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The Equilibria of Protonation Reaction of *N*,*N'*-Ethylenebis(salicylideneiminato)cobalt(II) and of Its Oxygenated Binuclear Complex by Perchloric Acid in Dimethyl Sulfoxide

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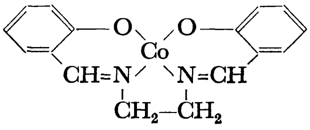
Acid dependence of oxygen uptake by Co(II)salen in DMSO was studied. As the concentration of perchloric acid increases in the absence of O_2, Co(II)salen forms 1: 1 and 1: 2 protonated complexes, with the formation constants $K_1=8.3\times10^3\ M^{-1}$ and $K_2=1.6\times10^3\ M^{-1}$ measured spectrophotometrically by the linearity method. The oxygen uptake ratio n of Co(II)salen in the absence of acid is 0.5, indicating formation of a 2: 1 O_2-bridged binuclear complex, with an immeasurably large formation constant K_3. The oxygenated complex is protonated by addition of acid with a formation constant $K_4=3.3\times10^5\ M^{-1}$ as observed again spectrophotometrically. When Co(II)salen is oxygenated in the presence of acid, n decreases considerably from 0.5 with increasing acid concentration. This is because the protonated Co(II)salen complexes are inert to oxygenation and both the rate of oxygenation of Co(II)salen and that of deoxygenation of oxygenated binuclear species are slow, as compared to the rapid processes of protonation.

In the last decade, much attention has been paid on the reversible oxygenation of some cobalt complexes by many investigators, especially on the reaction mechanisms and the electronic and the molecular structures of the oxygenated complexes,[1-3] because they have been taken as nice models for oxygen carriers in living systems. *N*,*N'*-Ethylenebis(salicylideneiminato)cobalt(II) (abbreviated as Co(II)salen below) was the first synthetic complex with a nature of reversible oxygenation,[4] which was mostly investigated in its solid state.[5] Recently, Floriani *et al.* found that Co(II)salen absorbs oxygen to form a binuclear complex Co(III)salen·O_2·-Co(III)salen in aprotic solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) at room temperature,[6] while Ochiai showed that Co(II)salen forms a 1: 1 complex with an oxygen molecule at 77 K and that the stability of oxygenated species depends upon the ligand which is situated at the *trans* position with respect to the oxygen.[7,8] However, since the function of acid existing in the organic solvents towards the oxygenation reaction is not known yet to date, we investigated the thermodynamic equilibria among Co(II)salen, O_2, and hydrogen ion in DMSO in the present paper.



Co(II)salen

Experimental

Materials. The purification of commercial DMSO and the preparation of DMSO solution of perchloric acid was carried out according to our previous procedure.[9] Co(II)salen was prepared by a method in the literature.[10] Sodium perchlorate was recrystallized twice from aqueous solution and was used for the purpose of adjusting the ionic strength of DMSO solutions.

Oxygen Uptake Measurements. The volume of oxygen absorbed by Co(II)salen was measured by the use of a Warburg apparatus at 25 °C and an ionic strength 0.25 M, by dissolving a weighed amount of crystalline Co(II)salen into DMSO of a given ionic strength, under various partial pressures of oxygen.

Spectrophotometry. The optical absorbances of complexes were measured by a Hitachi spectrophotometer Model 101 and a Hitachi recording spectrophotometer Model EPS-3T with a quartz cell of 10 or 1 mm light path. In the case of complexes containing no oxygen, the measurements were performed under nitrogen atmosphere.

Results

Absorption Spectra and Formation Constants of Mono- and Di-Protonated Complexes. Figure 1 shows absorption spectra of Co(II)salen (Curve a) and of partly proto-

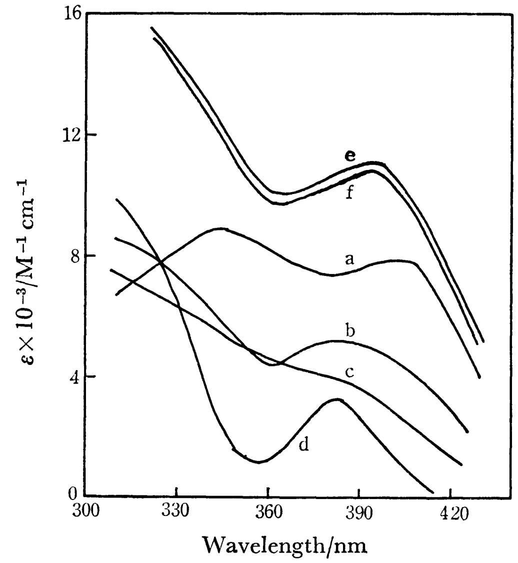


Fig. 1. Absorption spectra of Co(II)salen and its protonated and oxygenated species at $\mu=0.25$ M. (a) Co(II)salen, (b) $[Co(II)salen]_0=5.70\times10^{-4}$ M, $[HClO_4]_0=3.00\times10^{-4}$ M, (c) $[Co(II)salen]_0=5.70\times10^{-4}$ M, $[HClO_4]_0=2.00\times10^{-3}$ M, (d) Co(II)-salenH$^+$, (e) $(Co(III)salen)_2O_2$, (f) $[(Co(III)salen)_2O_2]_0=3.12\times10^{-4}$ M, $[HClO_4]_0=1.00\times10^{-4}$ M

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nated ones (Curve b for $[\mathrm{Co(II)salen}]_0=5.70\times10^{-4}$ M and $[\mathrm{HClO_4}]_0=3.00\times10^{-4}$ M and Curve c for $[\mathrm{Co(II)salen}]_0=5.70\times10^{-4}$ M and $[\mathrm{HClO_4}]_0=2.00\times10^{-3}$ M, where $[\ \ ]_0$ represents the total concentration). When acid concentration is lower than 3×10^{-4} M, an isosbestic point appears at 325 nm, indicating that there occurs a single species of protonated complex, although many curves between a and b passing the same isosbestic point are omitted in the figure. At higher acid concentrations, absorption spectrum gradually deviates from the isosbestic point because of probable occurrence of another protonated species.

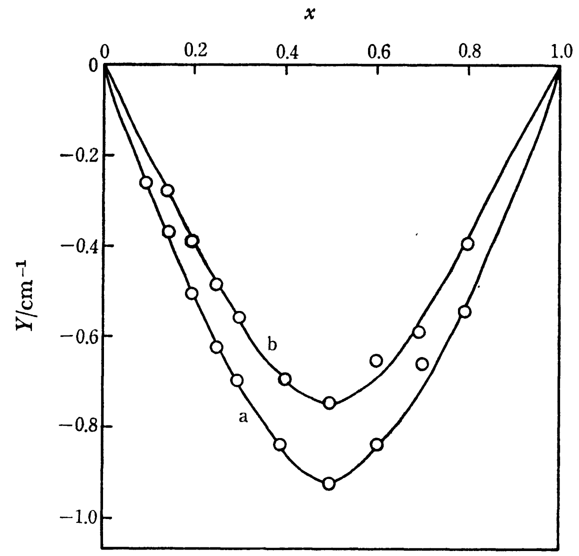


Fig. 2. Job's curves for Co(II)salen–$\mathrm{HClO_4}$ system at 410 nm and $\mu=0.25$ M.
(a) $[\mathrm{Co(II)salen}]_0+[\mathrm{HClO_4}]_0=5.00\times10^{-4}$ M
(b) $[\mathrm{Co(II)salen}]_0+[\mathrm{HClO_4}]_0=4.00\times10^{-4}$ M

According to Job's curves of continuous variation for solutions of Co(II)salen and perchloric acid observed at 410 nm as shown in Fig. 2, minimum points are recognized at concentrations of $[\mathrm{Co(II)salen}]_0=[\mathrm{HClO_4}]_0$, proving formation of a 1 : 1 complex, namely monoprotonated complex Co(II)salenH$^+$, holding an equilibrium,

$$\mathrm{Co(II)\ salen} + \mathrm{H^+} \rightleftarrows \mathrm{Co(II)\ salenH^+} \tag{1}$$

$$K_1 = \frac{[\mathrm{Co(II)\ salenH^+}]}{[\mathrm{Co(II)\ salen}][\mathrm{H^+}]} \tag{2}$$

In Fig. 2, the values of Y as defined below are plotted against the mole fraction of Co(II)salen, $x=[\mathrm{Co(II)salen}]_0/([\mathrm{Co(II)salen}]_0+[\mathrm{HClO_4}]_0)$ at two different total concentrations of Co(II)salen and acid.

$$\begin{aligned} Y &= \text{Absorbance} - \varepsilon_0[\mathrm{Co(II)\ salen}]_0 \\ &= \varepsilon_0[\mathrm{Co(II)\ salen}] + \varepsilon_1[\mathrm{Co(II)\ salenH^+}] \\ &\quad - \varepsilon_0[\mathrm{Co(II)\ salen}]_0 \\ &= (\varepsilon_1-\varepsilon_0)[\mathrm{Co(II)\ salenH^+}] \end{aligned} \tag{3}$$

Here, ε_0 and ε_1 stand for the molar absorptivity of Co(II)salen and Co(II)salenH$^+$, respectively. By adopting our method[11] to Curves a and b in Fig. 2, the values of K_1 and ε_1 are calculated which are listed in Table 1, along with other related data. By using the value of K_1, the absorption spectrum of Co(II)salenH$^+$ can be obtained which is shown as Curve d in Fig. 1. The absorption spectrum of Co(II)salen (Curve a) exhibits two peaks at 345 and 405 nm, while the absorption spectrum of Co(II)salenH$^+$ (Curve d) appears generally below that of Co(II)salen at the wavelength range longer than the isosbestic point 325 nm, having a single peak at 383 nm.

TABLE 1. FORMATION CONSTANTS AND MOLAR ABSORPTIVITIES OF PROTONATED Co(II)salen AT $\mu=0.25$ M AND 25 °C

Wave-length nm	K_1 M^{-1}	ε_1 M^{-1}cm^{-1}	K_2 M^{-1}	ε_2 M^{-1}cm^{-1}	Method
410	1.17×10^4	8.13×10^2	—	—	Job's
400	1.27×10^4	1.66×10^3	—	—	Job's
360	0.83×10^4	$1.0\ \times10^3$	1.6×10^3	5.9×10^3	Linearity

At higher acid concentration, however, Curve c represents an absorption spectrum of a probable mixture of mono- and di-protonated Co(II)salen. When the apparent molar absorptivity of the mixture and the molar absorptivity of Co(II)salenH$_2^{2+}$ are expressed by ε and ε_2 respectively, the following relationship may be established.[11]

$$\varepsilon = \varepsilon_1 + \frac{1}{K_1}\frac{\varepsilon_0-\varepsilon}{[\mathrm{H^+}]} + (\varepsilon_2-\varepsilon)K_2[\mathrm{H^+}] \tag{4}$$

$$\mathrm{Co(II)\ salenH^+} + \mathrm{H^+} \rightleftarrows \mathrm{Co(II)\ salenH_2{}^{2+}} \tag{5}$$

$$K_2 = \frac{[\mathrm{Co(II)\ salenH_2{}^{2+}}]}{[\mathrm{Co(II)\ salenH^+}][\mathrm{H^+}]} \tag{6}$$

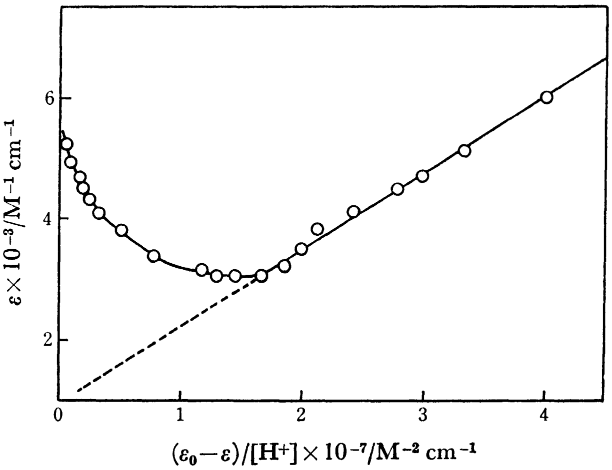


Fig. 3. Relationship between ε and $(\varepsilon_0-\varepsilon)/[\mathrm{H^+}]$ at $[\mathrm{Co(II)salen}]_0=5.50\times10^{-4}$ M, 360 nm, and $\mu=0.25$ M.

Therefore, a plot of ε against $(\varepsilon_0-\varepsilon)/[\mathrm{H^+}]$ gives a straight line at sufficiently low hydrogen ion concentration as shown in Fig. 3, from whose slope and intercept, K_1 and ε_1 are obtained. At higher hydrogen ion concentration, however, the plot deviates from the linearity, caused by occurrence of the considerable amount of diprotonated species. At this range of hydrogen ion concentration, another linearity between ε and $\Delta\varepsilon(1+K_1[\mathrm{H^+}])/K_1[\mathrm{H^+}]^2$ must hold from the modification of Eq. (4), as follows:

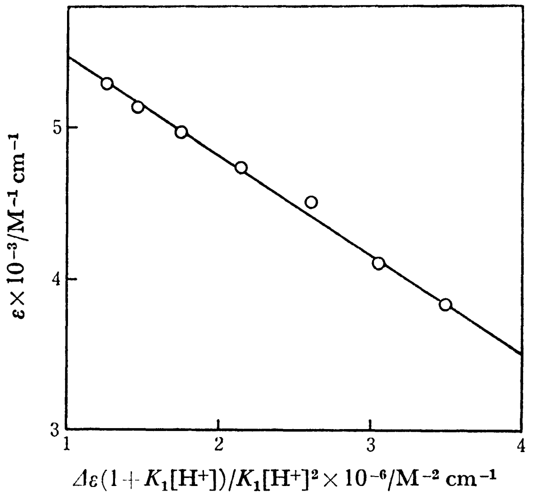


Fig. 4. Linear relationship between ε and $\Delta\varepsilon(1+K_1[H^+])/K_1[H^+]^2$ at $[Co(II)salen]_0=5.50\times 10^{-4}$ M, 360 nm, and $\mu=0.25$ M.

$$\varepsilon = \varepsilon_2 - \frac{1}{K_2}\,\frac{\Delta\varepsilon(1+K_1[H^+])}{K_1[H^+]^2} \qquad (7)$$

where $\Delta\varepsilon$ stands for the increment of ε caused by the occurrence of $Co(II)salenH_2^{2+}$. The linearity of Eq. (7) is shown in Fig. 4, from whose slope and intercept, K_2 and ε_2 are obtained. The values of K_1, K_2, ε_1, and ε_2 thus obtained are also listed in Table 1. The K_1 values from the two different methods agree with each other within experimental error.

Oxygen Uptake by Co(II)salen and Protonation of Oxygenated Complexes. The oxygen uptake by Co(II)-salen in the absence of acid in DMSO is very slow, the spectral change during the oxygenation being shown in Fig. 5. In the figure, it is seen that an absorption peak at 340 nm due to Co(II)salen gradually diminishes in the course of the oxygenation, while an alternative peak at 390 nm grows up due to the oxygenated species with an isosbestic point between the unoxygenated and oxygenated complexes at 325 nm. The mole ratio of oxygen uptake to the total Co(II)salen, $n=[\text{Absorbed } O_2]/[Co(II)salen]_0$ at infinite time is approximately 0.5 as listed in Table 2, which indicates the formation of a 2: 1 complex as represented by $(Co(III)salen)_2O_2$ at room temperature. Thus, a chemical equilibrium is established as follows:

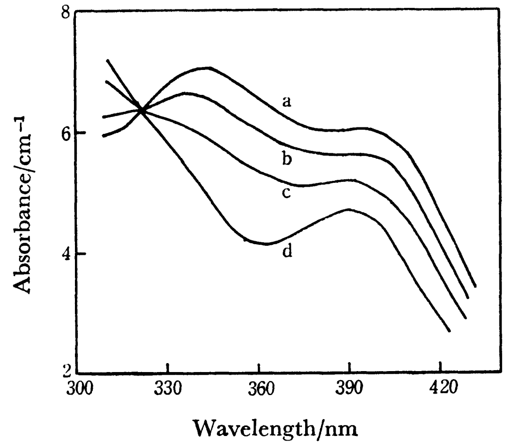


Fig. 5. Spectral change during the oxygenation of Co(II)salen at $[Co(II)salen]_0=8.20\times 10^{-4}$ M in an atmospheric air at room temperature. Time after initiation of the reaction, (a) 11 min, (b) 87 min, (c) 300 min, (d) ∞

TABLE 2. MOLE RATIO n OF O_2-UPTAKE TO THE TOTAL Co(II)salen UNDER AN ATMOSPHERIC AIR AT 25 °C

$[Co(II)salen]_0$ M	$[O_2\text{-uptake}]$ M	n
5.16×10^{-3}	2.60×10^{-3}	0.50
1.00×10^{-2}	4.88×10^{-3}	0.48
1.28×10^{-2}	6.50×10^{-3}	0.51
1.42×10^{-2}	7.04×10^{-3}	0.50

$$2Co(II)\,salen + O_2 \rightleftharpoons (Co(III)\,salen)_2O_2 \qquad (8)$$

$$K_3 = \frac{[(Co(III)\,salen)_2O_2]}{[Co(II)\,salen]^2[O_2]} \qquad (9)$$

The equilibrium constant K_3 must be immeasurably large under the present condition, so large that the reaction could be regarded to be irreversible.[7,8]

When perchloric acid was added to binuclear oxygenated complex, a slight spectral change but no release of oxygen was observed. Therefore, it is deduced that the protonation of $(Co(III)salen)_2O_2$ must have occurred and quickly attained to an equilibrium.

$$(Co(III)\,salen)_2O_2 + H^+ \rightleftharpoons (Co(III)\,salen)_2O_2H^+ \qquad (10)$$

$$K_4 = \frac{[(Co(III)\,salen)_2O_2H^+]}{[(Co(III)\,salen)_2O_2][H^+]} \qquad (11)$$

The equilibrium constant K_4 can be obtained by the method similar to the case of K_1 with ε_3, ε_4, and K_4 in place of ε_0, ε_1, and K_1 respectively and with ignoring the third term of the right-hand side in Eq. (4). The linearity of ε *vs.* $(\varepsilon_3-\varepsilon)/[H^+]$ is shown in Fig. 6 and the calculated data associated with the equilibrium 10 at 25 °C are as follows:

$$K_4 = 3.3\times 10^5\,M^{-1}$$

$$\left.\begin{aligned}\varepsilon_3 &= 1.11\times 10^4\,M^{-1}\cdot cm^{-1}\\ \varepsilon_4 &= 9.80\times 10^3\,M^{-1}\cdot cm^{-1}\end{aligned}\right\}\ \text{at 390 nm}$$

When Co(II)salen is oxygenated in the presence of perchloric acid, Reactions 1, 5, 8, and 10 might take

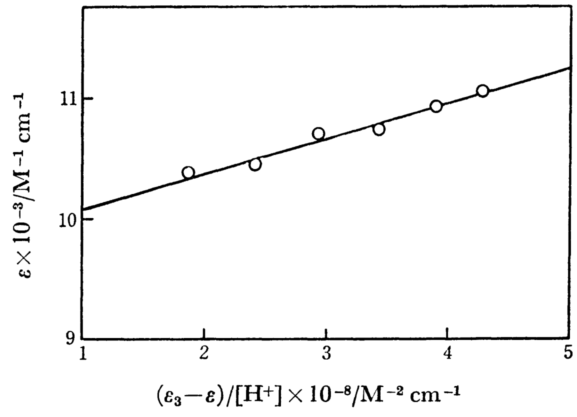


Fig. 6. Linear relationship between ε and $(\varepsilon_3-\varepsilon)/[H^+]$ at $[(Co(III)salen)_2O_2]_0=3.12\times 10^{-4}$ M, 390 nm, and $\mu=0.25$ M.

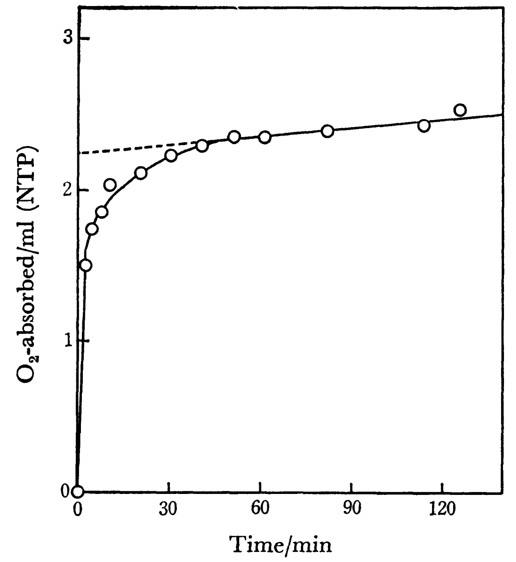


Fig. 7. Rate of oxygen uptake by Co(II)salen in the presence of perchloric acid under an atmospheric air at $[\mathrm{Co(II)salen}]_0=1.00\times10^{-2}$ M, $[\mathrm{HClO_4}]_0=2.19\times10^{-2}$ M, $\mu=0.25$ M, and 25 °C.

place altogether, among which only Reaction 8 proceeds very slowly. The rate of oxygen uptake in the presence of acid is drawn in Fig. 7. The curve consists of two parts with a rapid uptake at earlier stage of the reaction, followed by a very slow uptake at later one. This means that the primary and the secondary protonation reactions of Co(II)salen (Reactions 1 and 5) quickly reach their equilibria without regard to the presence of oxygen and then, on the gradual progress of Reaction 8, the deprotonation reactions (backward reactions of 1 and 5) produce again Co(II)salen to be oxygenated. The protonated species themselves, Co(II)salenH$^+$ and Co(II)salenH$_2^{2+}$, are inert to oxygenation. The observed apparent oxygen uptake ratio n at earlier stage

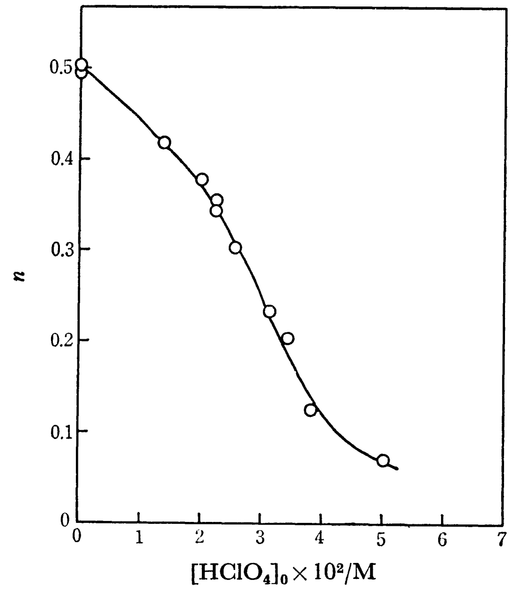


Fig. 8. Oxygen uptake ratio n, dependent upon acid concentration at $[\mathrm{Co(II)salen}]_0=1.00\times10^{-2}$ M, $\mu=$ 0.25 M, and 25 °C.

at various acid concentrations is represented in Fig. 8, in which n decreases with increasing acid concentration, being approximately expressed by a following equation, derived on the basis that the protonated species can not be oxygenated.

$$n=\frac{1}{2}\left(1-\frac{K_1(1+K_2[\mathrm{H^+}])[\mathrm{H^+}][\mathrm{Co(II)\,salen}]}{[\mathrm{Co(II)\,salen}]_0}\right) \quad (12)$$

Discussion

The mono- and di-protonated Co(II)salen are produced according to the acid concentration. The protonation may take place at lone electron-pairs on oxygen atoms of Co(II)salen, resulting in weakening the electron donating ability of oxygen atom to Co(II) and consequently of Co(II) which might have reduced O_2 to O_2^-. Therefore, the protonated species must be inert to oxygenation as observed above.

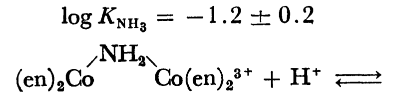
The reducing ability of Co(II) is known to be affected by the basic nature of X at low temperature as expressed in the reaction,

$$\mathrm{Co(II)\,salen\cdot X}+O_2 \rightleftarrows (O_2\mathrm{Co(II)\,salen\cdot X})^{*}$$
$$\rightleftarrows O_2^-\cdot\mathrm{Co(III)\,salen\cdot X} \quad (13)$$

the enthalpy of the reaction being in parallel with basicity of X in the order,[7] pyridine>DMSO>NCS$^-$> tetrahydrofuran > *N*, *N*-dimethylacetamide > CH_2Cl_2, where X coordinates with Co(II) at the site perpendicular to the salen plane. Thus, the basic nature of X assists Co(II)salen in reducing O_2 to O_2^-. Therefore, the inertness of the protonated species to the oxygenation is easily convinced by the fact that the proton is, say, of the least basic nature, although the attaching positions of X and H$^+$ are different to each other.

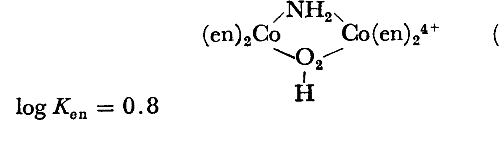
According to Ochiai,[8] the formation of 1: 1 superoxo or 2: 1 μ-peroxo complex by oxygen uptake depends upon the nature of solvent, ligand, and temperature. In our present case, the latter complex seems to be far more favored than the former in DMSO at room temperature, because of a considerably large negative free energy.[8]

The protonation of 2: 1 μ-peroxo complex, (Co(III)-salen)$_2$O$_2$ (Reaction 10), occurs at the bridging O_2^{2-} on producing hydroperoxo ion, HO_2^-. The formation constants of protonated μ-peroxo binuclear cobalt complexes are compared as follows. The ammine, ethylenediamine, and cyano complexes in aqueous solutions maintain chemical equilibria with respective equilibrium constants,[12,13]



$$(\mathrm{NH_3})_5\mathrm{Co}\text{-}O_2\text{-}\mathrm{Co(NH_3)_5}^{4+}+\mathrm{H^+}\rightleftarrows (\mathrm{NH_3})_5\mathrm{Co}\text{-}\underset{\substack{|\\ \mathrm{H}}}{O_2}\text{-}\mathrm{Co(NH_3)_5}^{5+} \quad (14)$$

$$\log K_{\mathrm{NH_3}}=-1.2\pm0.2$$



$$(\mathrm{en})_2\mathrm{Co}\overset{\mathrm{NH_2}}{\underset{O_2}{\diamond}}\mathrm{Co(en)_2}^{3+}+\mathrm{H^+}\rightleftarrows (\mathrm{en})_2\mathrm{Co}\overset{\mathrm{NH_2}}{\underset{\underset{\substack{|\\ \mathrm{H}}}{O_2}}{\diamond}}\mathrm{Co(en)_2}^{4+} \quad (15)$$

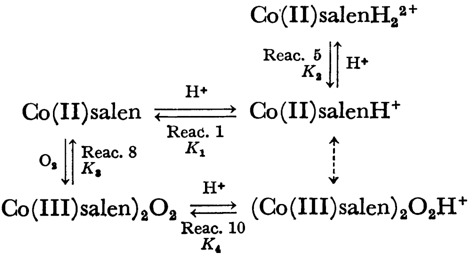
$$\log K_{\mathrm{en}}=0.8$$

$$(CN)_5Co\text{-}O_2\text{-}Co(CN)_5{}^{6-} + H^+ \rightleftarrows (CN)_5Co\text{-}\underset{\substack{|\\ H}}{O_2}\text{-}Co(CN)_5{}^{5-} \quad (16)$$

$$\log K_{CN} = 10.5$$

while $\log K_{\text{salen}}$ for Co(II)salen in DMSO ($=\log K_4$ in Eq. (11)) has been found to be 5.5. Although the solvent used only for Co(II)salen was different from others, the order of K's, $K_{NH_3}<K_{en}<K_{\text{salen}}<K_{CN}$, agrees with the reverse order of electric charges on Co-complexes, $4+_{NH_3}>3+_{en}>0_{\text{salen}}>6-_{CN}$, indicating that the reactions are largely retarded or favored by Coulombic repulsive or attractive force between the Co-complex and H$^+$, respectively. The dielectric constant of DMSO is 46.7, being small as compared to that of water 78, but the effect of the smallness of dielectric constant of DMSO might be minute because the oxygenated Co(II)salen complex is chargeless. Consequently, the magnitude of K_4 for Reaction 10 seems to be reasonable.

In conclusion, the reactions considered in the present study are summarized below.



Since the protonating site differs from each other among Reactions 1, 5, and 10, all reactions lie in a line with the protonated species being inhibited for direct oxygenation or deoxygenation, as shown by a dotted arrow. Only Reaction 8 is very slow with an apparent decrease in oxygenation ratio in acid DMSO.

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