Redox Chemistry and Valence Tautomerism of Cobalt-Quinone Complexes in Nonaqueous Solvents

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The electrochemistry and valence tautomerism of Co^{III}(*N-N*)(SQ)(Cat), [*N-N*=*N,N,N',N'*-tetramethylethylenediamine (TMEDA); SQ=3,5- or 3,6-di-*tert*-butyl-semiquinone, Cat=3,5- or 3,6-di-*tert*-butyl-catechol], have been investigated by spectroscopic, electrochemical, spectroelectrochemical methods in nonaqueous solvents under anaerobic condition. The transition temperature between tautomers is dependent upon the donation effect of substituted quinone ligand and solvent. It increases with the increase of donation effect of solvent and quinone ligand. Co^{III}(TMEDA)(SQ)(Cat) is reduced to $[Co^{II}(TMEDA)(SQ)(Cat)]^-$, and then reduces to $[Co^{II}(TMEDA)(Cat)_2]^{2-}$. Co^{III}(TMEDA)(SQ)(Cat) is oxidized to $[Co^{III}(TMEDA)(SQ)_2]^+$, but the stability of the oxidized form in DMF is dependent upon the solution temperature. With the increase of solution temperature the oxidized form may be converted to $[Co^{II}(TMEDA)(SQ)(BQ)]^+$ by intramolecular electron transfer from SQ ligand to Co^{III}.

Introduction

The electron-transfer chemistry of transition metal complexes *in nonaqueous* solvents has been of continuing major interest. The semiquinonate and catecholate ligands have partially filled and filled molecular orbitals that are close in energy to transition metal d orbitals. It is possible to change the charge distribution between quinone-derived ligand and transition metal in the metal complexes. The complexes of cobalt ion and quinone ligand containing nitrogen-donor coligand showed facile intramolecular charge transfer between cobalt and quinone ligand in solution and solid state.[1-9] A tautomeric equilibrium between Co^{III} and Co^{II}-quinone complexes having nitrogen-donor coligand is described in eq 1, where *N-N* is a bidentate nitrogen-donor ligand and SQ and Cat are the semiquinonate and catecholate, respectively.

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

Cobalt complexes with two *o*-quinone derived ligands have been shown to undergo a thermally driven valence tautomeric interconversion in toluene solution.[7-9] High spin Co^{II} complex dominates in toluene solution at higher temperature, and low spin Co^{III} complex is stabilized with the decrease of solution temperature. Tautomeric forms of the complex are related to the electron transfer between core metal and quinone ligand. Tautomeric isomers are electronically labile because two electronic states are nearly degenerate. Equilibria between valence tautomers occur in separate electron transfer and spin transition steps.[4-7] It has also been studied for the complexes of iron and manganese coordinating with quinone-derived ligands.[10-15]

Redox chemistry of quinones and metal complexes coordinating with quinone ligands has been investigated by electrochemical methods in nonaqueous solvents.[16-20] The electron transfer for metal-quinone complexes involves the ligand rather than the metal, and the redox processes of quinone ligands are very important for the understanding of their electrochemistry.[19-20] Until now the electrochemistry of transition metal complexes with quinone ligands containing nitrogen donor coligand has only been studied for iron complexes.[12-13]

It was reported that transition temperature (Tc) for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) is 310 K in toluene solution and above 400 K in solid state.[4] The valence tautomerism of cobalt complexes has been investigated in toluene solution. Since their electrochemistry can not be studied in toluene solvent, reasonable solvents are selected for electrochemistry. In the present study, we wish to report the redox chemistry of cobalt-quinone complexes containing TMEDA as a nitrogen-donor coligand, tautomeric equilibria for them, and their redox forms in several nonaqueous solutions.

Experimental

Material. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DBBQ) were purchased from Aldrich. Dicobaltoctacarbonyl was purchased from Strem Chemical Co. 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) was prepared using literature procedure.[21] Co(TMEDA)(3,6-SQ)(3,6-Cat) was synthesized by literature procedure.[4] Anhydrous acetonitrile (MeCN), methylene chloride (CH_2Cl_2), toluene, and dimethyl formamide (DMF) were used as received from Aldrich. Tetrabutyl-ammonium perchlorate (Bu_4NClO_4) was used as a supporting electrolyte.

Synthesis of Co(TMEDA)(3,5-SQ)(3,5-Cat). $Co_2(CO)_8$ (172 mg, 0.5 mmol) and TMEDA (116 mg, 1.0 mmol) were combined in 50 mL of toluene. The mixture was stirred for 5 min, and 3,5-DBBQ (440 mg, 2.0 mmol) was slowly added. The solution was stirred under argon for 2 h at room temperature. Evaporation of the solvent produced a dark blue residue of the complex in 76% yield. The complex was recrystallized from acetone solution.

Instumentation and methodology. The voltammetric measurements were accomplished with a three

electrode potentiostat (Bioanalytical Systems, Model CV-27) and a Rikadenki Model RW 21T recorder. A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary electrode. An Ag/AgCl electrode supplied by BAS was used as a reference electrode, and the potential is approximately −45 mV relative to a saturated calomel electrode (SCE). A 3.0 mm diameter glassy carbon and 1.6 mm diameter platinum were employed as a working electrode for the redox reactions of cobalt-quinone complexes. All working electrode surfaces were highly polished with alumina paste prior to each experiment. Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode via controlled potential electrolysis using CV-27 potentiostat with a three electrode system. Absorption spectra were recorded on a Jasco V-530 spectrophotometer equipped with a HMC-358 constant temperature cell holder. Infrared spectra were obtained in 5000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets. All experiments are carried out under anaerobic conditions.

Results

Electronic spectra of Co^{III}(TMEDA)(SQ)(Cat). Since Co^{III} and Co^{II} complexes have characteristic electronic spectra, optical spectroscopy has been used to monitor equilibria in different solvents over an appropriate temperature range. It was known that the complexes of Co^{III}(*N*-*N*)(SQ)(Cat) show characteristic absorptions in the 600-700 nm range of the visible region, and Co^{II}(*N*-*N*)$(SQ)_2$ complexes give characteristic absorptions in the 750-850 nm range.[4-7] Optical spectra for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) measured in a series of nonaqueous solvents are shown in Figure 1 at 293 K. Therefore the result indicates that Co^{III}

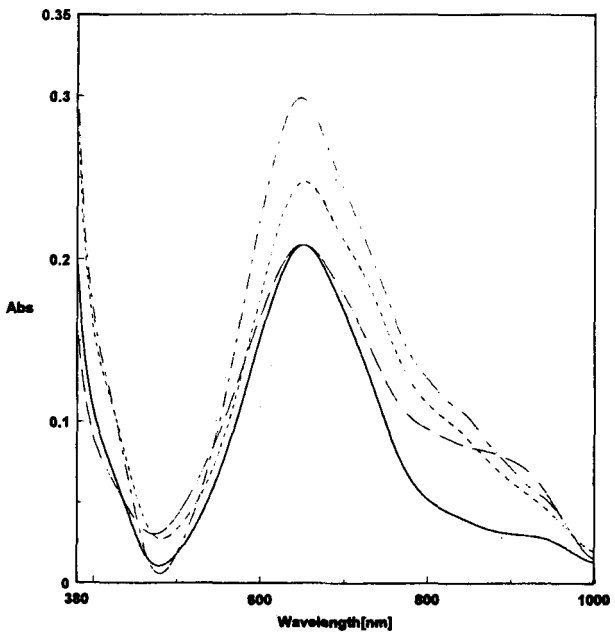


Figure 1. Electronic spectra of 0.15 mM Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) recored in toluene (-------), methylene chloride (- - - - -), acetonitrile (- - -), and dimethyl formamide (———) solutions at 293 K.

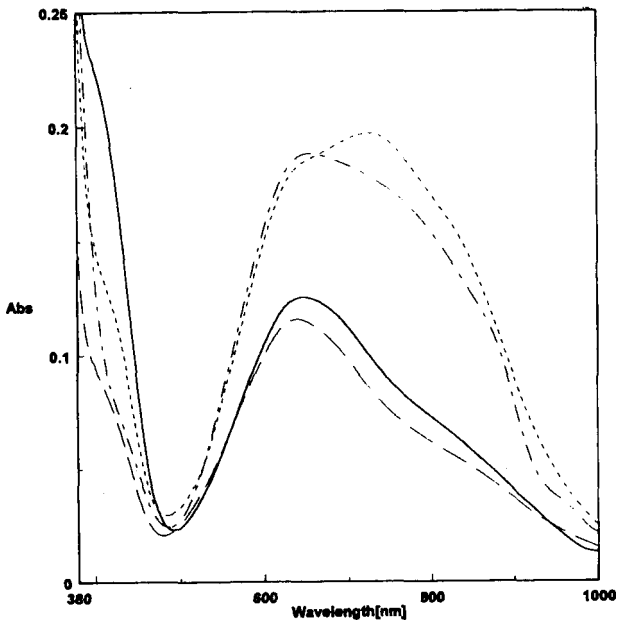


Figure 2. Electronic spectra of 0.15 mM Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) recored in toluene (-------), methylene chloride (- - - - -), acetonitrile (- - -), and dimethyl formamide (———) solutions at 293 K.

isomer is predominant rather than Co^{II}(TMEDA)$(3,6\text{-SQ})_2$ as a tautomeric form of the Co^{III} in all solvents. Systematic experiments confirm that transition temperature (T_c) between tautomers is about 310 K in toluene solution,[4] and demonstrate that Co^{III} isomer is still predominant until 373 K in DMF and 348 K in MeCN and 308 K in CH_2Cl_2. The T_c is defined as the approximate temperature at which concentrations of Co^{III} and Co^{II} forms of the cobalt complexes are equal in solution.

Figure 2 illustrates electronic spectra for Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) obtained in nonaqueous solvents at 293 K. Solution spectra recorded explain that Co^{III} isomer predominates in DMF and MeCN, and a mixture of Co^{III}/Co^{II} tautomers exists at equilibrium in toluene and CH_2Cl_2. The temperature-dependent spectra for Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) are shown in Figures 3 (in DMF) and 4 (in CH_2Cl_2). Co^{III} isomer is genarally decreased with the increase of solution temperature, and Co^{II} isomer is increased concomitantly. The T_c of Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) determined from systematic experiments with solution temperature may be about 280 K in toluene solution (approximately 300 K in CH_2Cl_2, 340 K in MeCN, 363 K in DMF).

According to previous result,[4] IR spectral characterization on Co^{III} complexes shows that an intense transition in the 4000 cm^{-1} region of the infrared appears characteristically for complexes of this charge distribution. This band is assigned as the charge transfer transition from Cat ligand to cobalt that is associated with the electron transfer step.

Electrochemistry of Co^{III}(TMEDA)(SQ)(Cat). Figure 5 illustrates the temperature-dependent cyclic voltammograms (CVs) for 3,6-DBBQ used as a ligand in DMF containing 0.1 M Bu_4NClO_4 (scan rate: 50 mV/sec). An initial negative scan yields two stepwise redox couples at −0.39 V *vs.* Ag/AgCl and −0.85 V for 3,6-DBBQ and at −0.38 V and −0.84 V for 3,5-DBBQ at GC electrode in

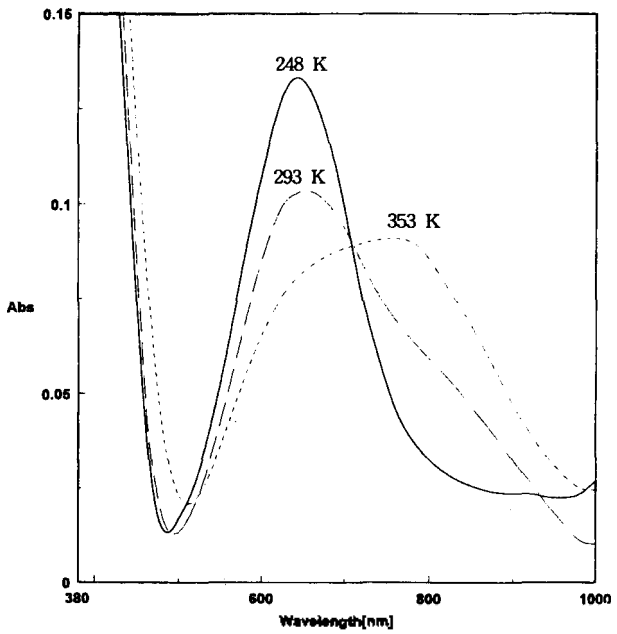


Figure 3. Electronic spectra of 0.15 mM Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) recored in dimethyl formamide solutions.

DMF at 293 K, and they are quasi-reversible processes. It is well known that the first reduction of benzoquinone (BQ) produces semiquinone anion-radical (SQ), and its second reduction gives catecholate dianion (Cat). The first reduction potential is independent upon the solution temperature, but the second reduction potential shifts to negative direction with the decrease of solution temperature. The cathodic current for the first reduction is slightly dependent on the solution temperature, but it for the second reduction largely decreases with the decrease of solution temperature and finally the second redox couple may disappear. The rate of charge transfer for second redox couple is dependent upon

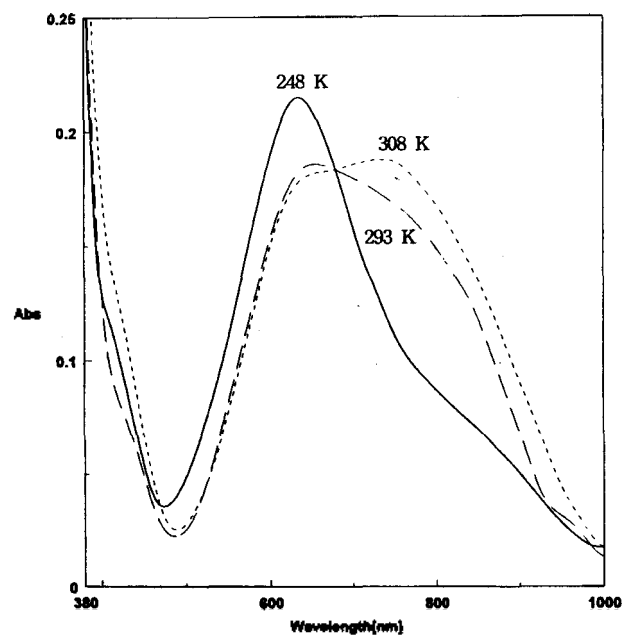


Figure 4. Electronic spectra of 0.15 mM Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) recored in methylene chloride solutions.

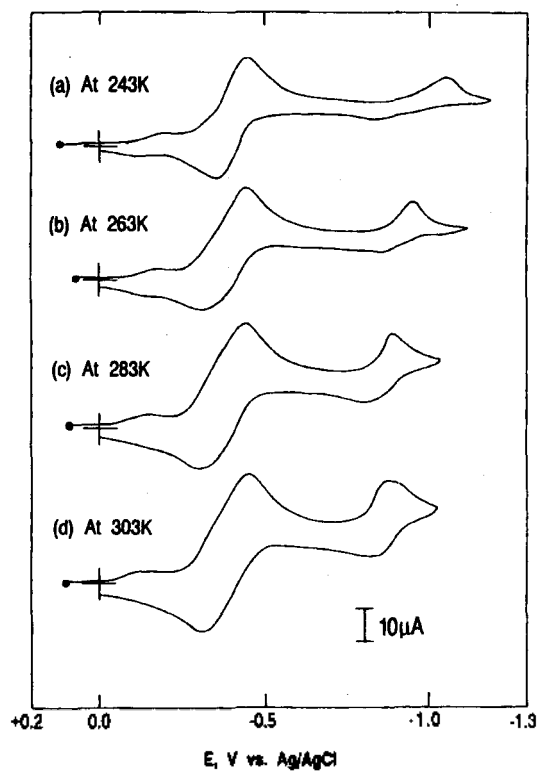


Figure 5. The temperature-dependent cyclic voltammograms of 3.0 mM 3,6-DBBQ in DMF containing 0.1 M Bu_4NClO_4 at glassy carbon electrode (scan rate, 50 mV/s).

solution temperature, and the rate becomes slow with the decrease of temperature. TMEDA used as an ancillary ligand of cobalt-quinone complexes doesn't show any redox peaks within potential window employed.

According to the result of electronic spectra, the complex exists as Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF below 373 K. Figure 6 illustrates the temperature-dependent cyclic voltammograms (CVs) for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1 M Bu_4NClO_4 (scan rate: 50 mV/sec). An initial negative scan yields two stepwise redox couples at higher temperature, but gives one redox couple at lower temperature. The cathodic current for the first reduction at a constant scan rate is linearly proportional to the concentration of the Co^{III} complex. The first reduction potential (−0.37 V) and the second reduction potential (−0.62 V) of the Co^{III} complex are independent upon the solution temperature. Because the peak separation between first reduction and its corresponding oxidation peak is about 60 mV, its electrode reaction is quasi-reversible and one-electron transfer. The peak separation between second reduction and its corresponding oxidation peak is also about 60 mV. The cathodic current for the first reduction is independent on the solution temperature, but it for the second reduction decreases with the decrease of solution temperature and finally the second redox couple disappears. The rate of charge transfer for second redox couple is dependent upon solution temperature, and the rate becomes slow with the decrease of temperature. On the basis of temperature-dependent redox chemistry of quinone-ligand, the first reduction seems to be a metal-centered and its second reduction a ligand-centered.

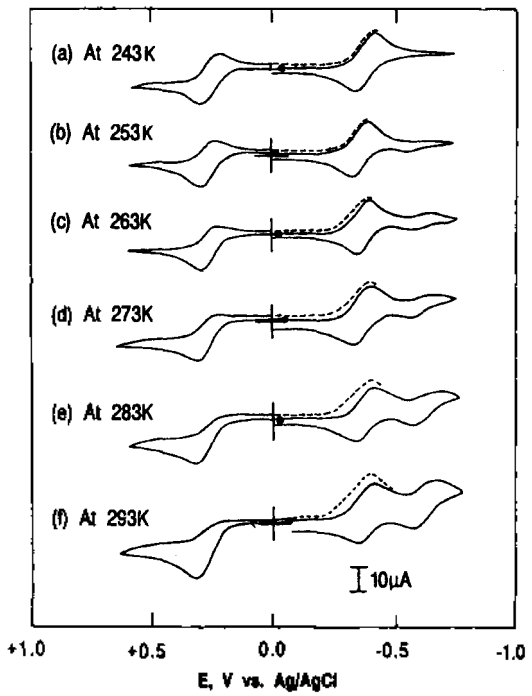


Figure 6. The temperature-dependent cyclic voltammograms of 3.0 mM Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1 M Bu_4NClO_4 at glassy carbon electrode (scan rate, 50 mV/s).

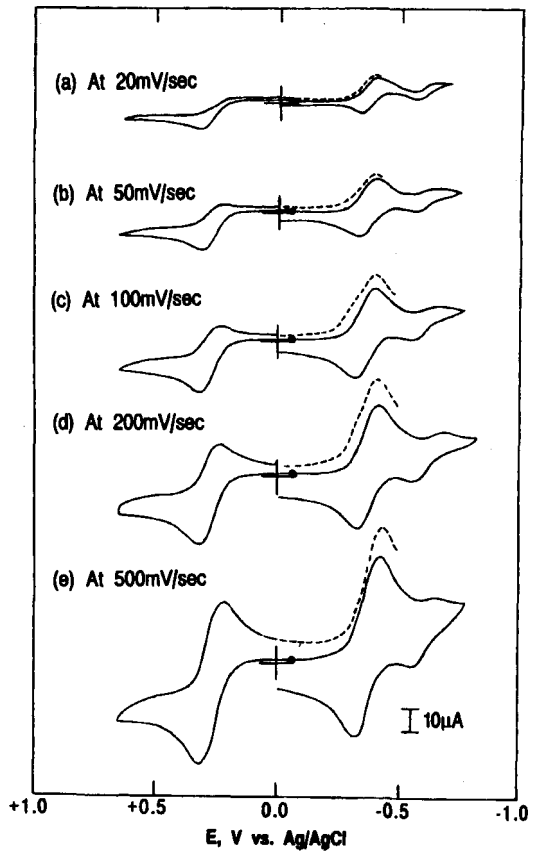


Figure 7. Cyclic voltammograms of 3.0 mM Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1 M Bu_4NClO_4 at glassy carbon electrode as a function of scan rate at 273 K.

According to Figure 6a at 243 K, an initial positive scan for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) yields a reversible redox couple at +0.27 V. The anodic current for the first oxidation is comparable to the cathodic current for the first reduction, and the peak separation between first oxidation and its corresponding reduction peak is about 60 mV. It can be concluded that the first oxidation is also one electron reaction and quasi-reversible. The reversibility decreases with the increase of solution temperature, and simultaneously new reduction peak at −0.28 V begins to make by reverse negative scan. The irreversible oxidation peak at +0.30 V is shown at higher temperature with new reduction peak at −0.28 V. The reversible oxidation potential (+0.27 V) is independent upon the solution temperature, and demonstrates stabilization for $[Co^{III}(TMEDA)(3,6\text{-}SQ)_2]^+$ complex as an oxidized form of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) by one-electron process with ligand-centered. The irreversible oxidation peak at +0.30 V shown at higher temperature indicates that because the oxidized $[Co^{III}(TMEDA)(3,6\text{-}SQ)_2]^+$ is unstable at the solution temperature, it may convert to $[Co^{II}(TMEDA)(3,6\text{-}SQ)(3,6\text{-}BQ)]^+$ by intramolecular electron transfer between Co^{III} and SQ ligand. The oxidation peak current at +0.30 V increases with the decrease of reversibility of first oxidation couple, and the increase of peak current (the addition of new oxidation current) is due to the oxidation of $[Co^{II}(TMEDA)(3,6\text{-}SQ)(3,6\text{-}BQ)]^+$ which generated by intramolecular electron transfer in $[Co^{III}(TMEDA)(3,6\text{-}SQ)_2]^+$ formed by first oxidation initially. The oxidation of $[Co^{II}(TMEDA)(3,6\text{-}SQ)(3,6\text{-}BQ)]^+$ produces $[Co^{III}(TMEDA)(3,6\text{-}SQ)(3,6\text{-}BQ)]^{2+}$ by metal-centered. The new reduction peak at −0.28 V seems to be generated by the reduction of $[Co^{III}(TMEDA)(3,6\text{-}SQ)(3,6\text{-}BQ)]^{2+}$. It can be concluded that the increase of oxidation current with the raise of solution temperature gives rise from ECE mechanism.

The cyclic voltammograms as a function of scan rate for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF are shown in Figures 7 (at 273 K) and 8 (at 293 K). The cyclic voltammograms for the first reduction of the Co^{III} complex are obtained at various scan rates, and the dependence of the cathodic current as a function of the square root of the scan rate is linear as expected from a diffusion-controlled process. The charge transfer for the second reduction is apparently slow compared to the first reduction. The first oxidation wave is dependent on scan rate, and it indicates that the fate of oxidized product is a function of time. The interconversion rate of oxidized product is a function of solution temperature. The rate apparently increases with the increase of solution temperature.

The redox chemistry for Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) is similar to those for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) except the temperature range. Table 1 summerizes the redox potentials for Co^{III}(TMEDA)(SQ)(Cat) complexes in DMF solutions.

Spectroelectrochemistry of Co^{III}(TMEDA)(SQ)(Cat). Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode. The spectrum of the first reduction product is obtained by holding the potential of −0.47 V. Figure 9 illustrates the spectroelectrochemical first reduction of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1

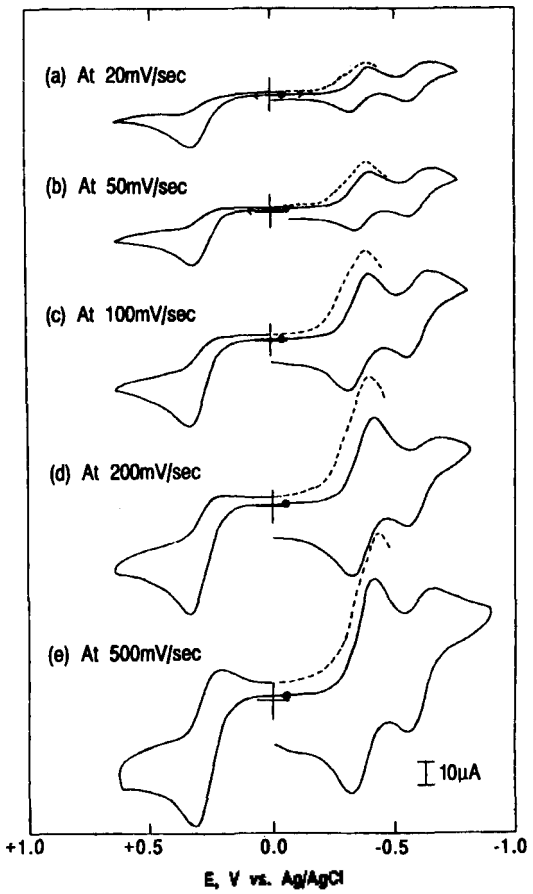


Figure 8. Cyclic voltammograms of 3.0 mM Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1 M Bu_4NClO_4 at glassy carbon electrode as a function of scan rate at 293 K.

Table 1. Voltametric redox potentials for substituted benzoquinones and Co^{III}(TMEDA)(SQ)(Cat) complexes in DMF solutions [0.1 M $(Bu_4N)ClO_4$]

Substrate	$E^{0'}$ (V *vs.* Ag/AgCl)			Temp. (K)
	1st Ox.	1st Red.	2nd Red.	
3,6-DBBQ	-	−0.39	−0.85	293
3,5-DBBQ	-	−0.38	−0.84	293
Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat)	+0.30[a]	−0.37	−0.62	293
Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat)	+0.27	−0.37	-	243
Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat)	+0.29[a]	−0.27	−0.58	293
Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat)	+0.25	−0.27	-	243

[a]Indicates irreversible oxidation peak potential.

M Bu_4NClO_4. The absorption band of the reduction product looks characteristically like Co^{II} complex, and it may be assigned as $[Co^{II}$(TMEDA)(3,6-SQ)(3,6-Cat)$]^-$. The spectroelectrocCo^{II}mical oxidation of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF is carried out as a function of temperature. The spectrum of the oxidation product illustrates the invariance of Soret absorption maximum in DMF. This result indicates that the oxidation state of cobalt center is invariant during the oxidation process. The spectroelectrochemical results of Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) are also similar to those obtained from Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) except the solution temperature.

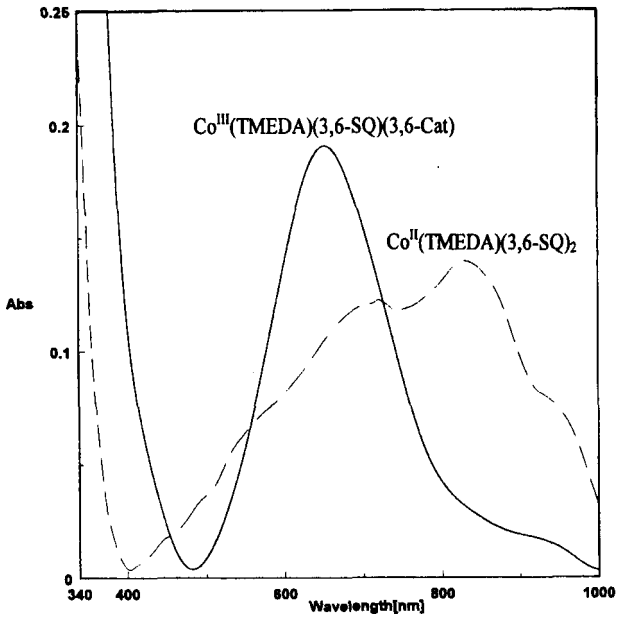
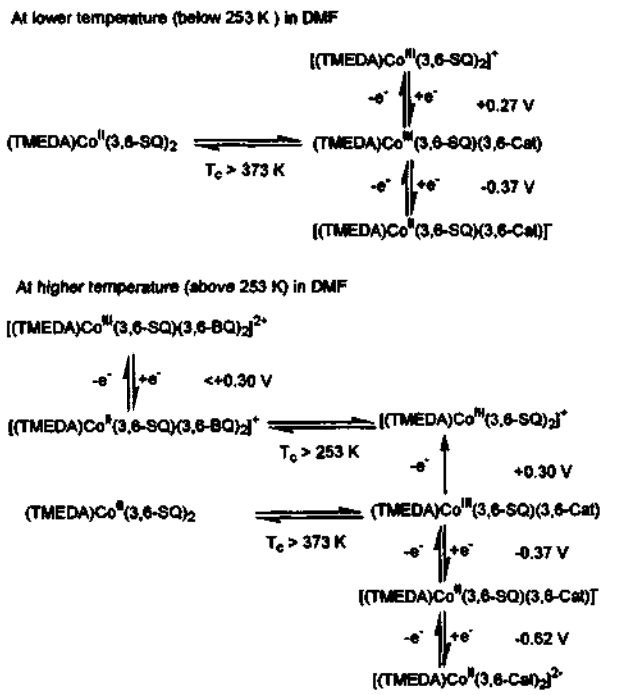


Figure 9. Spectroelectrochemical reduction of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF containing 0.1 M Bu_4NClO_4. Solid line for Co^{III} complex and dot for reduced Co^{II} complex.

Discussion and Conclusions

In a previous report,[4] we described the properties of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat). TMEDA as a hard-donor coligand stabilizes the cobalt-quinone complex, and is responsible for the relatively high transition temperature (T_c) of 310 K in toluene solution and above 400 K in solid state. Electronic spectra recorded in nonaqueous solutions at temperature where tautomeric forms of the complex exist show features that are characteristic of the Co^{II} and Co^{III} charge distributions. The temperature dependence of optical spectra has been used to provide information on the Co^{III}/Co^{II} transition temperature in solution. T_c of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) is about 310 K in toluene, but isn't measured in DMF, MeCN, and CH_2Cl_2 within temperature range employed. Whereas T_c for Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) is determined as about 280 K in toluene solution, 300 K in CH_2Cl_2, 340 K in MeCN, and 363 K in DMF. The T_c of Co^{III}(TMEDA)(3,5-SQ)(3,5-Cat) is lower value as 280 K than 310 K of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in toluene. Although T_c of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) isn't determined in the range of experiments, the results of T_c will be similar in the other solvents. These results demonstrate that the temperature range of the equilibrium is dependent upon the donation effect of substituted quinone ligand as well as solvent. T_c seems to be increased with the increase of donor number of solvent and the donation effect of quinone ligand which will be explained as the influence of electronic effects on substituted quinones. An *o,o*-substituted quinone of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) has stronger donation property than an *o,m*-substituted quinone of 3,5-DBBQ. A tautomeric equilibrium between Co^{III} and Co^{II}-quinone complexes containing TMEDA coligand may be described in Eq (2).

$$Co^{III}(TMEDA)(SQ)(Cat) \rightleftharpoons Co^{II}(TMEDA)(SQ)_2 \quad (2)$$



Scheme 1.

Co^{III}(TMEDA)(SQ)(Cat) can reduce to $[Co^{III}(TMEDA)(Cat)_2]^-$ with ligand-centered or $[Co^{II}(TMEDA)(SQ)(Cat)]^-$ with metal-centered, and then reduces to $[Co^{II}(TMEDA)(Cat)_2]^{2-}$. Co^{III}(TMEDA)(SQ)(Cat) can oxidize to $[Co^{III}(TMEDA)(SQ)_2]^+$. On the basis of the electrochemical and spectroelectrochemical results, Co^{III} isomer is predominant rather than Co^{II} in DMF used for the spectroelectrochemical studies. The possible redox reactions of Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat) in DMF may be summarized in terms of Scheme 1. The first reduction of Co^{III}(TMEDA)(SQ)(Cat) gives the formation of $[Co^{II}(TMEDA)(SQ)(Cat)]^-$ by one-electron process with metal-centered (see a spectrum of Figure 9), and then reduces to $[Co^{II}(TMEDA)(Cat)_2]^{2-}$. The oxidation of Co^{III} isomer gives different formation as a function of solution temperature. In DMF at lower temperature for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat), Co^{III}(TMEDA)(SQ)(Cat) oxidizes to $[Co^{III}(TMEDA)(SQ)_2]^+$ by one-electron process with ligand-centered. The redox couple between Co^{III}(TMEDA)(SQ)(Cat) and $[Co^{III}(TMEDA)(SQ)_2]^+$ in the oxidation region shown in Figure 6 demonstrates stabilization for $[Co^{III}(TMEDA)(SQ)_2]^+$ complex. However in DMF at higher temperature for Co^{III}(TMEDA)(3,6-SQ)(3,6-Cat), Co^{III}(TMEDA)(SQ)(Cat) may initially oxidize to $[Co^{III}(TMEDA)(SQ)_2]^+$ and then may convert to $[Co^{II}(TMEDA)(SQ)(BQ)]^+$ by intramolecular electron transfer from SQ ligand to Co^{III}. Tautomeric equilibra for oxidized form $\{[Co^{III}(TMEDA)(SQ)_2]^+\}$ are observed in DMF solutions. An equilibrium between Co^{III} and Co^{II}-quinone complexes containing TMEDA coligand for oxidized form $\{[Co^{III}(TMEDA)(SQ)_2]^+\}$ is shown in Eq. (3).

$$Co^{III}(TMEDA)(SQ)_2]^+ \rightleftarrows [Co^{II}(TMEDA)(SQ)(BQ)]^+ \quad (3)$$

Transition temperatures for the Co^{III}/Co^{II} equilibrium in DMF solution have been found to be dependent upon the substituted quinone ligand. The T_c of $Co^{III}(TMEDA)(3,6\text{-}SQ)_2]^+$ seems to be about 253 K and 233 K for $Co^{III}(TMEDA)(3,5\text{-}SQ)_2]^+$.

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