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Steric Control of Redox Potentials of Cobalt(II) Schiff Base Complexes with Phenyl Substituents

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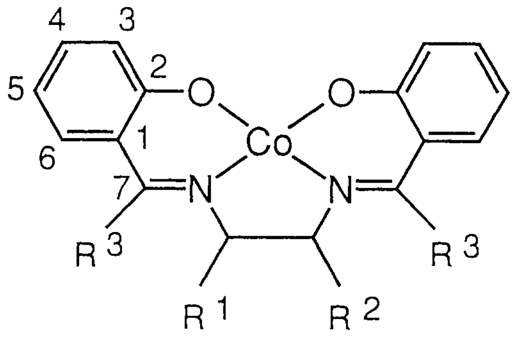
The structure of the cobalt(II) complex of the tetradentate Schiff base ligand derived from 2-hydroxybenzophenone and *rac*-1,2-diphenylethylenediamine was determined by the X-ray method to show that the phenyl groups in the N-N chelate moiety are in axial positions. The redox potential of the cobalt(II/III) couple in CH_3CN for the complex is shifted in a more positive direction by *ca.* 300 mV than that for [Co^{II}(salen)]. The significant anodic shift is ascribed to the steric effect of the axial phenyl groups.

Electronic effects of substituents in the ligand of metal complexes affect the redox potentials of the central metals.1) In this letter, we report that axially oriented phenyl groups in square planar cobalt(II) Schiff base complexes, [Co^{II}(SB)], make the Co^{II} center difficult to oxidize due to steric reasons. Since [Co^{II}(SB)] catalyzes the oxygenation of organic molecules,2) and it is known that the orientation of the phenyl groups plays an important role in asymmetric catalytic reactions,3) it is interesting to study the steric control of redox potentials by the phenyl substituents.

Figure 1 shows the redox potentials ($E^{\circ\prime}$) found for the cobalt(II/III) couple for [Co^{II}(salen)] (**a**, H_2salen= *N*,*N*'-disalicylideneethylenediamine) and the derivatives (**b**-**g**)4) as determined by averaging the anodic and cathodic peak potentials of cyclic voltammograms in acetonitrile solutions containing 0.1 M Bu_4NBF_4. The electrochemical cell was a three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/Ag$^+$ (Ag/0.1 M $AgNO_3$) reference electrode. All complexes show almost reversible one-electron waves; the peak-to-peak separation (ΔE_p) of 70-81 mV is slightly larger than the theoretical value (57 mV) and the peak ratio (i_{pc}/i_{pa}) is almost equal to unity. Under the



a $R^1 = H, R^2 = H, R^3 = H$
b $R^1 = Ph, R^2 = H, R^3 = H$ (*R*)
c $R^1 = Ph, R^2 = Ph, R^3 = H$ (*RR*)
d $R^1 = Ph, R^2 = Ph, R^3 = H$ (*meso*)
e $R^1 = H, R^2 = H, R^3 = Ph$
f $R^1 = Ph, R^2 = H, R^3 = Ph$ (*R*)
g $R^1 = Ph, R^2 = Ph, R^3 = Ph$ (*RR*)

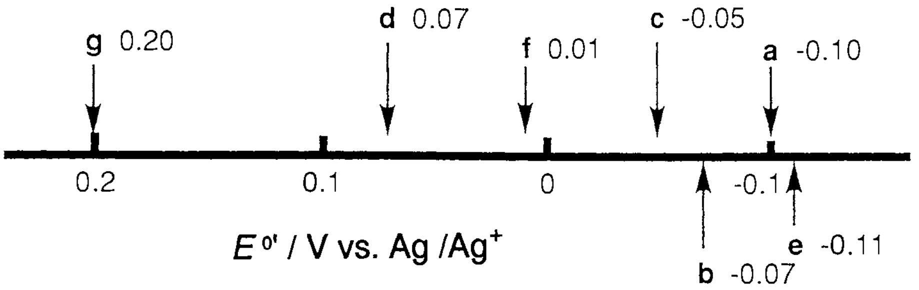


Fig. 1. Redox potentials ($E^{0\prime}$) for the cobalt(II/III) couple for [Co^{II}(Schiff base)].

same conditions, the Fc/Fc^+ (Fc=ferrocene) couple is observed at 0.085 V vs. Ag/Ag^+ with a ΔE_p value of 80 mV. That the substitution of H on the azomethine carbon atoms (R^3) with C_6H_5 gives only a small electronic contribution is demonstrated by the fact that **a** and **e** give closely similar values for $E^{0\prime}$ (-0.10 and -0.11 V, respectively). The most striking aspect of the data summarized in Fig. 1 is the remarkable change in the $E^{0\prime}$ value between **c** and **d**. The **c** and **d** complexes are diastereomers, and the electronic contributions of the two phenyl groups (R^1 and R^2) in the N-N chelate moiety should be the same, and thus, the large difference in $E^{0\prime}$ is solely attributed to the steric effects. In **c**, the two phenyl groups (R^1 and R^2) can take equatorial positions in the λ-gauche conformation. On the other hand, **d** has one axially disposed phenyl group irrespective of the conformation (λ- or δ-gauche) of the N-N chelate ring. This leads to a strong repulsion between the axial phenyl group and the apical ligand in the corresponding cobalt(III) complex.[6] A cobalt(III) complex has a strong tendency to take a 6-coordinate octahedral structure. Since the corresponding cobalt(II) complex is 4-coordinate and square planar, that interaction occurs only for the oxidized form of the complex. The resulting destabilization of the trivalent state causes a 120 mV increase for $E^{0\prime}$ for the cobalt(II/III) couple from -0.05 V to 0.07 V. The steric effects of substituents at the aromatic rings in the salen ligand in [Co^{II}(salen)] derivatives on the redox potentials of the cobalt(II/III) couple in DMF have been reported; *t*-butyl groups shifted the potentials to the more positive side and steric interactions with solvent molecules were indicated.[7] Kitaura *et al.*[8] have shown for [Co^{III}(salen)(pyridine)$_2$]$^+$ derivatives that *gem* di-substitution on the ethylene backbone of the salen ligand shifts the cobalt(III/II) reduction potential to the positive side, and the shift was attributed to the steric interaction between the substituted groups and the pyridine molecule coordinated at the apical site.

We realized that **g**, [Co^{II}{7-Phsal-(*RR*)-stien}] where all substituents (R^1-R^3) are phenyl groups, was not easily oxidized when we tried to prepare the cobalt(III) complexes. For example, **g** was not seemingly oxidized by air (oxygen) in the presence of 1-methylimidazole, on the other hand, **f** where R^1 and R^3 are phenyl groups, was easily oxidized to form [Co^{III}(Schiff base)(1-methylimidazole)$_2$]$^+$ under similar conditions. Actually, **g** had the most positive $E^{0'}$ value (+0.20 V vs. Ag/Ag$^+$) of the seven complexes studied.

In order to see the reason why **g** is so difficult to oxidize, we determined the molecular structure of [Co{7-Phsal-(*rac*)-stien}]·CH_3CN (*rac*-**g**) by the X-ray method.[9)]

Figure 2 shows an ORTEP drawing of *rac*-**g**. The geometry around the cobalt(II) ion is essentially square planar. A slight tetrahedral distortion is found; the mean deviation of the coordinating atoms, N(1), N(2), O(1), and O(2) from the N_2O_2 least-squares plane is 0.10 Å, which is comparable to those of the related complexes.[10,11)] In *rac*-**g**, the two phenyl groups (R^1 and R^2) are in the axial positions due to severe steric interactions with the phenyl groups on the azomethine carbon atoms (R^3). The two axially disposed phenyl groups should prevent the ligands from approaching the cobalt atom and make the oxidation to the cobalt(III) species very difficult. Since the substituents in the N-N chelate moiety exert little electronic effect on the redox potentials,[12)] the potentials can be used directly as a measure of the tendency of the substituents to axially dispose. The steric repulsion between the two phenyl groups (R^1 and R^3) in **f** is larger than that between the

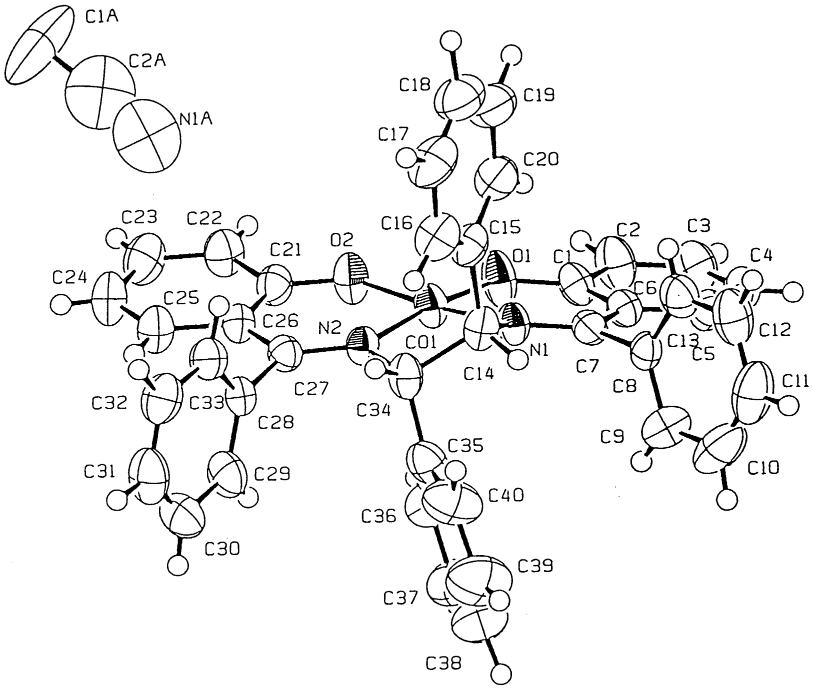


Fig. 2. ORTEP drawing of [Co{7-Phsal-(*rac*)-stien}]·CH_3CN (*rac*-**g**).

phenyl group (R^1) and hydrogen (R^3) in **b**, and the phenyl group (R^1) in **f** is more inclined to take the axial position than that in **b**, and thus the more positive $E^{0\prime}$ value for **f** (0.01 V) than for **b** (-0.07 V) is reasonably accounted for.

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4) The cobalt(II) complexes, **b-g** were prepared by the same method[5] as for [Co$^{\mathrm{II}}$(salen)] from Co(CH$_3$-COO)$_2$·4H$_2$O and the appropriate Schiff base ligands.

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6) The anion of supporting electrolyte seems to serve as the apical ligand. When Bu$_4$NCl is used instead of Bu$_4$NBF$_4$, for example, $E^{0\prime}$ for **c** is shifted in a more negative direction by 400 mV, and the result is consistent with the larger coordinating ability of Cl$^-$ than BF$_4^-$. However, the possibility that the solvent molecule serves as the apical ligand can not be ruled out.

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9) The crystal data are as follows: FW 670.67, monoclinic, $P2_1/n$, a=13.956(2), b= 14.703(2), c=17.808(3) Å, β=112.21(1)°, V=3383(2) Å^3, Z=4, D_x=1.317 g cm^{-3}, μ=0.544 mm^{-1} for Mo $K\alpha$ (λ=0.7107 Å). Intensity measurements were carried out for $2\theta \leq 50°$ on a Rigaku AFC-5R diffractometer at the X-Ray Laboratory of Okayama University. Among 6169 reflections (5966 were unique) measured in the range $-16 \leq h \leq 15$, $0 \leq k \leq 17$, $0 \leq l \leq 21$, those of 3972 had $I \geq 3\sigma(I)$. The structure was solved by the Patterson method and refined by a full matrix least squares procedure to R=0.045 and R_w=0.043. Full details of X-ray structure determination will be published separately.

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