Charge Distribution Dependent on the Chelating Ratio. [Co(μ-bpym)(dbbq)$_2$] vs. [{Co(dbbq)$_2$}$_2$(μ-bpym)] (bpym=2,2′-bipyrimidine; dbbq=3,6-di-*t*-butyl-1,2-benzoquinone)

Ok-Sang Jung,* Du Hwan Jo, Young-A Lee, Hee Kwon Chae,† and Youn Soo Sohn

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

†Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Korea

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The preparation and characterization of [Co(μ-bpym)(dbbq)$_2$] and [{Co(dbbq)$_2$}$_2$(μ-bpym)] (bpym = 2,2′-bipyrimidine; dbbq = 3,6-di-*t*-butyl-1,2-benzoquinone) have been established. The temperature-dependent magnetic moments (100—400 K) and variable-temperature near-infrared (NIR) absorption spectra are presented to show that the title complexes exhibit an equilibrium via a catechol to a cobalt intramolecular electron transfer. At temperatures below 200 K the mononuclear complex [Co(μ-bpym)(dbbq)$_2$] has a charge distribution of [Co^{III}(μ-bpym)(dbcat)(dbsq)] (dbsq = 3,6-di-*t*-butyl-1,2-semiquinonato; dbcat = 3,6-di-*t*-butylcatecholato), whereas at temperatures beyond 290 K the mononuclear complex is predominantly in the [Co^{II}(μ-bpym)(dbsq)$_2$] form. From 200—290 K a mixture of Co(III) and Co(II) redox isomers exists at equilibrium in the solid state. In particular, a thermal analysis of a solid sample of the mononuclear complex discloses that the transition for the Co(III)/Co(II) is accompanied by a change in the heat content of 36 kJ mol^{-1}, which may be closely related to the band at 3878 cm^{-1}, assigned as a dbcat to Co(III) charge transfer. In striking contrast, the dinuclear complex [{Co(dbbq)$_2$}$_2$(μ-bpym)] is locked in a charge distribution of [{Co^{II}(dbsq)$_2$}$_2$(μ-bpym)] when the temperature is 100—400 K.

One of the challenging issues in molecular chemistry deals with the use of molecular compounds in electronic devices and systems.[1—3] The structural changes that accompany shifts in the metal oxidation state have been applied to materials that exhibit photomechanical properties and optical-switching effects. Charge transfer, cis–trans isomerization, and proton transfer etc. have been investigated for some molecules with either structural mobility or chemical sensitivity.[4—6] Among the various systems, coordination complexes that exhibit intramolecular electron-transfer phenomena have been the subject of the most intense studies. In particular, small collections of these molecules could be expected to exhibit bistability, which can be switched from one state to another by an external perturbation.[7—13]

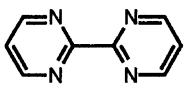
One of the most intriguing aspects of transition metal complexes containing 1,2-semiquinonato (sq) and catecholato (cat) ligands is a unique facility for intramolecular electron transfer between the metal and the chelated quinone ligands. This has been most prominently illustrated for a cobalt complexes, [Co^{III}(N–N)(sq)(cat)], where the temperature- or photo-induced equilibria between the following redox isomers have been observed in solution and in the solid state (Eq. 1).[14,15] One isomer consists of Co(III) with one semiquinonato, one catecholato ligand and a diimine ligand, and the other of Co(II) with two semiquinonato ligands and a diimine ligand. An intense band near 2500 nm (4000 cm^{-1}) assigned, as cat to Co(III) charge transfer, has been characteristically observed for Co(III) forms[16—19] Moreover, for such complexes, the transition temperature and bistability properties have been elucidated to be very sensitive to the nature of the diimine coligands.[19]

$$[Co^{III}(N\text{–}N)(sq)(cat)] \rightleftarrows [Co^{II}(N\text{–}N)(sq)_2] \quad (1)$$

In this paper, a study concerning the cobalt complexes of 2,2′-bipyrimidine (bpym) (Chart 1), which is a ligand that can serve as a delocalized π-system molecular bridge between metal centers,[20,21] is reported based on magnetic, spectroscopic, and thermal analyses. The charge-distribution difference between (μ-bpym)mono- and dicobalt complex is primarily discussed.

Experimental

Materials and Instrumentation. 3,6-Di-*t*-butyl-1,2-benzoquinone (dbbq) was prepared according to the literature procedures.[22] Dicobaltoctacarbonyl ($Co_2(CO)_8$) and 2,2′-bipyrimidine (bpym) were purchased from Strem and Alfa, respectively. An elemental analysis (C,H,N) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in the 5000—400 cm^{-1} range on a Perkin–Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets. Temperature-dependent magnetic measurements were



bpym

Chart 1.

made on a Quantum Design MPMS-5 SQUID magnetometer at a field of 10 kG. Electronic spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer equipped with an RMC-Cryosystems cryostat. The EPR spectrum was taken with an ESP-300S Bruker EPR Spectrometer. A thermal analysis was performed on a Stanton Red Croft TG 100 with a scanning rate of 20 °C min^{-1} when heating.

Synthesis of [Co(μ-bpym)(dbbq)$_2$]. $Co_2(CO)_8$ (171 mg, 0.50 mmol) and 2,2′-bipyrimidine (158 mg, 1.00 mmol) were combined in 30 mL of toluene. After the mixture was stirred for 5 min, dbbq (440 mg, 2.0 mmol) in 30 mL of toluene was added. The mixture was then stirred under dinitrogen for 2 h at room temperature. Evaporation of the solvent produced a dark-blue solid in 76% yield. The complex was recrystallized from a mixture of toluene and hexane. Found: C, 70.72; H, 6.99; N, 8.44%. Calcd for $C_{36}H_{46}N_4O_4Co$: C, 69.70; H, 7.05; N, 8.52%. IR (KBr) 2948 (s), 1552 (s), 1406 (s), 954 cm^{-1} (s).

Synthesis of [{Co(dbbq)$_2$}$_2$(μ-bpym)]. This compound was prepared by the same procedure with the 1 : 1 : 4 mole ratio of $Co_2(CO)_8$, bpym, and dbbq instead of above 1 : 2 : 4 mole ratio of the reactants. Recrystallization from toluene gave dark-green crystals as the toluene solvate in 74% yield. Found: C, 69.70; H, 7.67; 4.17%. Calcd for $C_{64}H_{86}N_4O_8Co_2 \cdot 2C_6H_5CH_3$: C, 69.32; H, 7.61; N, 4.15%. IR (KBr) 2952 (s), 1574 (m), 1442 (s), 954 cm^{-1} (s).

Results and Discussion

Synthesis. The synthetic procedures described in earlier studies[19] were used to synthesize the present complexes: The reaction of $Co_2(CO)_8$ with 3,6-di-*t*-butyl-1,2-benzoquinone in the presence of 2,2′-bipyrimidine (bpym) produced the present complexes in toluene at room temperature (Eq. 2). In particular, both mononuclear and binuclear products could be smoothly obtained by controlling the mole ratio of the reactants; a 1 : 2 : 4 mole ratio of $Co_2(CO)_8$, bpym, and dbbq afforded the monocobalt complex, whereas a 1 : 1 : 4 mole ratio of the reactants afforded the dicobalt complex. Each crystal recrystallized gave satisfactory chemical analyses. Spectral, thermal, and magnetic measurements of the two complexes were used to compare the properties of each complex.

$$n\cdot Co_2(CO)_8 + 2\cdot bpym + 4n\cdot dbbq \longrightarrow 2[\{\mathbf{Co(3,6\text{-}dbbq)_2}\}_n(\boldsymbol{\mu}\mathbf{\text{-}bpym)}] + 8n\cdot CO \quad (2)$$

$n = 1$ or 2

Magnetic and Spectroscopic Properties. The changes in the magnetic moments for solid samples of the two compounds are shown in Fig. 1. Although it was anticipated that the structural difference between [Co(μ-bpym)(dbbq)$_2$] and [{Co(dbbq)$_2$}$_2$(μ-bpym)] would be accompanied by a minor change in the magnetic properties, a dramatic change was observed, as shown in the figure. At temperatures below 200 K [Co(μ-bpym)(dbbq)$_2$] has an isomer of the low spin [Co^{III}(μ-bpym)(dbcat)(dbsq)] with an S=1/2 magnetic moment, due to the radical semiquinone ligand (1.7 μ_B). As the temperature is increased, a drastic shift to the high-spin [Co^{II}(μ-bpym)(dbsq)$_2$] redox isomer is observed with a transition temperature of 240 K (Eq. 3), which is lower than that (275 K) of the bipyridine analog, probably due to the relative basicity-decrease of the bpym ligand compared with bipyridine.[19] The magnetic moment for the [Co^{II}(μ-bpym)(dbsq)$_2$] isomer reflects the effects of a magnetic exchange between the radical ligands and the paramagnetic $S=3/2$ metal ion. The $S=3/2$ Co(II) center of the [Co^{II}(N–N)(dbsq)$_2$] isomer couples with the two $S=1/2$ radical ligands to give spin states of $S=5/2$, 3/2, or 1/2.[23] Metal dπ and dσ electrons may interact differently with the π radical spins, and the radical ligands may couple with each other. As a consequence, the temperature-dependent magnetic behavior may be complicated. In striking contrast, the dinuclear complex [{Co(dbbq)$_2$}$_2$(μ-bpym)] is locked in the [{Co^{II}(dbsq)$_2$}$_2$(μ-bpym)] form, and shows no transition to the Co(III) form at the same temperature range in the solid state. This is clear from its magnetic behavior, which remains nearly invariant at a high-spin value of 4.5 μ_B through the temperature range of 100—400 K. The magnetic-moment value is similar to that (4.6 μ_B) of [Co^{II}(dbsq)$_2$(NO$_2$-phen)].[16] For the complex, the locked Co(II) species may be ascribed to a weakening of the N donor strength induced by the presence of an angle constraint, to provide a suitable symmetric structure of the bpym ligand.

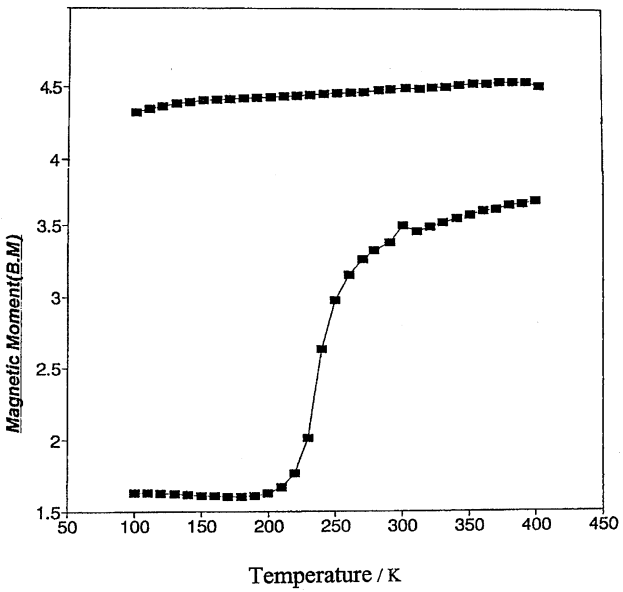
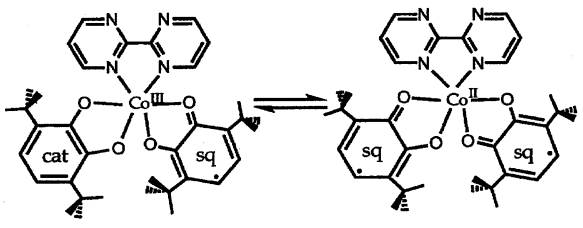


Fig. 1. Plots of the effective magnetic moment (μ_{eff}) vs. temperature on solid samples of [{Co(dbbq)$_2$}$_2$(μ-bpym)] (top) and [Co(μ-bpym)(dbbq)$_2$] (bottom).



(3)

The optical spectra on a solid sample of [Co(μ-bpym)-

$(dbbq)_2$] in the NIR region were obtained in order to show the solid-state equilibria have been monitored spectroscopically, especially by observing the intensity changes for a low-energy charge transfer transition that occurs characteristically for Co(III) isomers at ca. 2579 nm (ca. 3878 cm^{-1}). Figure 2 shows the increase in the intensity of the band with decreasing temperature. At temperatures below 200 K the mononuclear complex [Co(μ-bpym)$(dbbq)_2$] has a change distribution of [Co^{III}(μ-bpym)(dbcat)(dbsq)], whereas at temperatures beyond 290 K the mononuclear complex predominantly has the [Co^{II}(μ-bpym)$(dbsq)_2$] form. At 200—290 K a mixture of Co(III) and Co(II) redox isomers exist at equilibrium in the solid state, which is consistent with the above magnetic-moment measurements.

The complex shows a featureless first derivative EPR signal in a toluene solution at room temperature. The [Co^{III}(μ-bpym)(dbcat)(dbsq)] species contains low-spin Co(III), with the radical semiquinonato ligand as the paramagnetic center of the molecule. As the sample is cooled down, the signal sharpens and splits, and finally at toluene glass (77 K) the spectrum slightly shows anisotropy,[16] an effect that is common for delocalized organic radicals. It seems to consist of two components with g close to 2.00, each coupled to the cobalt nucleus (^{59}Co (I=7/2)) (Fig. 3). Thus, the spectrum also supports the presence of one ligand-based radical species of [Co^{III}(μ-bpym)(dbcat)(dbsq)] at low temperature.

Thermal Analysis. From a characteristic thermogravimetric analysis of the present two complexs, a similar pattern was observed in the thermal-degradation changes. The two complexes are thermally stable up to 210 °C, and are finally degraded to cobalt oxide through 210—425 K. For the complex of [{Co$(dbbq)_2$}$_2$(μ-bpym)], a signal relevant to the evaporation of solvated toluene was observed at 110—140 °C. In particular, mass-loss of 13% indicates that the crystal form of [{Co$(dbbq)_2$}$_2$(μ-bpym)] molecule contains two

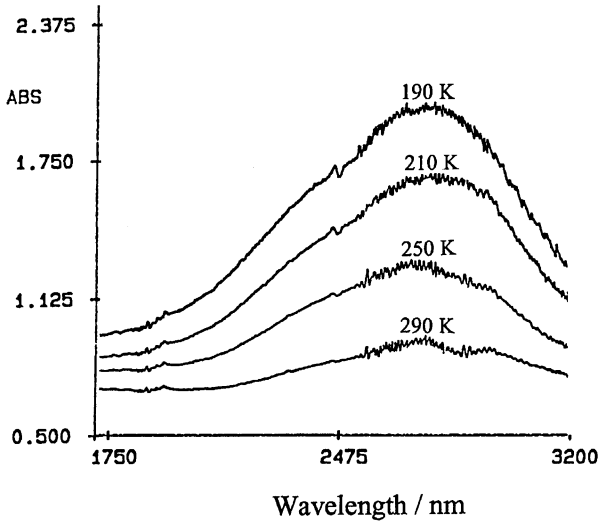


Fig. 2. Temperature-dependent changes in band intensity of the 2500 nm transition of [Co(μ-bpym)$(dbbq)_2$] in the solid state. Spectra were recorded on a sample prepared as a KBr pellet.

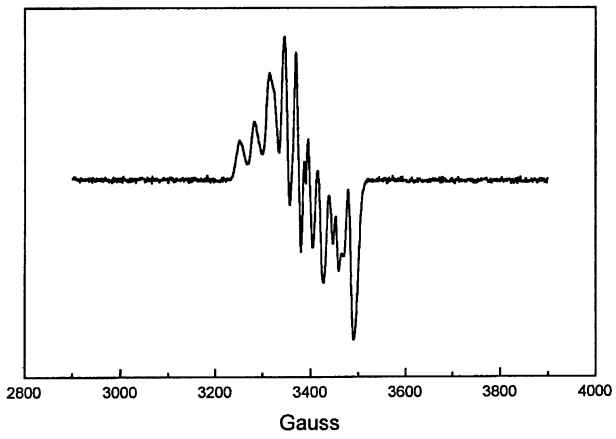


Fig. 3. EPR spectrum of [Co(μ-bpym)$(dbbq)_2$] recorded in toluene glass at 77 K.

solvated toluene molecules. A DSC curve of [Co(μ-bpym)-$(dbbq)_2$] is presented to disclose the change in heat content involved in the transition of Co^{III}/Co^{II}, and the thermogram at the range of 100—400 K is shown in Fig. 4. An endothermic peak with 36 kJ mol^{-1} was observed at 230 K. As can be seen from the scan, the endotherm appears at a temperature that is nearly in accord with the transition temperature obtained by a temperature-dependent magnetism measurement. The change in the heat content reveals that the transition of Co^{III}/Co^{II} is accompanied by a slight structural change via an intramolecular ligand to a cobalt electron transfer. In particular, the change in the heat content (36 kJ mol^{-1}) may be roughly related to the energy (46 kJ mol^{-1}) corresponding to the band at 3878 cm^{-1}, which was already assigned as a cat to Co(III) electron transfer.[19] However, for [{Co$(dbbq)_2$}$_2$(μ-bpym)], such an endotherm was not observed, implying that the complex is retained in [{$Co^{II}(dbsq)_2$}$_2$(μ-bpym)] in the temperature range of 100—400 K. Instead, an endothermic peak appeared at around 405 K, which is consistent with the evaporation-temperature of solvated toluene molecules.

In conclusion, for the title two complexes [{$Co^{II}(dbsq)_2$}$_n$-(μ-bpym)] (n=1,2), the charge distribution was prominently dependent on the stoichiometry of Co : bpym. The

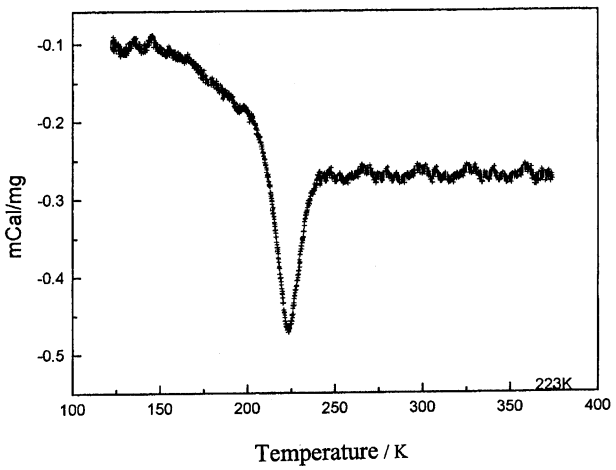


Fig. 4. DSC scan of [Co(μ-bpym)$(dbbq)_2$].

slight conformational flexibility of the bpym ligand seems to tune the charge distribution of the two complexes. Such a bistable system may also be anticipated by the absence or presence of an angle constraint of the diimine coligand.

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