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Molecular Switching Coordination Polymers. 4,4'-Chalcogenobispyridine Bridged Cobalt Benzoquinone Complexes

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The reaction of $Co_2(CO)_8$ with 3,6-di-*tert*-butyl-1,2-benzoquinone in the presence of the respective 4,4'-chalcogenobispyridine results in the coordination polymers of $[Co^{III}(4,4'-X(Py)_2)(DBSQ)(DBCat)]_n$ (X = S, Se, Te; Py = pyridine; DBSQ = 3,6-di-*tert*-butylsemiquinone; DBCat = 3,6-di-*tert*-butylcatechol). The title compounds undergo an intramolecular Cat → Co electron transfer, and thus change toward the $[Co^{II}(4,4'-X(Py)_2)(DBSQ)_2]_n$ at elevated temperature. The temperature-switching properties of the compounds directly depend upon the electronegativity of the chalcogen atom of the 4,4'-chalcogenobispyridine coligands. The spectroscopic data disclose that the properties of $[Co^{III}(4,4'-S(Py)_2)(DBSQ)(DBCat)]_n$ and $[Co^{III}(4,4'-Se(Py)_2)(DBSQ)(DBCat)]_n$ are similar each other in contrast to those of $[Co^{III}(4,4'-Te(Py)_2)(DBSQ)(DBCat)]_n$.

Introduction

An important facet in molecular chemistry is the applicability as electronic devices dealing with the treatment and storage of information.[1~3] Such devices have been concerned with the molecular switch properties, which may be defined as a molecular assembly existing under two stable (or metastable) electronic states in a given range of external parameters such as temperature, pressure, light energy, etc.[4~7] Examples of such a molecular switch have been known in the system of intramolecular electron transfer,[8~10] allosteric effect,[6] proton transfer,[11~12] and cis-trans isomerization[13] etc. Among the examples, an intramolecular electron transfer system has been widely investigated in recent years.

Cobalt-quinone complexes of $Co^{III}(N-N)(SQ)(Cat)$, where SQ and Cat are semiquinonate and catecholate forms, respectively, and N-N is a nitrogen donor coligand, exhibited equilibria between Co(III) and Co(II) species (1) in solution and in the solid state.[14~19] The metal ion of $Co^{III}(N-N)(SQ)(Cat)$

$$Co^{III}(N-N)(SQ)(Cat) \rightleftharpoons Co^{II}(N-N)(SQ)_2 \quad (1)$$

is in the form of low-spin Co(III), and $Co^{II}(N-N)(SQ)_2$ contains high-spin Co(II). The equilibrium between the two forms occurs in separate steps involving Cat → Co(III) electron transfer and Co(II) spin transition. Optical charge transfer occured at an unusually low energy of 4000 cm^{-1} region, and the transitions appeared characteristically for the $Co^{III}(N-N)(SQ)(Cat)$ complexes. Both steps of the equilibrium have been sensitive to the balance of quinone and metal orbital energies, and coligand donation effects have been investigated for a series of various bidentate coligands.[20]

In order to understand and expand the chemistry, a series of cobalt-quinone complexes of potentially bridged chalcogenobispyridine have been synthesized and their properties were elucidated based on physicochemical properties.

X = S, Se, Te
4,4'-Chalcogenobispyridine
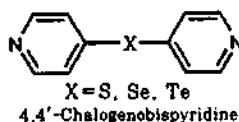
Experimental

Materials and Physical Measurement. 3,6-Di-*tert*-butylbenzoquinone (3,6-DBBQ)[21] and 4,4'-chalcogenobispyridine (chalcogen = S,[22] Se,[23] Te[24]) were prepared according to literature procedures, and dicobaltoctacarbonyl ($Co_2(CO)_8$) was purchased from Strem.

Elemental analysis (C, H, N, S) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in 5000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets. Temperature-dependent magnetic measurements were made on a Quantum Design MPMS-5 SQUID magnetometer. EPR spectra were recorded on a Bruker Quantum Design MPMS 5 and referenced to DPPH as the g value standard. Thermogravimetric analysis (TGA) was performed after drying each sample by using a Stanton Red Croft TG 100.
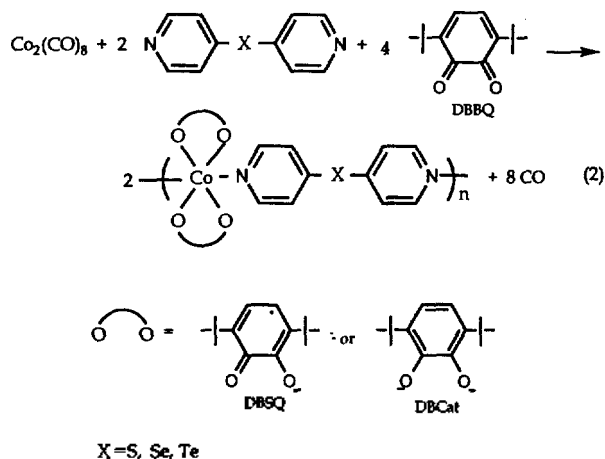
$[Co^{III}(4,4'-S(Py)_2)(3,6-DBSQ)(3,6-DBCat)]_n$. $Co_2(CO)_8$ (171 mg, 0.50 mmol) and 4,4'-thiobispyridine(188 mg, 1.0 mmol) were combined in 50 mL of toluene. The mixture was stirred for 5 min, and 3,6-DBBQ (440 mg, 2.0 mmol) in 30 mL of toluene was further added. The mixture was then stirred under N_2 for 2 hrs at room temperature. The dark violet solid precipitated was filtered and washed with excess hexane. The microcrystalline solid was obtained in 85% (680 mg) yield. Anal. found (calcd. for $C_{38}H_{48}N_2O_4SCo$): C, 66.60 (66.36); H, 6.84 (7.03); N, 3.65 (4.07); S, 4.34 (4.66). IR (KBr, cm^{-1}): 4290 (br, s), 2952 (s), 1590 (s), 1548 (s), 1478 (s), 1278 (s), 1206 (m), 972 (s).

$[Co^{III}(4,4'-Se(Py)_2)(3,6-DBSQ)(3,6-DBCat)]_n$. The selenium analog was also prepared by the procedure above. Anal. found (calcd. for $C_{38}H_{48}N_2O_4SeCo$): C, 61.88 (62.12); H, 6.42 (6.59); N, 3.63 (3.81). IR (KBr, cm^{-1}): 4288 (br, s), 2950 (s), 1590 (s), 1548 (s), 1478 (m), 1412 (s), 1206 (m), 972 (s).

$[Co^{III}(4,4'-Te(Py)_2)(3,6-DBSQ)(3,6-DBCat)]_n$. The same procedure was used to prepare the tellurium analog. Anal. found (calcd. for $C_{38}H_{48}N_2O_4TeCo$): C, 58.02 (58.26); H, 5.98 (6.18); N, 3.43 (3.58). IR (KBr, cm^{-1}): 3676 (br, s), 2952 (s), 1586 (s), 1546 (s), 1478 (s), 1282 (s), 1154 (s), 974 (s).

Results and Discussion

Synthesis. The reaction between $Co_2(CO)_8$ and 3,6-di-*tert*-butyl-1,2-benzoquinone carried out in the presence of the respective 4,4′-chalcogenobispyridine resulted in the formation of the present coordination polymers of $[Co^{III}(4,4'-X(Py)_2)$ $(DBSQ)(DBCat)]_n$, (X=S, Se, Te)(2), which are stable and insoluble solids in common organic solvents, in contrast to the discrete analogs.[25] The reaction was smoothly performed in toluene as a solvent at room temperature.

$$Co_2(CO)_8 + 2 \quad \overset{}{N}\text{—}X\text{—}N + 4 \quad DBBQ \longrightarrow$$

$$2 \quad \left[\begin{array}{c} O \\ Co \\ O \end{array} \right]\text{—}N\text{—}X\text{—}N\text{—} _n + 8\,CO \quad (2)$$

DBSQ   DBCat

X =S, Se, Te

Physicochemical Properties. IR spectra in the region of 5000-400 cm^{-1} at room temperature are designated in Figure 1. The IR spectra show the characteristic band at around 4000 cm^{-1} assigned as Cat→Co charge transfer and exhibited in only Co^{III} system[20] along with appreciable bands in the finger print region. The bands of the present compounds exist in 4290 cm^{-1}, 4288 cm^{-1} and 3676 cm^{-1} for X=S, Se, Te compound, respectively. First of all, the bands indicate the presence of $[Co^{III}(4,4'-X(Py)_2)(DBSQ)(DBCat)]_n$ species at room temperature. In particular, the band position and shape of X=Se compound is similar to that of S analog, rather than the band of tellurium analog. The band intensity of the tellurium analog is the strongest, indicating that tellurium compound remains exclusively in Co(III) form compared to other two analogs at room temperature.[20] Such results reflect that the 4,4′-Te(Py)₂ is the strongest donor ligand, which is linearly expected from the electronegativity of the chalogen atom (Pauling's electronegativity : S=2.58, Se=2.53, and Te=2.1).[26] Figure 2 shows temperature-dependent IR spectra of $[Co^{III}(4,4'-S(Py)_2)(DBSQ)(DBCat)]_n$. As temperature increases, the band intensity at 4290 cm^{-1} was decreased, reflecting the change of structure, *i.e.* the transformation of $[Co^{III}(4,4'-S(Py)_2)(DBSQ)(DBCat)]_n$ into $[Co^{II}(4,4'-S(Py)_2)(DBSQ)_2]_n$. However, the drastic change was not observed for the present polymers in contrast to discrete analog molecules, which will be published separately,[25] at the range of the temperature. In case of the polymers, the range of the transition temperature seems to be somewhat wide, which is well consistent with temperature-dependent magnetism measurement as will be explained below.

The magnetic moment and molar susceptibility of $[Co^{III}(4,4'-Te(Py)_2)(DBSQ)(DBCat)]_n$ over the temperature range of 100-400 K are shown in Figure 3. Magnetic measurement has been an effective means of following the equilibrium due
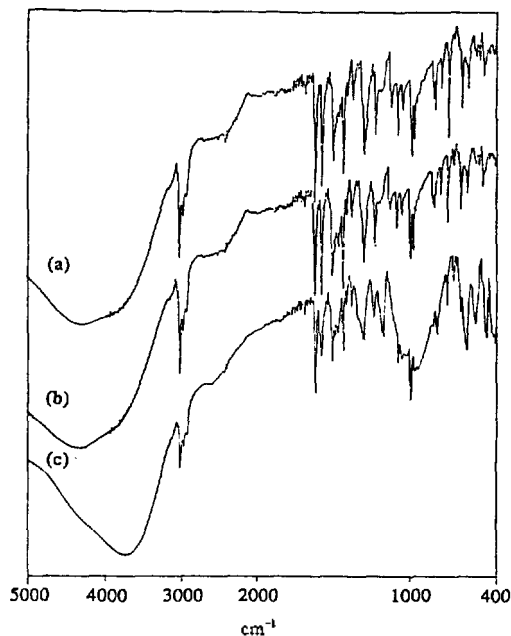

Figure 1. IR spectra of $[Co^{III}(4,4'-X(Py)_2)(DBSQ)(DBCat)]_n$, X=S (a), Se(b), Te(c) as KBr pellets.

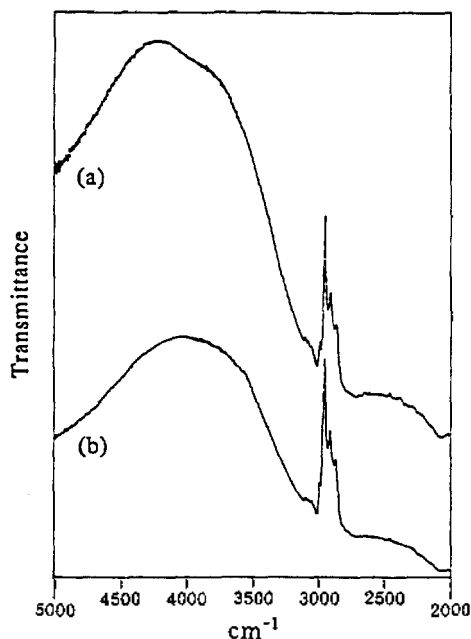**Figure 2.** Temperature-dependent IR spectra of $[Co^{III}(4,4'-S(Py)_2)(DBSQ)(DBCat)]_n$ at room temperature (a) and 85 ℃ (b).

to the change in metal spin state as well as the shift in charge distribution. Electron transfer from the DBCat ligand to the cobalt metal of $[Co^{III}(4,4'-Te(Py)_2)(DBSQ)(DBCat)]_n$ is accompanied by a spin transition of the resulting Co(II)ion. The S=3/2 high spin Co(II) center of the $[Co^{II}(4,4'-Te(Py)_2)(DBSQ)_2]_n$ product couples with the two S=1/2 radical ligands to give spin states of S=5/2, 3/2, or 1/2. The values obtained at below 300 K is 1.6-1.8 μ_B, approximately the value expected for an S=1/2 molecule. This agrees

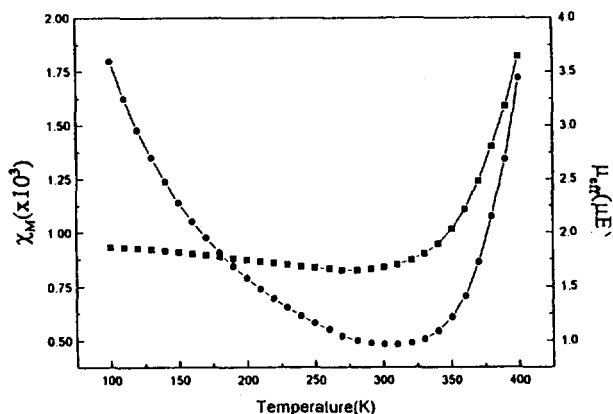**Figure 3.** Changes in magnetic moment (■) and magnetic susceptibility (●) of [Co^{III}(4,4'-Te(Py)$_2$)(DBSQ)(DBCat)]$_n$.
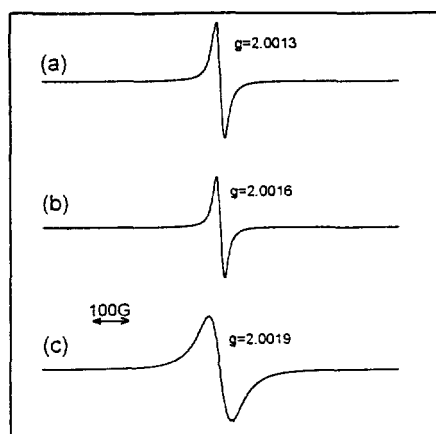
Figure 4. EPR spectra of [Co^{III}(4,4'-X(Py)$_2$)(DBSQ)(DBCat)]$_n$, X=S(a), Se(b), Te(c) recorded in the solid state at 280 K.

with the result of a diamagnetic Co(III) metal center with a single S=1/2 semiquinone ligand. Thus, the magnetic moment of the compound indicates that the [Co^{III}(4,4'-Te(Py)$_2$) (DBSQ)(DBCat)]$_n$ is the dominant form at temperature below 300 K. As the temperature is increased to above 300 K, the magnetic moment changes toward the Co^{III}/Co^{II} equilibrium with the formation of [Co^{II}(4,4'-S(Py)$_2$)(DBSQ)$_2$]$_n$. The value of 3.7 μ$_B$ at 400 K (limit of its stability) corresponds to the weak antiferromagnetic exchange between the S=3/2 Co and the two S=1/2 ligands. However, at above 400 K the increase of the magnetic moment is anticipated, and will finally approach to ferromagnetic exchange. The magnetic moment of sulfur analog revealed a similar pattern. In contrast, the Co^{III}/Co^{II} transition temperature of the sulfur analog began at T$_c$=280 K and the slope was more or less smooth due presumably to the delicate difference of the chalcogen atoms. Thus, the nature of interacting organic radicals in the bulk polymers hints a chance to synthesize materials that show cooperative magnetic effect.

As powder samples, all the complexes exhibit a strong signal with g values close to 2.00, which indicate the presence of one ligand-based radical species of [Co^{III}(4,4'-X(Py)$_2$) (DBSQ)(DBCat)]$_n$ in range of 77 K~280 K. Figure 4 represents the EPR spectra of the title compounds at around 280

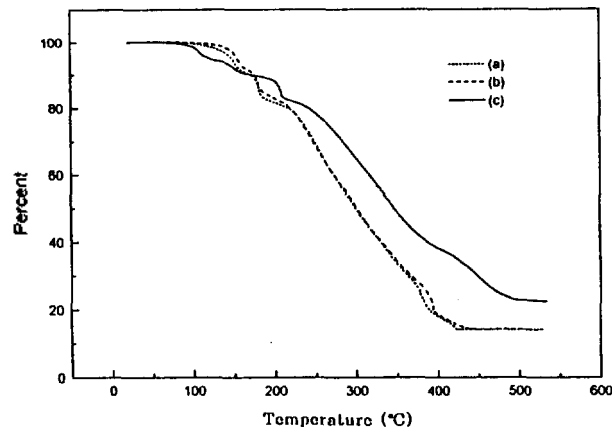**Figure 5.** TGA curves of [Co^{III}(4,4'-X(Py)$_2$)(DBSQ)(DBCat)]$_n$, X=S(a), Se(b), Te(c).

K. However, they do not show hyperfine coupling with ^{59}Co (I=7/2) even at 773 K, in contrast to discrete analogs.[26] The signals at 77 K sharpened compared to those at 280 K. Band width of tellurium coordinatin polymer is characteristically different from S, and Se analogs, due presumably to electronic effect of the chalcogen atom. The magnetic susceptibility and no epr hyperfine splitting in the range of 100-300 K suggest that there is no exchange interaction between low-spin Co^{III} (S=0) and DBSQ ligand (S=1/2) in the temperature range.

TGA curves of [Co^{III}(4,4'-X(Py)$_2$)(DBSQ)(DBCat)]$_n$ are shown in Figure 5. The TGA curve indicates that the polymers are stable up to 110, 155, and 150 °C for X=S, Se, and Te, respectively, and then are slowly decomposed. In addition, the degradation temperature (155 °C) of [Co^{III}(4,4'-Se(Py)$_2$)(DBSQ)(DBCat)]$_n$ is much far from the boiling point of water, implying that the intense low-energy band does not stem from the O-H stretching frequency of trace water in the sample or KBr. Another important fact from the TGA curve is that the transition between Co^{III}/Co^{II} is not accompanied by mass-loss. The title polymeric complexes seem to be changed to cobalt oxide at about 400 °C.

In conclusion, the present coordination polymers revealed the temperature-switching properties by an catechol to cobalt intramolecular electron transfer (3). Differences in chalcogen

$$[Co^{III}(4,4'-X(Py)_2)(DBSQ)(DBCat)]_n \rightleftharpoons$$
$$[Co^{II}(4,4'-X(Py)_2)(DBSQ)_2]_n \qquad (3)$$
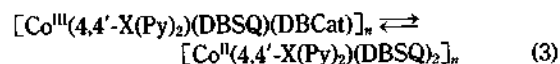
atom of the coligand may be used to modulate the orbital energy of the central cobalt atom permiting investigation of the dependence of the molecular switching properties. It may be assumed that the subtle change of the electronic properties of the nitrogen donor coligands directly depend on the development of new materials that exhibit desirable switching properties.

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Vapor-Phase Chlorination of Chlorobenzene over Solid-Acid Catalysts

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Catalytic chlorination of chlorobenzene was studied in vapor phase using various solid-acid catalysts such as silica-alumina, alumina, zeolite and a modified clay prepared by impregnating bentonite with ferric chloride. The conversions of both chlorine gas and chlorobenzene showed high over silica-alumina, alumina and modified clay catalysts. However relatively large amounts of polychlorinated benzene derivatives were also observed. The active species of catalytic activity in chlorination of chlorobenzene in vapor phase were proved to be as Lewis acid sites by *in-situ* IR experiments. The strength of Lewis acid sites which were effective for the vapor-phase chlorination seemed to be having Hammett acidity Ho> −3.0. The selectivity to dichlorobenzenes was proved to be high over the zeolite catalyst due to their shape-selective properties. *p*-Dichlorobenzene or dichlorobenzene selectivities were improved more or less by changing the reaction conditions.

Introduction

Chlorination of aromatics has long been investigated using Lewis acid catalyst such as ferric chloride or antimony pentachloride.[1] Recently, solid-acid catalysts have been utilized in the catalytic chlorination of benzene and/or benzene derivatives.[2] The high *para*-selectivity of dichlorobenzene could be expected by using solid-acid catalysts comparing with Lewis acid catalysts such as $FeCl_3$, $AlCl_3$, $MnCl_2$ and $SbCl_5$,

etc..[3] Many studies have been carried out for the effects of modification of zeolites by cation exchange or addition of various additives to improve the *para*-selectivity among dichlorobenzenes.[4-7] Zeolite L, offretite and erionite were reported to exhibit the high *para*-dichlorobenzene selectivity by combination of additives such as aliphatic carboxylic acid, sulfur compound and ether.[8] van Bekkum *et al.*[4] reported that L type zeolite could produce *para*-dichlorobenzene with high selectivity due to its particular pore structure. In addition, Miyake *et al.*[9] observed the salt bearing effect using inorganic salts on NaY zeolite which narrow the NaY pore