Electrochemical and Spectroelectrochemical Studies of Cobalt Salen and Salophen as Oxygen Reduction Catalysts

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Electrochemical and spectroelectrochemical studies of cobalt-Schiff (Co-SB) base complexes, Co(salen) [N-N'-bis(salicylaldehyde)-ethylenediimino cobalt(II)] and Co(salophen) [N-N'-bis(salicylaldehyde)-1,2-phenylenediimino cobalt(II)], have been carried out to test them as oxygen reduction catalysts. Both compounds were found to form an adduct with oxygen and exhibit catalytic activities for oxygen reduction. Comparison of spectra obtained from electrooxidized complexes with those from Co-SB complexes equilibrated with oxygen indicates that the latter are consistent with the postulated complex formed with oxygen occupying the coaxial ligand position, namely, Co(III)-SB·O_2^-. The catalysis of oxygen reduction is thus achieved by reducing Co(III) in the oxygen-Co-SB adduct, releasing the oxygen reduction product, *e.g.*, O_2^-, from the Co(II)-SB complex.

Introduction

Coordination cobalt complexes that can reversibly coordinate dioxygen have been the subjects of extensive studies.[1-4] Organic ligands for these complexes include macrocyclic compounds such as porphyrin and phthalocyanine derivatives as well as Schiff bases. It has also been demonstrated that these metal complexes act as catalysts for the electroreduction of oxygen,[5-9] which is an important cathodic reaction in energy conversion systems such as fuel cells and batteries. Since cobalt-Schiff base complexes were reported to be synthetic reversible oxygen carriers by Tsumaki,[10] many investigators have conducted extensive studies in relation to the oxygen-carrying property of these complexes.[1-4] Moreover, based on this property, investigators pointed out that these compounds would be promising electrocatalysts for the reduction of oxygen in addition to cobalt porphyrins and cobalt phthalocyanines.[11-13]

Among the cobalt-Schiff base complexes, the best known is N,N'-bis(salicylaldehyde)-ethylenediimino cobalt(II), commonly called Co(salen), which has a low-spin configuration with a square planar donor atom symmetry.[14-17] It has been well established that its base adduct [Co(salen)L], where L could be a solvent molecule such as pyridine (Py) and dimethylsulfoxide (DMSO), and its derivatives have a ground state electron configuration in which a single unpaired electron occupies the d_{z^2} orbital.[15-18] Ochai *et al.*[16,18] suggested from their studies on the kinetic and thermodynamic aspects of the oxygenation of Co(salen) in various solvents that its electronic configuration should be $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^2(d_{z^2})^1$ $(d_{xy})^0$ when solvents with high donor strengths, such as DMSO and Py, are incorporated as a coaxial ligand. They indicated that the oxygenation of Co(II)L complex forms

either O_2·CoL (1 : 1 adduct) or LCo·O_2·CoL (2 : 1 adduct), of which the 2 : 1 adduct is thermodynamically favored. Busseto *et al.*[19] and Hitchman[17] identified electronic absorption bands in the near infrared region corresponding to the d-d transition from their studies on the electronic structures of low-spin Co(II)-Schiff base complexes. They assigned one or more charge transfer transitions of high molar absorptivities in the UV-Vis region. Hipp *et al.*[15] in their studies of Co(II) complexes using electronic and circular dichroism assigned the bands at about 300-351 nm to the $\pi \rightarrow \pi^*$ ligand transition and that at about 410-490 nm to d $\rightarrow \pi^*$ metal-ligand charge transfer (MLCT) transitions.

We have been studing mechanisms involved in oxygen reduction reactions and their catalysis under various experimental conditions.[20-24] As an extension of these studies, we report the results of electrochemical and spectroelectrochemical experiments on Co(salen) and its derivative N-N' bis(salicylaldehyde)-1,2-phenylenediimino cobalt(II) monohydrate, Co(salophen)·H_2O, as model compounds for reversible oxygen carriers and also, for oxygen reduction catalysts. The study has been conducted first in non-aqueous solutions and extended to their adsorbed states on carbon electrodes in an effort to assess and understand their catalytic activities for oxygen reduction in aqueous solutions.

Experimental Section

Aldrich's Co(II)(salen) and Co(II)(salophen), whose chemical structures are shown in Figure 1, were used as received. EM Science's Omnisolve, glass distilled dimethylsulfoxide (DMSO) was used after fractional distillation after drying over activated molecular sieves. Southwestern Analytical's (Austin, Texas) electrometric grade tetra-n-butylammonium perchlorate (TBAP) was used as a supporting electrolyte after drying on a vacuum line overnight. For recording linear sweep voltammograms in aqueous solutions, Baker Analyzed KCl or Alfa Product's ultra pure potassium hydroxide was

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[†]Deceased in 1998.
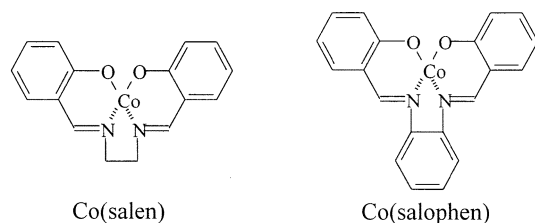[*]To whom correspondence should be addressed: Fax: +82-562-279-3399, E-mail: smpark@postech.edu

Figure 1. Structures of Co(salen) and Co(salophen).

used. Aqueous electrolyte solutions were prepared using doubly distilled, deionized water.

A single compartment cell housing working, reference, and counter electrodes was used for both electrochemical and spectroelectrochemical measurements. A platinum disk electrode with an area of 0.031 cm^2 was used for voltammetric measurements, while a reflective platinum disk electrode with an area of 0.33 cm^2 was used for spectroelectrochemical measurements. Either a silver wire pseudo-reference or Ag/AgCl (in satured KCl) reference electrode was used depending on the medium. For measurements in aqueous solutions, a modified carbon paste (area = 0.24 cm^2) or glassy carbon (GC) disk (area = 0.28 cm^2) working electrode, an Ag/AgCl (in saturated KCl) reference electrode, and a platinum wire spiral counter electrode were used. Carbon paste electrodes were prepared first by mixing 95% (w/w) of graphite powder (Alfa Products, below 325 mesh) with 5% (w/w) of a cobalt Schiff base complex intimately. This was then mixed with the same weight of wax at an elevated temperature of about 70 °C. The electrode was made by filling a glass tube with this mixture and heating it in an oven to about 70 °C, followed by cutting the carbon paste outside the tube flush to the perpendicular long axis and subsequent polishing.[11] The glassy carbon electrode was modified by first dipping a Co(salophen) solution in pyridine and drying it. This method was not successful for Co(salen) due to its high solubility in aqueous alkaline media.

A Hewlett-Packard model 8452A photodiode array spectrophotometer was used for the transmittance spectral measurements. The solution spectra of Co(salen) and Co(salophen) were obtained in a transmittance mode by this spectrophotometer. A Princeton Applied Research (PAR) model 173 potentiostat-galvanostat along with a PAR 175 universal programmer was used for the spectroelectrochemical measurements and to record cyclic voltammograms (CVs). An Oriel Instaspec® IV with a charge coupled device (CCD) detector assembled in a near normal incidence reflectance mode using a bifurcated optical fiber was used for the spectroelectrochemical measurements of both solution and surface species. In these spectroscopic measurements, transmittance or reflectance of blank solutions were first measured and used for background corrections. Details of the instrumentation for spectroelectrochemical experiments have been described elsewhere.[25-28]

Results and Discussions

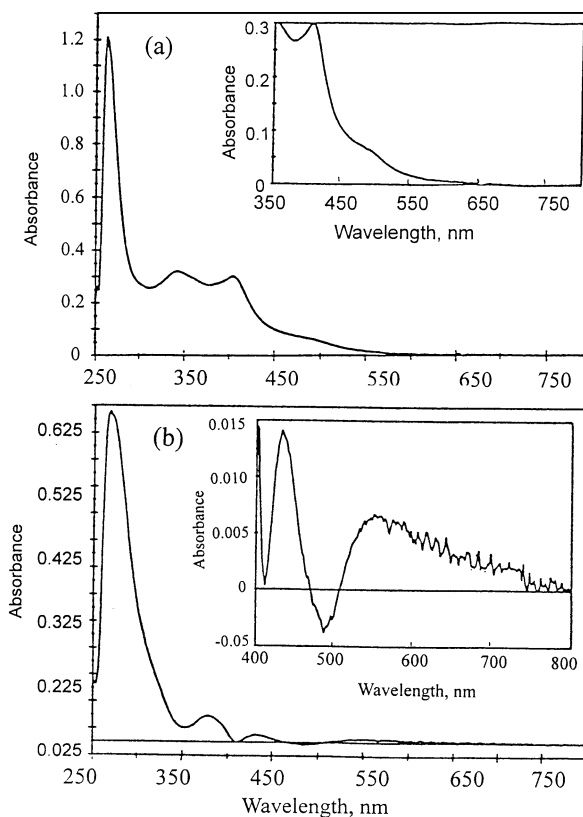**Spectroscopic Studies**.   Figure 2 shows: (a) an absorp-

Figure 2. UV-Vis Spectrum recorded in DMSO solution under an inert atmosphere for (a) 0.035 mM Co(salen) and (b) difference spectrum obtained by substracting the spectrum under the inert atmosphere from that under the oxygen atmosphere. The inset shows an expanded spectrum between 400 and 800 nm.

tion spectrum of 3.5×10^{-5} M Co(II)(salen) in deaerated DMSO and (b) a difference spectrum obtained between a spectrum recorded in the oxygen saturated solution and that shown in Figure 2a, respectively. The inert atmosphere was obtained by saturating the solution with nitrogen gas after we found that the spectrum obtained for Co(salene) under an argon atmosphere was identical to that obtained under the nitrogen atmosphere. The Co(salen) spectrum obtained without oxygen present (Figure 2a) shows three well defined bands and a shoulder at about 490 nm. The band at 266 nm is assigned to the $\pi \to \pi^*$ transition, that at 345 nm to $n \to \pi^*$, and the one at 405 nm to $d \to \pi^*$, respectively.[15,29] The broad shoulder at around 490 nm arises from the $d \to d$ transition according to Hitchman.[17] The difference spectrum shown in Figure 2b indicates that the $\pi \to \pi^*$ and $n \to \pi^*$ band undergo increases in their absorbance, while a slight decrease in absorbance is seen for the $d \to d$ transition at about 490 nm upon its exposure to oxygen. Also noticed is a new broad weak band with its peak absorbance at about 530 nm (see the spectrum shown in the inset of Figure 2b), which was assigned to the d-d band and much studied.[17,30] The decrease in the $d \to d$ transition at about 490 nm (see the inset of Figure 2b), albeit small, indicates that Co might be in +3 state. That the central Co ion might be in the +3 state will be clearer for Co(salophen) as will be discussed in detail below. The spectra shown in Figures 2 and 3 were obtained
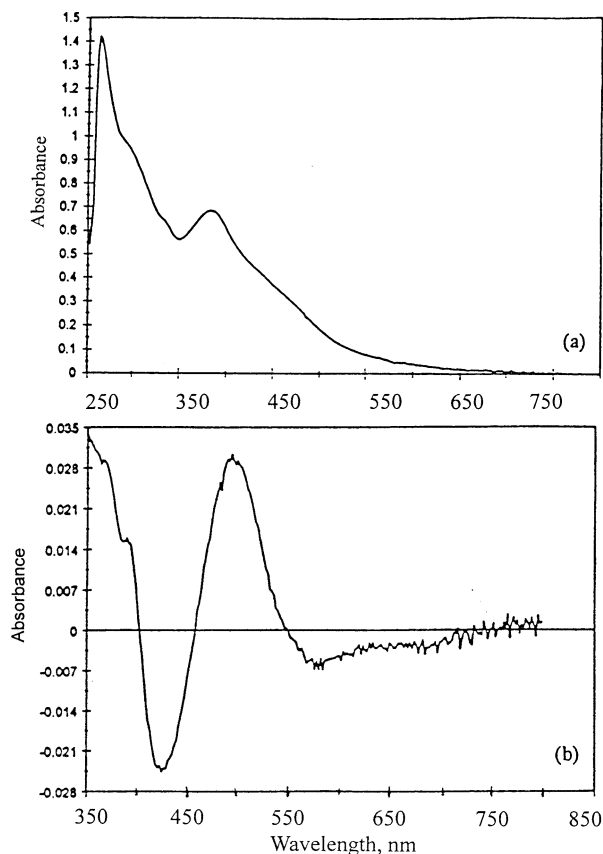
Figure 3. UV-Vis Spectrum recorded in DMSO solution under an inert atmosphere for (a) 0.025 mM Co(salophen) and (b) difference spectrum obtained by substracting the spectrum under the inert atmosphere from that under the oxygen atmosphere.

Table 1. Summary of Spectroscopic Data[a]

Co(salen), 3.5×10^{-5} M			Co(salophen), 2.5×10^{-5} M		
λ_{max}, nm	Absorbance	Transition	λ_{max}, nm	Absorbance	Transition
266	1.25	$\pi \rightarrow \pi^*$	264	1.43	$\pi \rightarrow \pi^*$
345	0.35	$n \rightarrow \pi^*$	296	0.95	$n \rightarrow \pi^*$
405	0.33	$d \rightarrow \pi^*$	385	0.675	$d \rightarrow \pi^*$
490	0.07	$d \rightarrow d$	425	0.300	$d \rightarrow d$

[a]Measurements made by transmittance experiments in a 1.00 cm cell with the solvent used as a spectral reference.

in the transmittance mode; the spectral data are summarized in Table 1.

The spectrum of Co(II)(salophen) recorded under the nitrogen atmosphere (Figure 3a) has similar spectral features as those of Co(salen), except that bands are generally blue shifted compared to Co(salen) and not resolved as well as for Co(salen) (see Table 1). The higher electron density on the salophen molecule due to an extra benzenoid ring is believed to cause the blue shift as it interacts, or donates its electrons more strongly to the central metal ion. The poor resolution is explained by more extensive conjugation through the extra benzenoid between two otherwise isolated π-systems, which makes differences between energy levels on the ligand molecules less separated. Due to the benzenoid group,

salophen became a 11 π-system, whereas two 4π-systems are separated by an ethylene group in the salen molecule.

When oxygen is saturated in the solution containing Co(salophen), the difference spectrum obtained (Figure 3b) is essentially the same as that for Co(salen), except that the decrease in the $d \rightarrow d$ band at about 425 nm is much more dramatic. While the absorbances arising from $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $d \rightarrow \pi^*$ transitions increase, the $d \rightarrow d$ band at 425 nm and another at about 565 nm show decreases in their intensities upon formation of the oxygen adduct. In general, the observation may be summarized as increases in $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $d \rightarrow \pi^*$ transitions and decreases in $d \rightarrow d$ transitions. This suggests that the coordination of oxygen in the axial position leads to localization of the electron density onto the oxygen molecule through a bond similar to the inoic bonding. From the similarity of the spectral features obtained from the Co-SB·O$_2$ adduct with those of the electrochemically oxidized Co-SB with oxygen absent (*vide infra*), we conclude that the Co ion in the adduct is in the +3 state.

The spectral changes observed for Co(salen) and Co(salophen) in the absence and presence of oxygen are reversible, indicating that the formation of the adduct is also reversible. Spectral changes were reversible for many repeated recordings, at least more than three times.

Figure 4 shows the absorbance spectra of the Co(salophen) film adsorbed on the glassy carbon surface without potentials applied to see how the spectrum would be affected in an aqueous 0.10 M KCl solution in the absence (a) and presence (b) of oxygen. This and the other spectra shown hereafter were recorded in a near normal reflectance mode using an optical fiber probe. In general, the spectral features are similar to those observed in solution, except that fairly large red shifts and band broadenings are observed. The spectrum under the inert atmosphere (Figure 4a) shows two bands, one at 405 nm ($d \rightarrow \pi^*$ transition) and the other at 475 nm ($d \rightarrow d$ transition). Compared to the spectrum recorded in solution (Figure 3a), it is seen that both bands underwent red shifts by about 20-50 nm. Also, the spectral bands are much broader than those observed in the solution. The band broadening observed here suggests that Co-SBs undergo oligomerization or polymerization reactions when adsorbed on carbon surfaces. Very similar observations have been made for iron and cobalt phthalocyanines also.[24] More importantly, the relative oscillator strength of the $d \rightarrow d$ transition became significantly higher compared to that of $d \rightarrow \pi^*$ on the carbon surface. The extensive red shifts in spectral bands and the increase in the $d \rightarrow d$ absorption in comparison to that in solution indicate that carbon surfaces may act as an electron donor in the axial position. In other words, the Co ion may be in a partially reduced state on the carbon surface. It was pointed out in recent reports[31,32] that the adsorption of planar molecules with the π system onto the carbon surface may take place *via* a $\pi \rightarrow \pi$ interaction between the π system of the planar molecule and the π system of the carbon; the adsorption on the carbon surface would render the central metal ion (Co(II)) more reduced, resulting in an increase in the MLCT band. The band broadening and spectral shifts
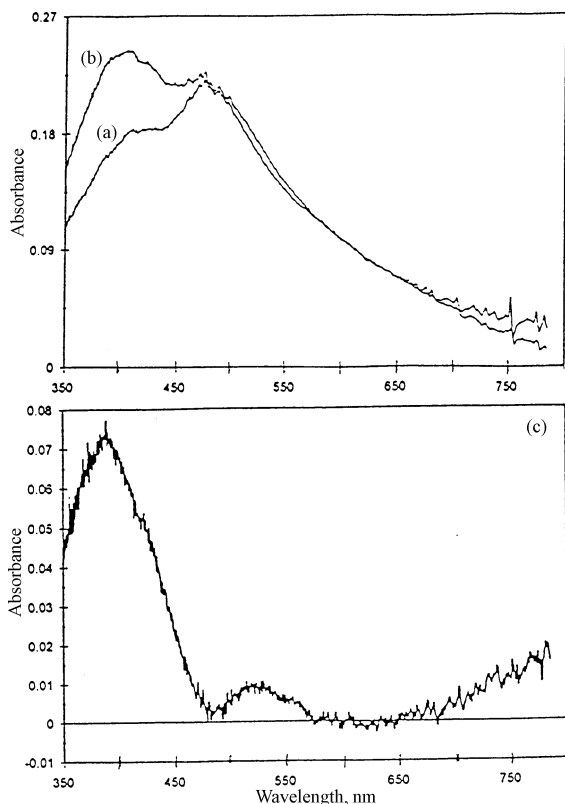
Figure 4. Absorption spectra recorded for Co(salophen) adsorbed on glassy carbon in 0.1 M KCl: (a) under an inert atmosphere, (b) under an oxygen atmosphere, and (c) difference spectrum obtained by substracting (a) from (b).

must have resulted from the formation of aggregates that these species tend to form.[33,34]

The spectrum of Co(salophen) film recorded in an oxygen-saturated solution (Figure 4b) shows slight increases in the d → π* (~405 nm) and d → d (~480 nm) transitions along with some spectral shifts. The differences in the spectral behavior displayed upon addition of oxygen are shown more clearly in the difference spectrum in Figure 4c. A similar behavior was observed in the solution spectra in the presence of oxygen, except that the d → π* band at about 480 nm is almost not affected. Due to the localization of the electron density onto the oxygen molecule in the axial ligand position, the Schiff base ligands become more detached from the central metal ion and, thus, shows a stronger n → π* transition ab about 375 nm as can be seen from Figure 4c. The π back-bonding from the molecular oxygen to the Co ion makes electronic transitons of Co d-electrons easier, resulting in slight increases in d → d transitions at about 480 and 570 nm.

Electrochemical Studies.   Figure 5 presents typical cyclic voltammograms of Co(salen) (a) and Co(salophen) (b) in DMSO under an inert atmosphere. The voltammetric characterisics are listed in Table 2. From the peak separation values (ΔE_ps) and the cathodic-to-anodic or anodic-to-cathodic peak current ratios, we conclude that the electron transfer processes are chemically reversible, one electron transfer processes. Also, the scan rate dependencies of the peak currents support that the electron transfer is a diffusion-controlled process. Diffusion coefficients were calculated to be 1.4 ($\pm$ 0.3)$\times 10^{-6}$ cm^2/s for Co(salen) and 3.0 ($\pm$ 0.4)$\times 10^{-6}$ cm^2/s for Co(salophen), respectively, from the slopes of the i_p *vs.* v$^{1/2}$ plots, where i_p is the peak current and v is the scan rate. The slope of the i_p *vs.* v$^{1/2}$ plot has the form,

$$\text{slope} = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^* \tag{1}$$

for a reversible electrochemical reaction, where $n = 1$ (see Table 2), A is the electrode area, D is the diffusion coefficient, and C^* is the bulk concentration of the compound.[35] It is interesting that Co(salophen) has a larger diffusion coefficient than Co(salen). Unfortunately, we have no explanation for this anomaly although one might speculate that the molecule with a planar salophen ligand might feel less resistive for the medium than with a less planar salen ligand.

Chronocoulometric experiments were carried out in order to obtain kinetic parameters for the electron transfer reactions. These experiments were carried out at lower potentials than the diffusion limited region. According to Christie *et al.*,[36,37] a faradaic charge ($Q(t)$) *vs* $t^{1/2}$ plot for a redox process is linear and follows the relation

$$Q(t) = nFAk_f C_o^* \left[\frac{2t^{1/2}}{H\pi^{1/2}} - \frac{1}{H^{1/2}} \right] \tag{2}$$

where $H = \pi^{1/2}/(2t_i^{1/2})$ with t_i the intercept on the time axis when $Q(t) = 0$. The k_f values can be obtained from the slope at various potentials. From the k_f values thus obtained, the exchange rate constant k^0 is calculated using the equation,

$$k_f = k^0 \exp\left[\frac{\alpha n F}{RT}(E - E^{0'}) \right] \tag{3}$$

where α is the transfer coefficient, E is the applied potential, and $E^{0'}$ is the formal potential estimated from the average of the cathodic and anodic CV peak potentials. The exchange rate constant (k^0) values calculated from plots shown in Figure 6 are 4.2$\times 10^{-3}$ cm/s and 3.6$\times 10^{-3}$ cm/s with α values of 0.33 and 0.48 for reducing Co(salen) and Co(salophen), respectively. These values place the electrochemical reduc-

Table 2. Summary of Voltammetric and Coulometric Experiments

Compounds	$E_1^{0'}$, V^a	$\Delta E_{p,1}$, mV^b	$n_{app,1}^c$	$E_2^{0'}$, V^a	$\Delta E_{p,2}$, mV^b	$n_{app,2}^c$
Co(salen)	0.030	60	1.11 $\pm$ 0.08	-1.13	60	0.97 $\pm$ 0.02
Co(salophen)	0.051	60	1.07 $\pm$ 0.03	-1.03	60	0.95 $\pm$ 0.02

^{a}Formal potentials ($E^{0'}s$) were estimated by taking averages of anodic and cathodic CV peak potentials measured with respect to the Ag/AgCl (in saturated KCl) electrode for Co(III)/Co(II) (subscript 1) and Co(II)/Co(I) (subscript 2) redox pairs. $^b\Delta E_p$s are defined by the difference of potentials for anodic and cathodic processes. ^{c}number of electrons transferred determined by coulometric experiments.
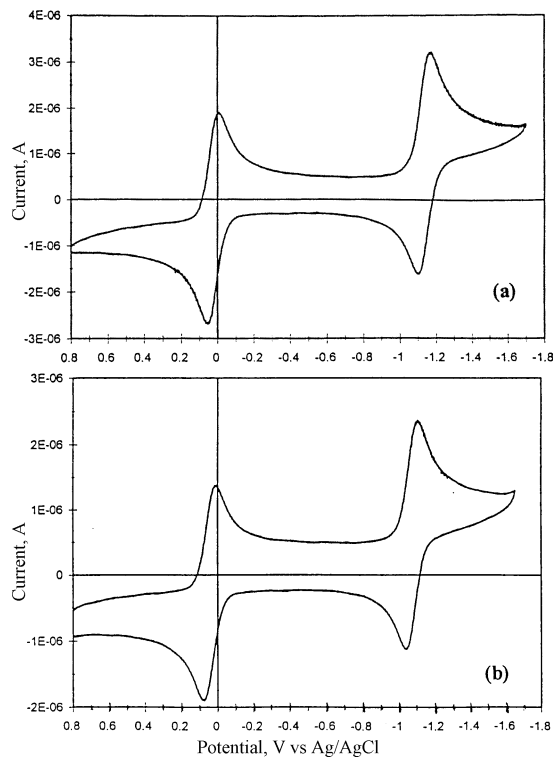
Figure 5. Cyclic voltammograms recorded at 50 mV/s in DMSO solutions containing (a) 1.36 mM Co(salen) and (b) 1.10 mM Co(salophen) under an inert atmosphere.

Figure 6. The $\ln k_f$ *vs* overpotential plots for reduction of the (a) Co(salen) and (b) Co(salophen).

tion of these compounds in the category of electrochemically quasireversible electron transfer.

The modified carbon paste electrodes were prepared using graphite powder. Linear sweep voltammograms (LSVs) recorded at these electrodes without oxygen present in aqueous KOH solutions showed similar behaviors to those shown by adsorbed cobalt phthalocyanines, in which low irreversible current traces of Co-SB reduction appeared (not shown).[24] When oxygen was saturated, the current due to Co-SBs were suppressed and the LSVs as shown in Figure 7 were obtained. As can be seen, significant catalytic activities are observed from these electrodes for oxygen reduction as evidenced by the potential shifts for oxygen reduction by 180 and 160 mV at Co(salen) and Co(salophen) modified electrodes, respectively. A larger potential shift by Co(salen) than that by Co(salophen) suggests that the Co(salophen)·O$_2$ adduct has a higher thermodynamic stability than Co(salen)·O$_2$. The variations in peak currents at the Co(salen) and Co(salophen) modified electrodes reflect the difficulty in precise control of surface areas of carbon paste electrodes.

Spectroelectrochemical Studies. Spectroelectrochemical measurements were conducted on Co(salen) and Co(salophen) solutions in DMSO. The difference spectra were recorded in a near normal incidence reflectance mode at various applied potentials with spectra recorded at open circuit potentials used as references. Thus, the difference spectra obtained show the difference in spectral features caused by applying potentials with respect to the open circuit potential.

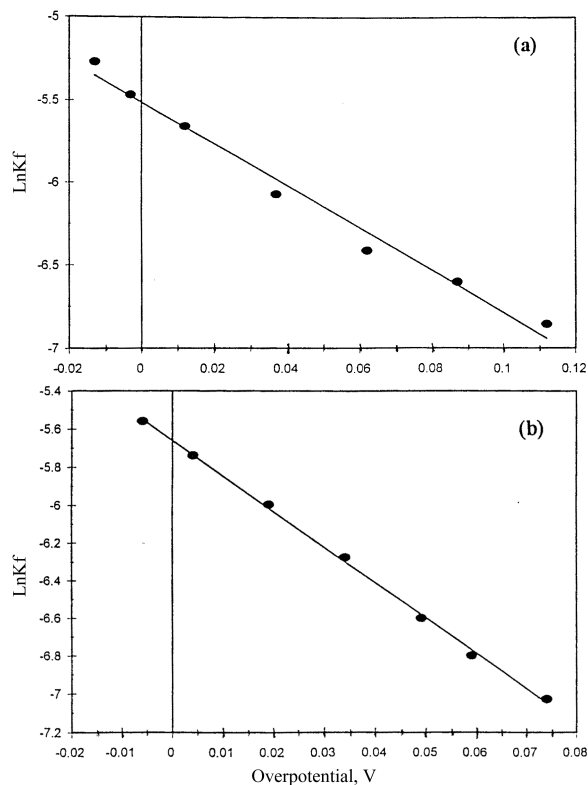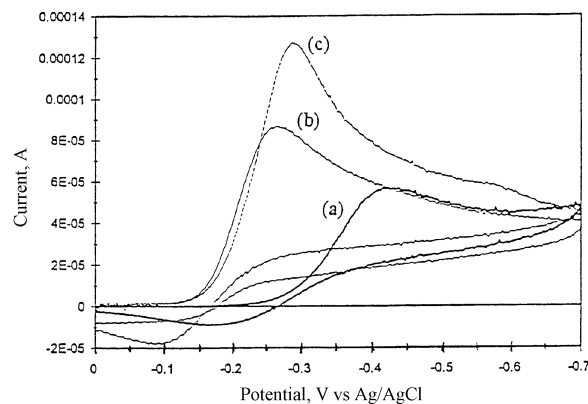Figure 8a shows the difference spectrum of 0.35 mM

Figure 7. Single sweep voltammograms for oxygen reduction in 1 M KOH saturated with oxygen recorded at (a) a bare carbon paste electrode, (b) a Co(salen) modified electrode, and (c) a Co(salophen) modified electrode.

Co(salophen) in DMSO while it is reduced at -1.2 V in an inert atmosphere. These spectroelectrochemical measurements were made in a reflectance mode such that all the Co(salophen) molecules above the electrode surface, which underwent electrochemical reactions, are integrated in the form of absorbance. The $\pi \to \pi^*$, n $\to \pi^*$, and d $\to \pi^*$ bands are not significantly affected by the reduction, while the d $\to$ d bands in both the high (~480 nm) and low (~610 nm) energy regions are suppressed. It should be pointed out here that the spectroelectrochemical behavior shown by the Co-Schiff base complexes described here is in stark contrast to those shown by its phthalocyanine counterparts. The metal-
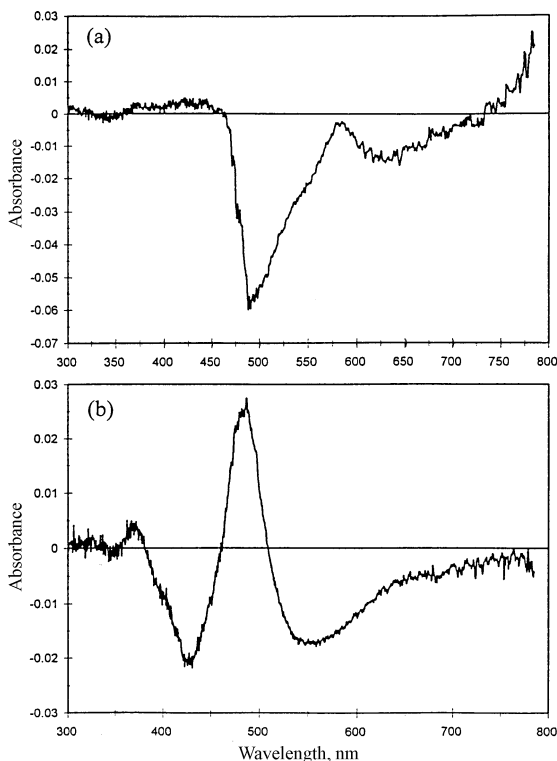
Figure 8. Difference spectra recorded from 0.35 mM Co (salophen) while it is reduced at -1.2V (a) and oxidized at +0.2 V *vs* Ag (b) in DMSO containing 0.1 M TBAP under an inert atmosphere. The reflective platinum electrode was used for spectroelectrochemical measurements.

lophthalocyanines exhibit an intense metal-ligand charge-transfer (MLCT) band upon reduction to Co(I).[23] However, the MLCT band, *i.e.*, d → π^* transition here, is not much affected when Co(salophen) is reduced. There appears to be a slight increase in the d → π^* transition (Figure 8(a)) but we are not certain whether this is the increase in signal or an experimental artifact due to noise. An extra electron added to the complex may be stabilized through an extensive conjugation through three benzene rings which are linked by, and thus conjugated *via*, two -CH = N- double bonds. The decrease in the d-d transitions in both energy regions (~480 nm and ~610 nm) upon reduction suggests that the addition of the extra electron goes to the d_{xy} orbital, which makes the electronic transition from the occupied d-orbitals more difficult. This must be why the d-d transitions are suppressed, while the MLCT band is not affected significantly.

When Co(salophen) is oxidized (Figure 8b), it shows a very similar spectral changes to the case when it forms an adduct with oxygen (Figure 3b). This behavior is consistent with the fact that the Co ion in the adduct must be in the +3 oxidation state, as already pointed out. When oxidized, the MLCT bands are suppressed while the absorbance of the d → d band is increased.

Our results from the spectroscopic studies on Co(II) Schiff base complexes show that their electronic structure is sensitive not only to the molecular structure of the Schiff base ligand but also to the type of the axial ligand. The solution

spectra recorded from Co(salen) and Co(salophen) in aprotic media in the presence of oxygen show basically the same spectral features as those of electrochemically oxidized Co-Schiff base complexes, indicating that the central cobalt ion is in the +3 state in Co-SB·oxygen adducts. This supports the widespread view[1-4,10,15,18] that the adduct is in the form of Co(III)-SB·O_2^-.

The two Co-SB complexes studied here undergo quasi-reversible one-electron transfers for both oxidation and reduction. Also, the Co-SB modified electrodes on a graphite powder support clearly exhibit catalytic effects.

Conclusions

From the spectroelectrochemical results, we conclude that d-orbital energies of the metal ion center are affected by the oxidation state of the metal, explaining the changes in MLCT and d → d bands in these complexes. The decrease/increase in absorbance of the d → d transition depending on whether the complex is reduced or oxidized (Figure 8(a)) suggests that the d → d band arises from the d_{z^2} → d_{xy} transition. According to Ochai,[16,18] Co(salen) dissolved in a strong donor solvent such as DMSO has an unpaired electron localized in d_{z^2} orbital; hence, an electron removed would be from this orbital. This transition should be in the 450-550 nm region in this energy level scheme.

The oxidation state of the Co ion in the oxygen saturated solutions of Co(salen) and Co(salophen) is shown to be Co(III) from the similarity of their difference spectra to those recorded when these complexes are electrochemically oxidized under the nitrogen atmosphere. Hence, the presence of Co(III)·O_2^- in the dioxygen adduct is consistent with results obtained from these experiments.

Finally, our observation is consistent with a catalytic mechanism, in which the catalytic effect is attained *via* the adduct formation of Co-SB with dioxygen, *i.e.*, Co(III)-SB·O_2^-. The adduct is then reduced and the product is released according to the reaction,

$$Co(III)\text{-}SB\cdot O_2^{-\cdot} + e^- \rightarrow Co(II)\text{-}SB + O_2^{-\cdot}. \qquad (4)$$
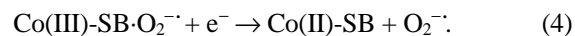
The Co(II)-SB thus reduced is reoxidized by forming the adduct again in solution with oxygen, repeating the catalytic process. The reduction potential of the adduct is more positive than that of oxygen reduction, making the overpotential for oxygen reduction smaller. The reactive intermediate species, superoxide ion, will then find its way to go to the final product, *e.g.*, either peroxide or water, depending on the reaction medium.

We proposed the above mechanism in our earlier study of the catalytic mechanism for oxygen reduction using Co(II)-disalophen as a catalyst.[11] In our current study, we have identified the intermediate species, *i.e.*, an adduct formed between Co-SB and O_2, using spectroscopic and spectroelectrochemical techniques, and present it as evidence for it.

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