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High Dioxygen Uptake by Hetero-Metal Binuclear Co(II)-Fe(II)-Schiff Base Complexes Systems in Dimethyl Sulfoxide

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Reactions of N,N'-ethylenenbis(salicylideneiminato)-cobalt(II), Co(salen), and its ring-substituted analogues with Fe^{2+} ion under nitrogen atmosphere in dimethyl sulfoxide readily afforded hetero-metal binuclear Co(II)-Fe(II)-Schiff base complexes, which have much higher uptake for dioxygen than do only the Co(II) Schiff base complexes.

Cobalt(II) complexes with Schiff base ligands, such as Co(salen) and its analogues have been the first and the most extensively investigated as reversible dioxygen carriers.1-3) Much attention has been paid on the reaction mechanisms and the electronic and the molecular structures of the oxygenated complexes.3-5) The molecular structure of some 1:2 adducts of dioxygen with Co(salen) was confirmed in solutions by ESR studies5) and dioxygen uptake measurements.3) Four-coordinated planar cobalt(II) Schiff base complexes readily bind dioxygen by the addition of suitable monodentate Lewis bases such as amines and solvents. These results are based on the additional stabilization of the cobalt(II)-O_2 bond through increase in electron density at the metal center provided by the axial ligands.6) However, the effect of metal ions or complexes coexisting in solutions towards dioxygen affinities of cobalt(II) Schiff base complexes is not known yet to date. Hence, we examined the reaction of Co(X-salen) (X=H, 5-Cl, 5-Br, 3-MeO), where H-salen represents salen, with Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, $Fe(C_5H_5)_2$, and $[Co(NH_3)_6]^{3+}$ in dimethyl sulfoxide(DMSO) under nitrogen and air by spectrophotometry, cyclic voltammetry, and dioxygen uptake measurements.

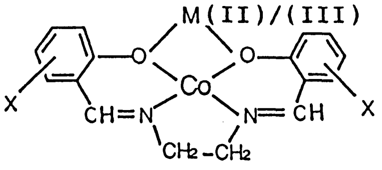

Fig. 1. Provable structure of hetero-metal binuclear $[Co(X\text{-}salen){\bullet}M]^{2+/3+}$ (X=H, 5-Cl, 5-Br, 3-MeO) in DMSO solution.

All complexes except for Schiff base complexes and $Fe(C_5H_5)_2$ were prepared as perchlorate salts. Figure 2 (A) shows the spectral changes accompanying the addition of Fe^{2+} ion to $1x10^{-4}$ M (1 M= 1 mol dm^{-3}) Co(salen) DMSO solution in N_2, essentially similar data being also obtained for the other metal ions. According to the curves of continuous variation for solutions of Co(X-salen) (X=H, 5-Cl, 5-Br, 3-MeO) and Fe^{2+} ion obtained at 310 nm as shown in Fig. 2 (B), maximum points are recognized at 0.5, proving the formation of the 1:1 hetero-metal binuclear complexes in accordance with Reaction (1). Similar results were obtained for the case of the other metal ions.

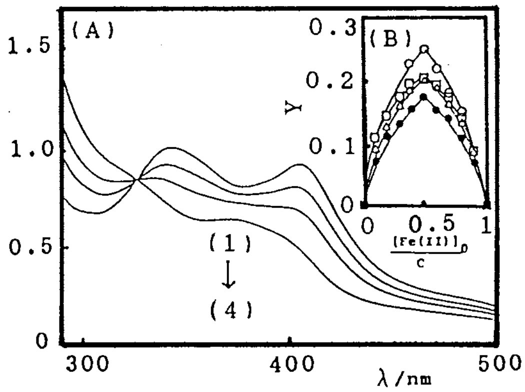

Fig. 2. (A) Spectral changes of Co(salen) accompanying the addition of Fe^{2+} ion at $[Co(salen)]_0$= 0.1 mM and 25 °C in N_2. $[Fe(II)]_0$ / mM : (1) 0 (2) 0.01 (3) 0.02 (4) 0.04 . (B) Continuous variation for Co(X-salen)-Fe^{2+} system in N_2. (1): C=0.01 mM, X=H(○) (2)-(4): C=0.1 mM, X=5-Cl(□), 5-Br (△), 3-MeO(●).

$$Co(X\text{-}salen) + M^{2+/3+} \rightleftarrows [Co(X\text{-}salen)\cdot M]^{2+/3+} \qquad (1)$$

On the other hand, the spectrum of Co(H-salen) was little influenced by the addition of $Fe(C_5H_5)_2$, suggesting no-complex formation between Co(X-salen) and $Fe(C_5H_5)_2$ in DMSO solution. Preliminary experiments revealed that the formation constants(K) by continuous variation method and reaction rates of Reaction (1) obtained by the stopped flow measurement are very large. These results indicate that Co(X-salen) complexes react very fast with used metal ions to be almost converted into the hetero-metal binuclear complexes. Provable structure of binuclear $[Co(X\text{-}salen)\cdot M]^{2+/3+}$ complex in solution is shown in Fig. 1 since Schiff base complexes in the crystals are known to coordinate to a metal halide MX_2 with two phenolic oxygens.7-8) The slightly spectral changes of Co(salen) with $[Co(NH_3)_6]^{3+}$ suggested the hydrogen-bond formation between two phenolic oxygens and the protons of NH_3 in solution.

Figure 3 shows the rates of dioxygen uptake of Co(salen) in the absence and presence of various metal ions and complexes, respectively. In the absence of the metal ions and complexes, the mole ratio of dioxygen uptake to the total Co(salen), n=[Absorbed O_2]/$[Co(salen)]_0$ at infinite time, being approximately 0.5 (the closed circles in Fig. 3), indicate the formation of a 2:1 complex, $[Co(X\text{-}salen)]_2O_2$ as follows:

$$2Co(X\text{-}salen) + O_2 \rightleftarrows Co(X\text{-}salen)\text{-}O_2\text{-}Co(X\text{-}salen) \qquad (2)$$

On the other hand, the n values except for Fe^{2+} ion under the condition of $[Co(salen)]_0=[M(0)/(II)/(III)]_0$ are smaller than 0.5 obtained in the absence of the metal ions and complexes. However, the n value for Fe^{2+} ion is larger than 0.5, indicating that only the binulcear $[Co(salen)\cdot Fe]^{2+}$ complex among the binuclear $[Co(salen)\cdot M]^{2+/3+}$ complexes exhibits the high dioxygen uptake rather than only the Co(salen) complex. The order of dioxygen uptake is follows: Fe^{2+}(○)>Ca^{2+}(▽)~$Fe(C_5H_5)_2$(◇)>Mn^{2+}(□)>Co^{2+}(△)>$[Co(NH_3)_6]^{3+}$(⦶)>Zn^{2+}(□)>Ni^{2+}(◇)>Fe^{3+}(○)>Cu^{2+}(⊗).

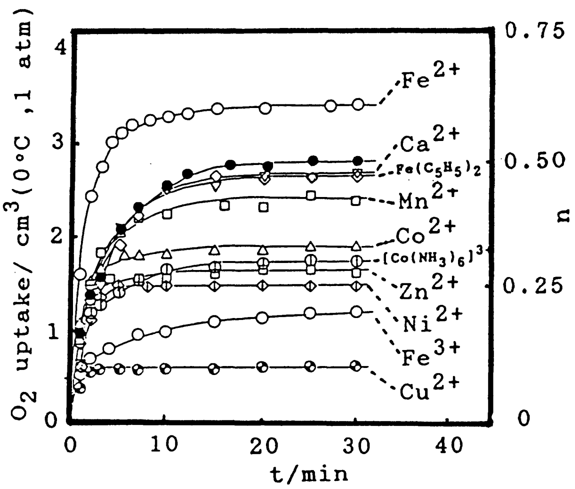

Fig 3. The rates of dioxygen uptake for Co(salen) and Co(salen) - M(O)/M(II)/M(III) systems in air. $[Co(salen)]_0$ = 10 mM,$[M(O)/(II)/(III)]_0$=10 mM

The spectra during dioxygen uptake of Co(salen) in the absence of Fe^{2+} ion changed with the isosbestic point at 325 nm. On the other hand, the hetero-metal binuclear $[Co(salen)\cdot Fe]^{2+}$ complex was oxygenated with the isosbestic points at 350 nm and ca. 400 nm between the unoxygenated and oxygenated complexes under the condition of $[Co(salen)]_0=[Fe(II)]_0$. For the presence of an excess of $[Fe(II)]_0$ over $[Co(salen)]_0$, the isosbestic points were obtained at 300 nm and 390 nm . Thus, the reaction paths would be expressed by the following Reactions (3) and (4):

$$[Co(X\text{-}salen)\cdot Fe]^{2+} + O_2 \rightleftharpoons [Co(X\text{-}salen)\cdot Fe\cdot O_2]^{2+} \quad (3)$$

$$[Co(X\text{-}salen)\cdot Fe\cdot O_2]^{2+} + Fe^{2+} \rightleftharpoons [Co(X\text{-}salen)\cdot Fe\cdot O_2\cdot Fe]^{4+} \quad (4)$$

The dependence of n on $m=[Fe(II)]_0/[Co(salen)]_0$ in Fig. 4 is interpreted as follows: at m=0, Reaction (2) takes place in DMSO solution, followed by Reaction (1) and (3) when 0<m<1, and at m=1 the reactions occur mainly by Reactions (1) and (3), followed by Reaction (4) at m>1, where the existence of $[Co(X\text{-}salen)\cdot Fe\cdot O_2]^{2+}$ is negligibly small.

Cyclic voltammograms of Co(salen), Fe^{2+} ion, and Co(salen) in the presence of Fe^{2+} ion at a glassy-carbon electrode in 0.1 M $n\text{-}Bu_4NClO_4$ DMSO solution in N_2 are shown in Fig. 5. Cyclic voltammogram for Co(salen) reveals two reversible redox waves at $E_{1/2}$=-0.08 and -1.25 V vs. Ag/AgCl, which are assigned to the Co(III)/Co(II) and Co(II)/Co(I) redox processes, respectively. In the case of Fe^{2+} ion, reversible and irreversible waves are attributed to the

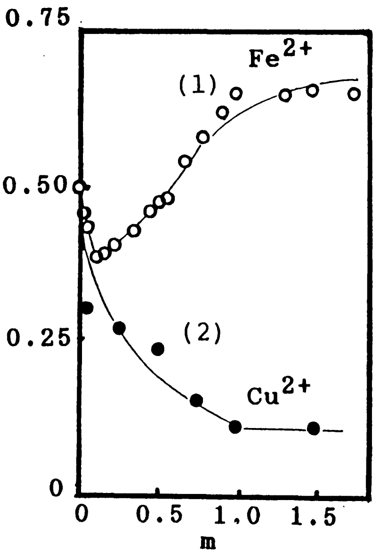

Fig. 4. Plots of n vs. m in air. (1) $[Co(salen)]_0$ =13 mM (2) $[Co(salen)]_0$ =10 mM

the redox of the Fe(III)/Fe(II) ($E_{1/2}$=+0.22 V) and Fe(II)/Fe(0) (negative region) couples, respectively. In the Co(salen) solution containing Fe^{2+} ion, the irreversible wave due to the Fe(II)/Fe(0) couple is lost, supporting the formation of the hetero-metal binuclear complex in solution. We attributed three new redox waves to the binuclear Co(III)-Fe(III)/Co(III)-Fe(II), Co(III)-Fe(II)/Co(II)-Fe(II), and Co(II)-Fe(II)/Co(I)-Fe(II) couples, respectively. As shown in Fig. 5, the redox potential of binuclear Co(III)-Fe(II)/Co(II)-Fe(II) couple ($E_{1/2}$ = -0.39 V) is more negative than that of the mononuclear Co(III)/Co(II) couple ($E_{1/2}$ = -0.08 V). On the other hand, the redox potential of Co(III)-M(II)/Co(II)-M(II) couple except for Fe^{2+} ion was similar to that of the mononuclear Co(III)/Co(II) couple. The results may be interpreted in the change in electron density at Co^{2+} ion provided by the coordination of M^{2+} ion to the two phenolic oxygens in Co(salen) complex. The binuclear $[Co(salen)\cdot Fe]^{2+}$ complex has higher uptake for dioxygen than does the other binuclear $[Co(salen)\cdot M]^{2+}$ complex. This reason may be interpreted on the stabilization of the dioxygen complexes through increase in electron density at Co^{2+} ion produced by the coordination of Fe^{2+} ion in the binuclear complexes.

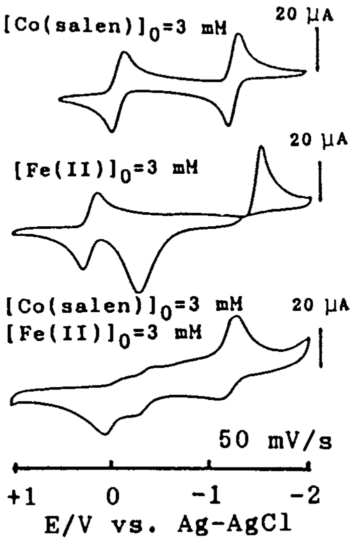

Fig. 5. Cyclic voltammograms of Co(salen), Fe^{2+}, and Co(salen)-Fe^{2+} systems in N_2.

In conclusion, cobalt(II) Schiff base complexes reacted rapidly with Fe^{2+} ion in DMSO solution to afford the hetero-metal binuclear Schiff base complexes. Moreover, these binuclear cobalt(II) Schiff base complexes exhibited high uptake for dioxygen compared to the corresponding starting complexes. Further studies on the detailed structure of the hetro-metal binulcear and the corresponding dioxygen complexes in solution are now in progress.

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