

# (ビス (サリシルアルデヒド) -o-フェニレンジイミナト) コバルト (II) の DMF 溶液過渡吸収

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## Transient Absorptions of DMF Solution of (Bis (salicylaldehyde) -o-phenylendiiminato) cobalt (II)

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### INTRODUCTION

Since the first report about a reversible oxidation of the Co (II)(salen) in the solid state<sup>1)</sup>, the cobalt (II) complexes with salen and the related Schiff bases as ligand molecules have been investigated on the basis of various experimental results, that is, electron paramagnetic resonance, vibration spectra, visible absorption spectra, X-ray analysis of the crystal and molecular structures, and kinetic measurements. Reversible oxidation is an interesting and an important phenomenon chemically and biologically<sup>2)</sup>. The ability of the cobalt (II) Schiff base complexes was also observed in solutions of coordinating solvents. Coordination of a solvent molecule to the cobalt (II) ion was considered to strengthen a bonding of a dioxygen molecule in the trans position of the solvent molecule. In the present work, the author have utilized nanosecond spectroscopy to measure the transient absorptions of cobalt (II)(saloph) complex in DMF and find that two absorptions with different lifetimes occur. Together with the other experimental results, it is discussed that the transient species give an information of solvation.

### EXPERIMENTAL SECTION

#### Materials

(Bis (salicylaldehyde) -o-phenylendiiminato) cobalt (II), abbreviated to Co (II)(saloph), was synthesized by the literature<sup>3)</sup>. The complex was stored under nitrogen and the sample solutions of  $\sim 10^{-4}$  mol / l were prepared under nitrogen atmosphere by the use of nitrogen-purged solvents. DMF (N,N' -dimethylformamide) of spectroscopic grade was used after distillation under nitrogen.

Measurements. The measurements of transient difference spectra were carried out by a system of a nitrogen laser (Molelectron, UV 14, 4mJ / pulse) and a pulsed Xenon lamp (pulse width less than 1ms) in 2 mm cell and at 20°C. A scanning of a monochromator and a data-transferring

from a storagescope (Iwatsuu, TS-8123) were controlled by a personal computer. The scales of the difference spectra ( $\Delta OD$ ) shown are normalized for the absorbances of 2 mm optical path at excitation wavelength (337.1 nm) to be 1. Near-infrared spectra were measured by a spectrophotometer (Shimadzu, MPS-5000).

## RESULTS AND DISCUSSION

### 1. Transient Absorption of salophH<sub>2</sub> and saloph<sup>2-</sup>.

Figure 1 shows the absorption spectra, and the transient difference spectra of bis (salicylaldehyde) -o-phenylenediamine (salophH<sub>2</sub>) and saloph<sup>2-</sup> in DMF. For salophH<sub>2</sub>, the lifetime of the transient absorption was longer than 1 ms in a nitrogen-purged DMF and decreased to 235  $\mu$ s by an aeration of the solution. Then the observed transient species can be assigned to the lowest triplet  $\pi\pi^*$  state. The transient absorption is located 8000  $\text{cm}^{-1}$  lower than the lowest singlet  $\pi\pi^*$  transition, so that it is assigned to a new transition from the lowest  $\pi^*$  to a higher  $\pi^*$  orbital.

When NaOH was added to a DMF solution of salophH<sub>2</sub>, an equilibrium between salophH<sub>2</sub> and saloph<sup>2-</sup> was confirmed from the visible absorption spectra. Since the absorption band of saloph<sup>2-</sup> shifted by 4000  $\text{cm}^{-1}$  to lower energy side than that of salophH<sub>2</sub>, the transient absorption corresponding to that of salophH<sub>2</sub> at 480 nm was expected in a longer wavelength region. However, for saloph<sup>2-</sup> a transient absorption was observed at 450 nm and no other band was found in a region to 700 nm. The observed  $\Delta OD$  of saloph<sup>2-</sup> is weaker than that of salophH<sub>2</sub>. The decay was not observed during 1 ms range of the monitoring light pulse even in the aerated DMF solution. These results suggest that the transient absorption of saloph<sup>2-</sup> has a different character from that of salophH<sub>2</sub>.

### 2. The Transient Absorption of Co (saloph) in DMF.

Figure 2 shows the absorption spectra and the  $\Delta OD$  of Co (saloph) in the nitrogen-purged DMF. The absorption spectrum exhibited a slow time-dependence, reaching the stable one after 160 minutes. In the oxygen-purged DMF solution, the same time-dependence of the spectra was observed but by the use of DMF without distillation the spectral change appeared faster (within 15 min). The reported result that very small amounts of dimethylamine added to the DMF solutions of Cobalt Schiff base complexes makes the rate of oxygen uptake increase<sup>4)</sup> shows a role of impurities to accelerate a rate of DMF solvation.

The  $\Delta OD$  also showed a time-dependence. Figure 2 exhibits the spectra at 0, 4 and 8  $\mu$ s after the excitation. It should be noted that the isosbestic points of the absorption spectra (408, 443, 522 nm) appeared also in the  $\Delta OD$  spectra. The  $\Delta OD$  showed a two-exponential decay with lifetimes of 8  $\mu$ s and 200  $\mu$ s, the longer liferime less accurate because of its weak intensity. The decay behavior did not exhibit a significant change whether DMF was purged by nitrogen or not and distilled or not.

### 3. Solvation of Co (saloph).

It was reported that DMF coordinates to Co (II) Schiff base complexes in solution.<sup>5)</sup> The isolated DMF-adducts of Co (II) Schiff base complexes were a stable dimeric form of Co (salen)<sub>2</sub> O<sub>2</sub>

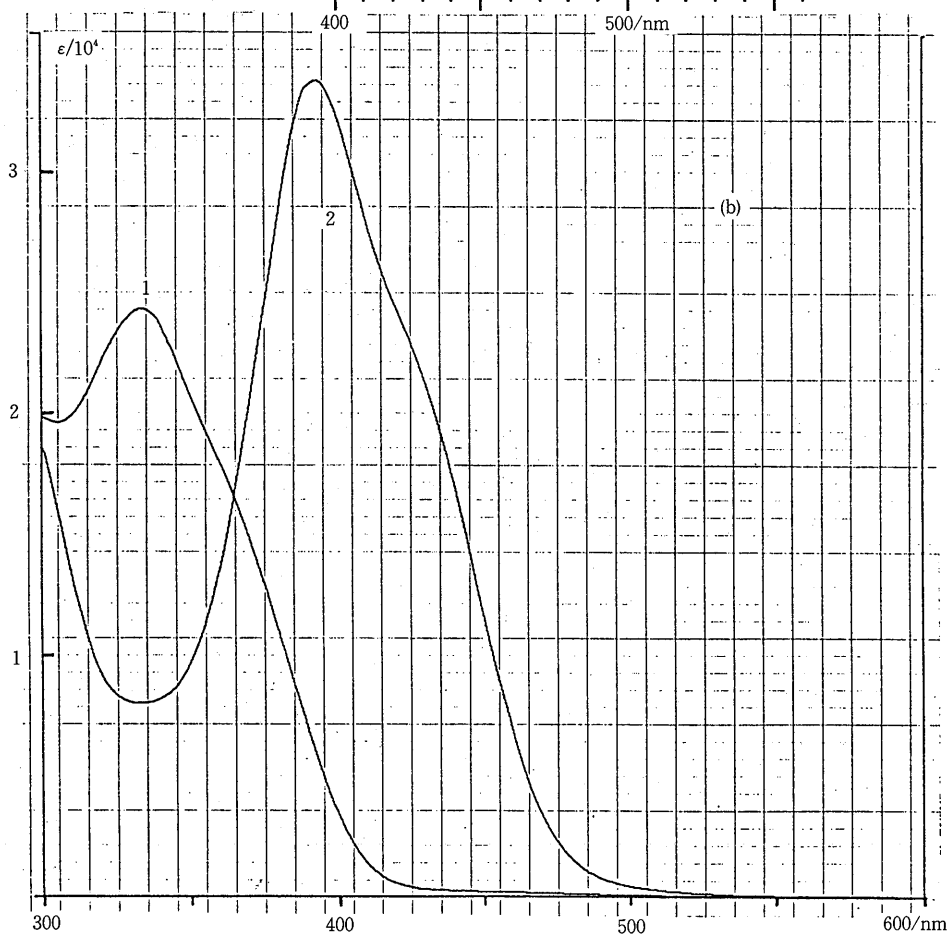
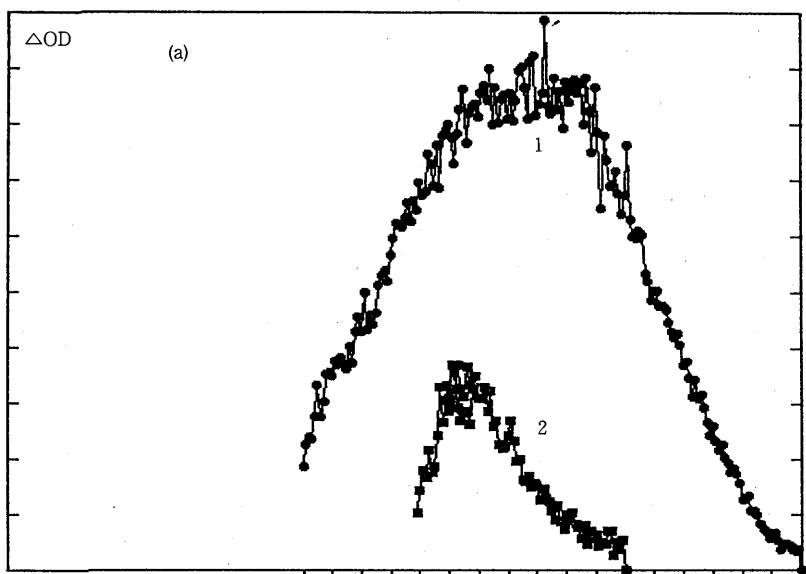


Figure 1. Transient difference spectra (a) and absorption spectra (b) of salophH<sub>2</sub> (1) and saloph<sup>2-</sup> (2) in nitrogen-purged DMF.

(DMF)<sub>2</sub><sup>5a</sup>) and an unstable monomeric form of Co (acacen) O<sub>2</sub> (DMF)<sup>5b</sup>, which both contain a dioxygen in the trans position against DMF.

In the present solutions containing no oxygen, possible DMF adducts are Co (saloph) DMF and Co (saloph)(DMF)<sub>2</sub>. By addition of pyridine (py) to a deaerated dichloromethane solution of Co

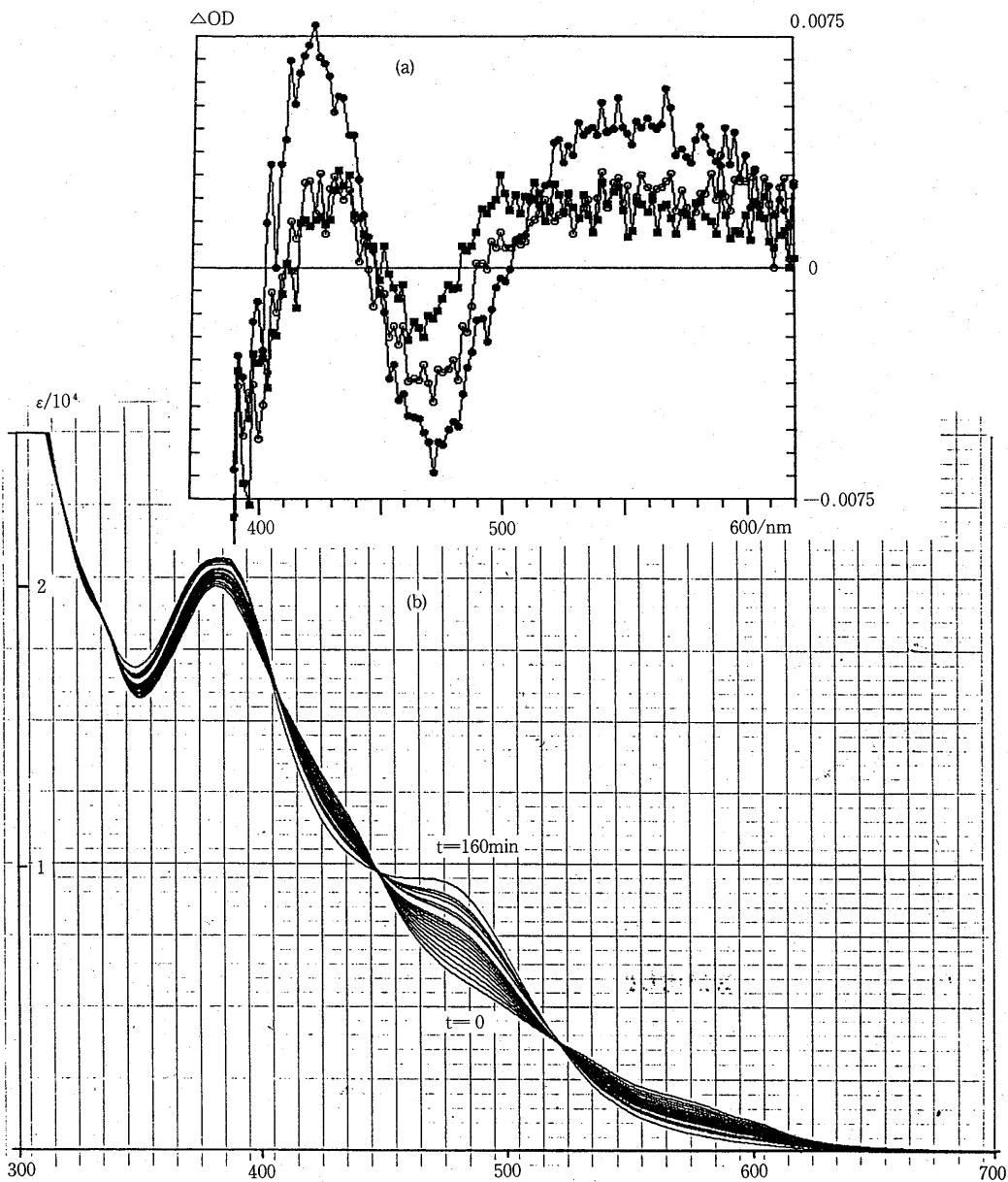


Figure 2. Transient difference spectra (a) at 0 (●) , 4 (○) and 8 (■)  $\mu s$  after excitation, and absorption spectral change (b) by 2 min step of Co (saloph)( $\times 10^{-4} M$ ) in nitrogen-purged DMF.

(saloph), the formation of  $\text{Co}(\text{saloph})\text{py}$  was reported<sup>6</sup>). In this condition, we could not find  $\text{Co}(\text{saloph})(\text{py})_2$  until after several hours spectroscopically. Pyridine is a much stronger donating solvent than DMF, so that the DMF adduct observed present within several ten minutes is impossible to be  $\text{Co}(\text{saloph})(\text{DMF})_2$ .

The near-infrared absorption spectrum of 900-2200 nm region of  $\text{Co}(\text{saloph})$  was observed, having a band at 1240 nm ( $\epsilon = 12$ ) in the dichloromethane solution. In the DMF solution a weaker and broad band at 1270 nm ( $\epsilon = 6$ ) was observed. In comparison with the report that

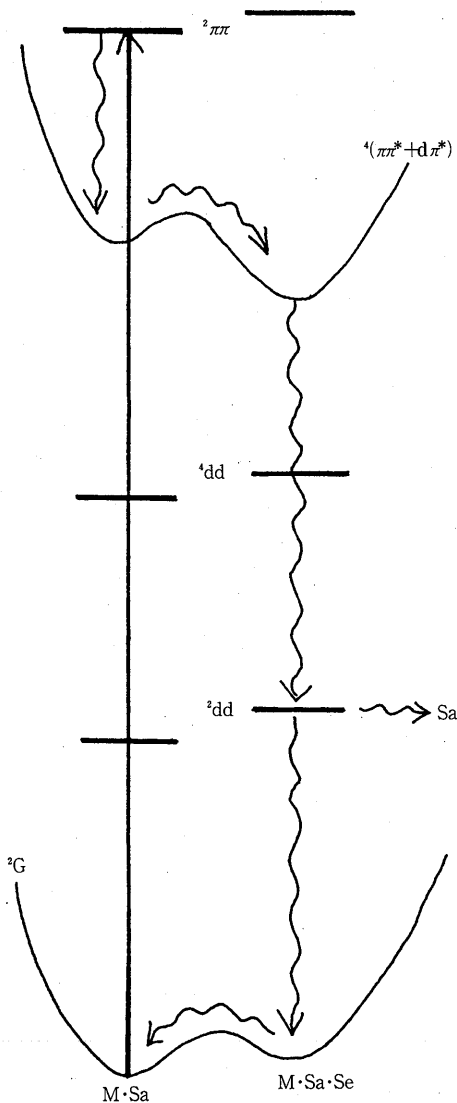


Figure 3. Schematic energy diagram. M : Co (saloph), Sa : axially coordinated DMF and Se : equatorially coordinated DMF.

the 1140 nm band of Co (salen) disappeared by a formation of the py-adduct<sup>4)</sup>, DMF-cobalt interaction is revealed to be weaker than py-cobalt one.

#### 4. Character of Transient of Co (saloph).

The transient difference spectra exhibited the same isosbestic points with an inverse direction of change relating to the absorption spectrum. Therefore, an explanation is possible that the DMF-coordinating Co (saloph) releases DMF through the excited processes and that the released DMF recombines with lifetime of 8  $\mu$ s.

It is reasonable that the lowest electronic excited state at 1270 nm promoting a d electron to the axial direction makes the axial DMF decompose (Fig. 3).

The longer component of the transient absorption was weak and broad. We carried out preliminary measurements of transient absorptions of dichloromethane and diethyleneglycol-methylether solutions of Co (saloph). Both spectra exhibited analogous weak bands at 480 nm with lifetimes of several hundreds  $\mu$ s. These solvents are non-coordinating solvents and as expected the time-depending transient absorption was not observed.

One of models of the transient species is a DMF adduct of Co (saloph), in which DMF solvates to oxygen anions of saloph<sup>2-</sup>. Supporting results are (1) saloph<sup>2-</sup> without cobalt (II) ion also shows a similar transient absorption, (2) a trichloromethane adduct of Co (salen) was reported to combine for a hydrogen atom of trichloromethane at oxygen anions of salen by X-ray analysis,<sup>7)</sup> (3) a flash photolysis of dichloromethane solutions of a hexacyanocobalt (III) salt results in a transient absorption with lifetime of the order of seconds, the transient species being attributed to a dichloromethane adduct by a scavenging experiment.<sup>8)</sup>

The equatorial addition of DMF affects the transition energies of ligand  $\pi\pi^*$  transitions but less the  $d\pi^*$  or  $dd$  transitions. Therefore, the observed transient difference absorption is assigned to a lower shifted  $\pi\pi^*$  transition of the equatorially solvated Co (saloph). The solvated complex decomposes to an unsolvated form with lifetime of several hundreds  $\mu$ s. The lower  $dd$  states cannot interact enough with the  $\pi\pi^*$  or  $d\pi^*$  states because of large energy separations and difference of orbital symmetry. Therefore, it is probable that the equatorial solvation occurs in the lowest  $\pi\pi^*$  state mixing a  $d\pi^*$  state to some extent (Fig. 3).

This work showed a useful utilization of measurements of transient absorptions to get informations about weak solvation.

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