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Temperature-Dependent Redox Isomerism via Intramolecular Electron Transfer. Synthesis and Properties of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ (dmppz=1,4-dimethylpiperazine; 3,6-dbq=3,6-di-*tert*-butyl-1,2-quinone)

Ok-Sang Jung*, Du Hwan Jo, Sung Ho Park, and Youn Soo Sohn

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

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The preparation and characterization of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ (dmppz=1,4-dimethylpiperazine; 3,6-dbq=3,6-di-*tert*-butyl-1,2-quinone) are established. Temperature-dependent magnetic moments (100-400 K), variable-temperature IR, and electronic spectra are presented to show that the title complex exhibits an equilibrium via a catechol to cobalt intramolecular electron transfer. At temperatures below 350 K, the charge distribution of the complex is $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})(3,6\text{-dbcate})$ (3,6-dbsq=3,6-di-*tert*-butyl-1,2-semiquinonato; 3,6-dbcate=3,6-di-*tert*-butylcatecholato) whereas at the temperature beyond 390 K, the complex is predominantly $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ form in the solid state. At the temperature range of 350-390 K a mixture of Co(III) and Co(II) redox isomers exist at equilibrium. The transition temperature (T_c) of Co(III)/Co(II) in solution is approximately 50° lower than that in the solid state. In particular, thermal analysis on solid sample of the complex discloses that the transition for the Co(III)/Co(II) is accompanied by the change in heat content of 12.30 kcal/mol.

Introduction

The striking facet of the challenging issues in molecular chemistry deals with the use of molecular compounds in electronic devices and systems.¹⁻³ Small collections of these molecules could be expected to exhibit bistability which can be switched from one state to another by an external perturbation.⁴⁻¹⁰ For instance, structural changes that accompany shifts in metal oxidation state have been applied to materials that exhibit photomechanical and optical switching signal creating an addressable memory effect. Charge transfer, *cis-trans* isomerism, proton transfer, and *etc.* have been investigated for some molecules with either structural mobility or chemical sensitivity.¹¹⁻¹³ Among the various systems, coordination metal complexes that exhibit intramolecular electron transfer phenomena have been the subjects of most intense study.

One of the most intriguing aspects of transition metal complexes containing 1,2-semiquinone (sq) and catechol (cat)¹⁴ ligands is a unique facility for intramolecular electron transfer between the metal and chelated catechol ligands. This has been most prominently illustrated for the cobalt complexes, $\text{Co}^{\text{III}}(\text{N-N})(\text{sq})(\text{cat})$ where temperature- or photo-induced equilibria between the following redox isomers have been observed in solution and in the solid state (1).^{15,16} One isomer consists of Co(III) with one semiquinonate and one catecholate ligand and a diimine ligand, and the other

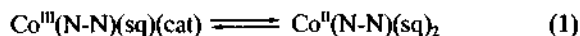
of Co(II) with two semiquinonate ligands and a diimine ligand. The intramolecular electron transfer is a consequence of charge localization within the molecule and the close energy separation between localized quinone and metal electronic levels. In particular, an intense band near 2500 nm (4000 cm^{-1}) assigned as cat to Co(III) charge transfer has been characteristically observed for Co(III) forms.¹⁷⁻²⁰ Moreover, for such complexes, the bistability and its T_c have been elucidated to be very sensitive to the nature of the diimine coligands.²⁰ In the present report, we describe the synthesis and characteristic properties of the $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ based on spectroscopic, magnetic, and thermal analyses. The physicochemical properties induced by the bistability of the complex is primarily discussed.



dmppz

Experimental

Materials and Instrumentation. Dicobaltoctacarbonyl ($\text{Co}_2(\text{CO})_8$) and 1,4-dimethylpiperazine (dmppz) were purchased from Strem and Aldrich, respectively. 3,6-Di-*tert*-butyl-1,2-benzoquinone (3,6-dbbq) was prepared according to literature procedure.²¹ Elemental analysis (C,H,N) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in $5000\text{-}400\text{ cm}^{-1}$ range on a Perkin Elmer 16F PC FTIR spectrophotometer with sample prepared as

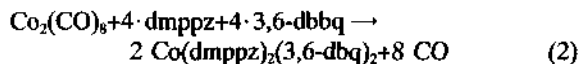


KBr pellet. Temperature-dependent magnetic measurement was recorded on a Quantum Design MPMS-5 SQUID magnetometer at a field of strength 10 kG. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with a RMC-Cryosystems cryostat. Thermal analysis was performed on a Stanton Red Croft TG 100 with a scanning rate of 20 °C/min when heating.

Synthesis of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$. $\text{Co}_2(\text{CO})_8$ (171 mg, 0.50 mmol) and dmppz (228 mg, 2.00 mmol) were combined in 30 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 added. The mixture was then stirred under dinitrogen atmosphere for 2 h at room temperature. Evaporation of its solvent produced a dark blue solid in 94% yield. The crude product was recrystallized in a mixture of toluene and hexane to afford dark blue crystals. Found: C, 70.90; H, 9.25; N, 6.20. Calcd for $\text{C}_{40}\text{H}_{68}\text{N}_4\text{O}_4\text{Co} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$: C, 71.10; H, 9.28; N, 6.14. IR (KBr, cm^{-1}): 4326 (s, br), 2950 (s), 1550 (s), 1457 (s), 1398 (s), 1274 (s), 1152 (s), 956 (s), 796 (s), 658 (s), 6109 (s), 488 (s).

Results and Discussion

Synthesis. Synthetic procedure described in an earlier paper²⁰ has been used for the title complex: the reaction of $\text{Co}_2(\text{CO})_8$ with 3,6-dbbq in the presence of dmppz produced the product in toluene at room temperature (2).



The product was easily obtained as solvated crystals in a mixture of toluene and hexane. A striking feature is that the reaction unexpectedly affords discrete molecules with two monodentate dmppz ligands as established by chemical analysis and preliminary X-ray analysis.²² In contrast, our previous papers on pyrazine,¹⁸ 4,4'-chalcogenobispyridine,²³ and 1,2-bis(4-pyridyl)ethane²⁴ analogs have shown that the amine ligand-bridged coordination polymeric species are formed under the same reaction condition. Furthermore, for the present reaction, only the product was isolated regardless of the reaction condition such as the mole ratio of the reactants and the reaction time. The formation of the discrete molecules seems to stem from intrinsic properties such as geometry of nitrogen atom and steric hindrance of dmppz ligand. The solvated toluene molecules in the crystals are easily evaporated to collapse the crystallinity in air. The product is soluble in common organic solvent, which is remarkably different from coordination polymeric analogs.

Spectroscopic Properties. IR spectra in the region of 5000–400 cm^{-1} are designated in Figure 1. The spectrum at room temperature shows a strong and broad band at 4326 cm^{-1} assigned as 3,6-dbcat to cobalt charge transfer and exhibited in only Co^{III} system.²⁰ First of all, the band discloses that the compound exists exclusively as $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})(3,6\text{-dbcat})$ species in the solid state at room temperature. The band position was shifted to high energy relative to that (4166 cm^{-1}) of $\text{Co}^{\text{III}}(\text{tmeda})(3,6\text{-dbsq})(3,6\text{-dbcat})$,²⁰ indicating that the dmppz ligand is weaker donor than tmeda. In particular, the featural temperature-dependent change of the band may be used to follow shifts in the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ equilibrium that occur in the solid state. As tem-

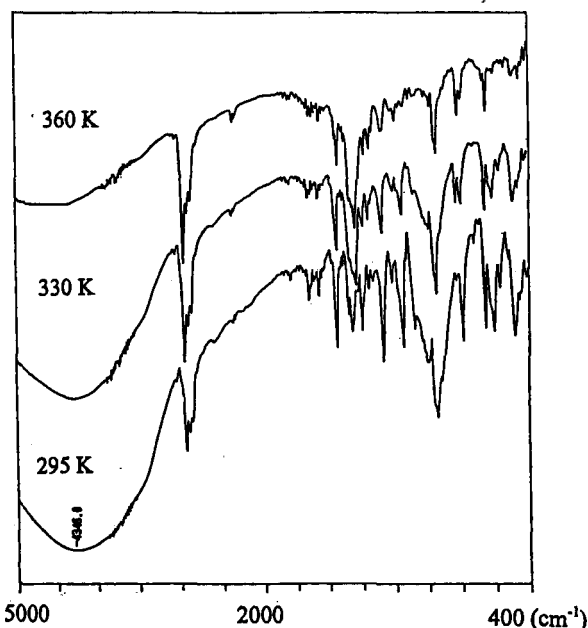
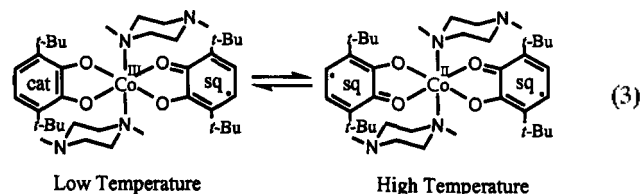


Figure 1. Temperature-dependent IR spectra: changes in band intensity of the 4326 cm^{-1} of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ in the solid state. Spectra were recorded on a sample prepared as a KBr pellet.

perature increases, the band intensity at 4326 cm^{-1} was decreased, reflecting the change of structure, *i.e.* the transformation of $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})(3,6\text{-dbcat})$ into $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ (3). Thus, Co^{II} species is predominant



at above 360 K, which is well consistent with magnetism measurement as will be explained below.

In order to scrutinize the behavior of the cobalt complex in solution, electronic spectra (300–1150 nm) over the temperature range of 180–300 K were measured in toluene. The spectra depicted in Figure 2 show prominent reversible temperature-dependence with two isosbestic points at 737 nm and 887 nm. The band at 790 nm of the low spin Co^{II} species decreases at reduced temperatures, and is replaced by the transitions at 620 nm which is associated with the high spin Co^{III} species.¹⁷ Thus, the electronic spectra indicate that the complex exists as a tautomeric mixture of the Co^{III} and Co^{II} charge distributions in toluene solution at room temperature.

The transition temperature (T_c) of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ in solution is approximately 50° lower than that in the solid state. The electronic spectrum on $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})(3,6\text{-dbcat})$ in toluene at 180 K resembles its spectrum in the solid state at room temperature.

Magnetic Properties. Change in magnetic moment recorded on desolvated solid sample of the present compound is shown in Figure 3. At temperatures below 350 K, $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ is in the low spin $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})_2$

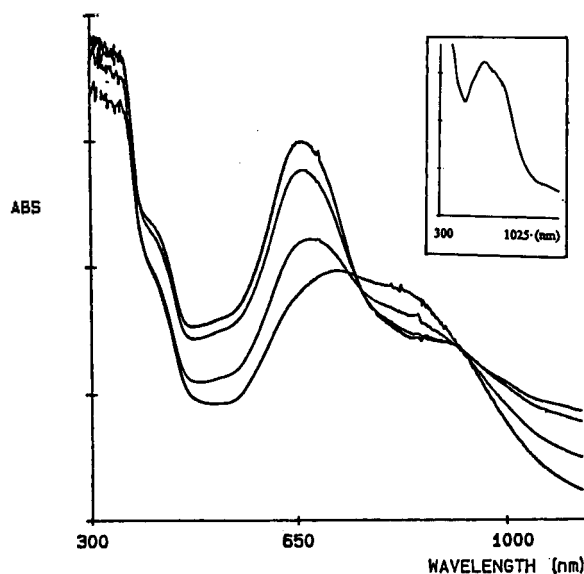


Figure 2. Electronic spectra of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$: spectra recorded in toluene solution ($C=5 \times 10^{-4}$ M) at temperatures of 180 K, 220 K, 260 K, and 300 K from top to bottom for the band at 620 nm. Electronic spectrum in box was taken on the solid sample as a KBr pellet.

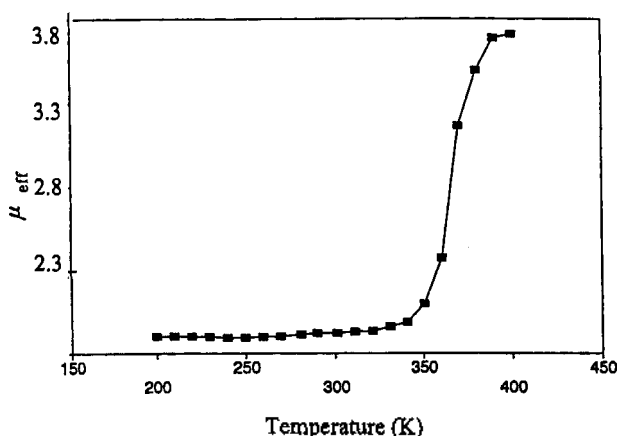


Figure 3. Plots of the effective magnetic moment (μ_{eff}) vs temperature on a solid sample of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$.

(3,6-dbcat) isomeric form with $S=1/2$ magnetic moment due to the radical semiquinone ligand ($1.7 \mu\text{B}$) as the paramagnetic center of the molecule.²⁵ As the temperature is increased, drastic shift to the high-spin $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ redox isomer is observed with T_c of 360 K. Magnetic moment for the $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ isomer reflects the effects of magnetic exchange between the radical ligands and the paramagnetic $S=3/2$ metal ion. Electron transfer from the 3,6-dbcat ligand to the metal of $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})_2(3,6\text{-dbcat})$ is accompanied by a spin transition of the resulting $\text{Co}(\text{II})$ ion. The $S=3/2$ $\text{Co}(\text{II})$ center of the $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ isomer couples with the two $S=1/2$ radical ligands to give spin states of $S=5/2$, $3/2$, or $1/2$.²⁶ Metal $d\pi$ and $d\sigma$ electrons may interact differently with the π radical spins and the radical ligands may couple with one another. As a consequence, temperature-dependent magnetic behavior may be complicated, and the use of magnetic data

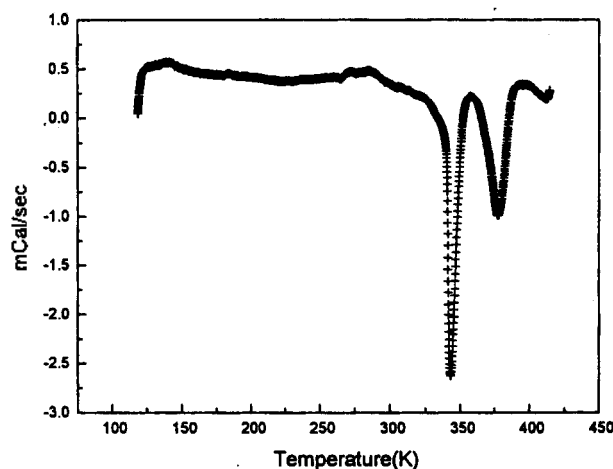


Figure 4. DSC scan of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$.

to give a value for T_c in the solid state may be tenuous. However, for the present compound, the temperature-dependent magnetic data were abruptly changed. Further complicating magnetic behavior may be the dependence of the spin transition on solid state effects such as partial solvation and intermolecular interaction.

Thermal Analysis. From featural thermogravimetric analysis, the compound itself is thermally stable up to 573 K, and finally seems to degrade to cobalt oxide over the temperature range of 573–723 K. However, a signal relevant to evaporation of solvated toluene molecules is clearly observed. In particular, mass-loss of 11% level indicates that two toluene molecules are solvated in the crystals. A DSC curve of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ is presented to disclose the change in heat content involved in the transition of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$, and the thermogram at the range of 100–400 K is shown in Figure 4. An endothermic peak with 12.30 kcal/mol was observed at 355 K. As can be seen from the scan, the endotherm appears at temperature that is nearly in accord with the transition temperature obtained by afore-mentioned temperature-dependent magnetism ($T_c=360$ K) and IR measurements. The change in heat content reveals that the transition of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ is accompanied by the slight structural change *via* an intramolecular catecholate to cobalt electron transfer. An additional endothermic peak appeared at 342 K, which is well consistent with evaporation-temperature of solvated toluene molecules.

In conclusion, the present reaction smoothly afforded discrete molecules of $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ in contrast to diimine bridged coordination polymers. Its charge distribution was prominently dependent on temperature: at temperature below 350 K, $\text{Co}(\text{dmppz})_2(3,6\text{-dbq})_2$ is the charge distribution of $\text{Co}^{\text{III}}(\text{dmppz})_2(3,6\text{-dbsq})_2(3,6\text{-dbcat})$ whereas at the temperature beyond 390 K the complex is predominantly $\text{Co}^{\text{II}}(\text{dmppz})_2(3,6\text{-dbsq})_2$ form. The transition temperature (T_c) of $\text{Co}(\text{III})/\text{Co}(\text{II})$ in solution is approximately 50 °C lower than that in the solid state. Such a system is a rare stable complex containing monodentate amine ligand that obviously exhibits temperature-bistability.

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Isolation of Epidioxysteroids from a Sponge of the Genus *Tethya*

Youngwan Seo, Jung-Rae Rho, Ki Woong Cho, Chung J. Sim¹, and Jongheon Shin*

Marine Natural Products Chemistry Laboratory, Korea Ocean Research & Development Institute
Ansan P.O. Box 29, Seoul 425-600, Korea

¹Department of Biology, Han Nam University, Taejon 300-791, Korea

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Four steroids including two novel compounds have been isolated from a sponge of the genus *Tethya*. All of the compounds possess a 5 α ,8 α -epidioxo functionality as a common structural feature. Two new steroids, **1** and **2**, possess a cyclopropyl ring at C-24(26) of the side chain. The structures of these compounds have been determined by combined spectroscopic methods.

Introduction

Sponges (phylum Porifera) are widely recognized as the most prolific sources of both structurally unique and biologically active marine natural products.¹ In a recent literature survey conducted by this group, more than 40% of mar-

ine-originated metabolites have been isolated from these animals.² Metabolites of sponges are consisting of compounds originated from various biogenetic origins; steroids, terpenoids, peptides, polyketides, purines and pyrimidines, and mixed biosynthetic products.^{1,3} In addition, numerous compounds have been reported to exhibit potent and diverse