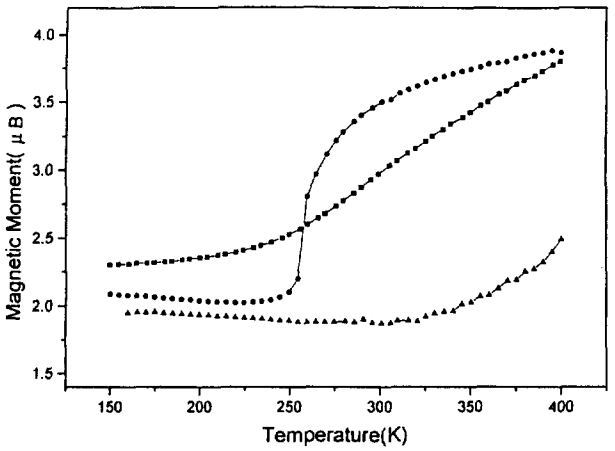

Figure 1. Temperature-dependent changes in magnetic moment (μB) for Co(Cl-phen)(3,6-DBSQ)(3,6-DBCat)(▲) and Co(Me_2-phen)(3,6-DBSQ)(3,6-DBCat)(■) along with Co(phen)(3,6-DBSQ)(3,6-DBCat) (●).

Results and Discussion

The reaction between $Co_2(CO)_8$ 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).

$$Co_2(CO)_8 + 2(N\text{-}N) + 4(3,6\text{-}DBBQ) \rightarrow 2Co^{III}(N\text{-}N)(3,6\text{-}DBSQ)(3,6\text{-}DBCat) + 8CO \quad (2)$$

Magnetic measurements[24] 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 Me_2-phen complex indicates that the Co^{III} charge distribution, $Co^{III}(Me_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$, 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 μB. As the sample temperature is increased to above 200 K, magnetic moment changed toward the Co^{II}/Co^{III} equilibrium with the formation of $Co^{II}(Me_2\text{-phen})(3,6\text{-DBSQ})_2$. Coupling between the $S=3/2$ metal ion and two radical ligands resulted in complicated magnetic behavior. The magnetic moment of 3.9 μB 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 Co^{II}/Co^{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 cm^{-1}) of the present complexes at room temperature. The intense low-energy transition, which has been tentatively assigned as a Cat→Co atom charge-transfer band as a general property for the $Co^{III}(N\text{-}N)(DBSQ)(DBCat)$,[1,11,22] has been observed for the present complexes. Thus, for the present complexes, the charge distribution seems to be predominatly $Co^{III}(N\text{-}N)(DBSQ)(DBCat)$ form at room temperature, which is consistent with the result obtained earlier from the magnetic moment measurements. The low-energy band of Cl-phen complex (3733 cm^{-1}) appeared to be red shifted by 204 cm^{-1} compared with that of the Me_2-phen analog (3937 cm^{-1}). This

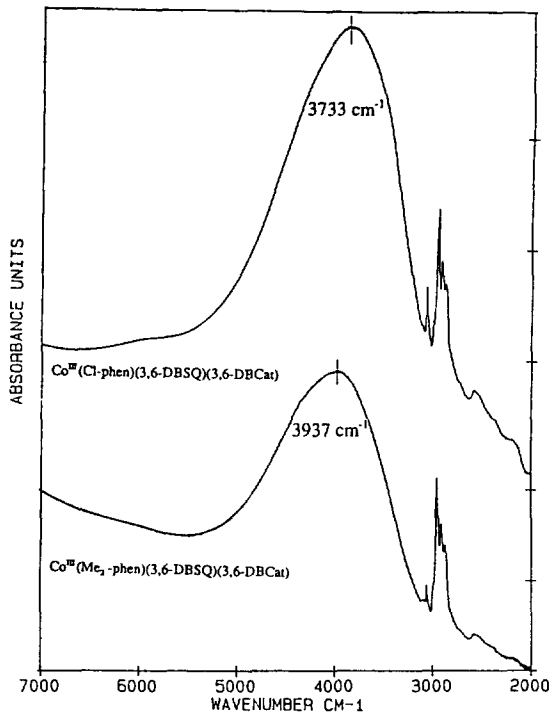

Figure 2. NIR spectra of Co^{III}(Cl-phen)(3,6-DBSQ)(3,6-DBCat) (top) and $Co^{III}(Me_2\text{-phen})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ (bottom) in the range of 7000-2000 cm^{-1} at room temperature.

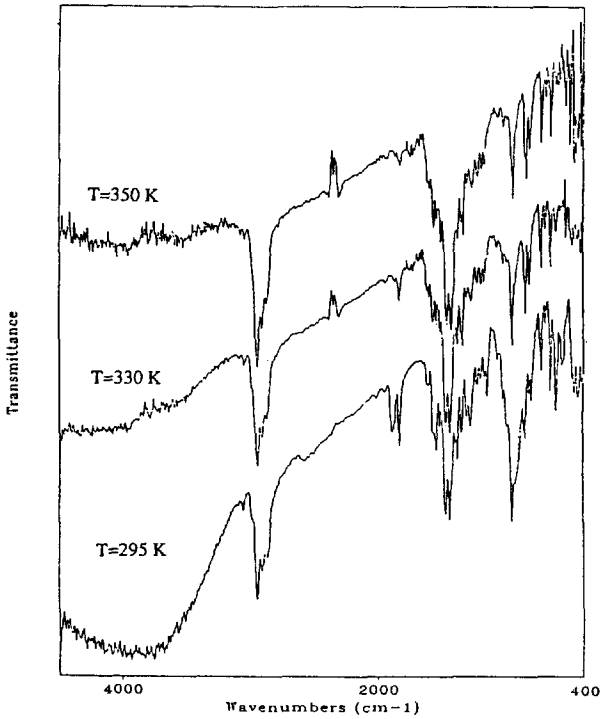

Figure 3. Temperature-dependent changes in the intensity of Cat→Co(III) charge transfer band of Co(Me_2-phen)(3,6-DBSQ)(3,6-DBCat).

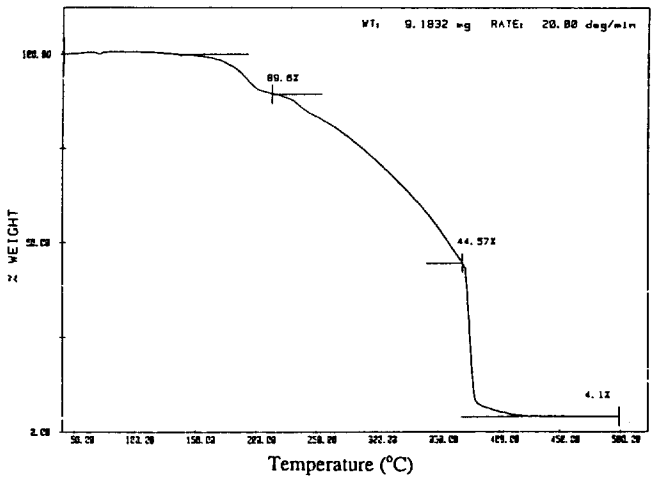

Figure 4. Thermogravimetric curve of Co(Me_2-phen)(3,6-DBSQ)(3,6-DBCat).

shift indicates that the intense low-energy band is also very sensitive to a electronic property of the diimine ligands. In particular, the band of Me_2-phen complex is relatively weaker than that of Cl-phen analog owing probably to bigger ratio of Co^{II}/Co^{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 Co^{III}(Me_2-phen)(3,6-DBSQ)(3,6-DBCat) showed reversible decrease with increasing temperature within the range of easily accessible temperature. Thus, shift in the Co^{II}/Co^{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 Me_2-phen complex is shown in Figure 4, indicating that the complex dose not degradate upto 170℃ at all (T_{10}=213℃). 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 Co^{II}/Co^{III} is not accompanied by mass-loss.

In conclusion, the present complexes revealed bistable properties in contrast to the NO_2-phen analog investigated in ref. 1. The bistable properties for a series of the complexes significantly depend on the diimmine ligand. It may be assummed that the electronegativity values of functional groups attached to diimine ligands be the key in the development of molecule that exhibit desirable switching properties in the range of accessible temperature.

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