

[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)のメタノール溶液の過渡吸収と基底状態吸収

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Transient and Ground-State Absorptions of [Bis(salicylaldehyde)-*o*-phenylenediiminato] cobalt(II) in Methanol

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Introduction

The reversible coordination of molecular oxygen to cobalt(II) Schiff base complexes has been intensively studied from interests relevant to biological oxygenations.¹⁾ It has been pointed out that solvents play an important role in the reactions. In the solid states oxygen adducts of these planar Co(II) complexes were reported to have an electron donating solvent molecule at an opposite side of molecular oxygen.²⁾ In solutions the structures of the coordinated oxygen molecule have been investigated by means of electron spin resonance but little were discussed coordination structures of solvent molecules. Recently, with respect to one of such complexes, [Bis(salicylaldehyde)-*o*-phenylenediiminato] cobalt(II) ([Co(saloph)]), we have observed the photo-induced transient absorptions in *N,N'*-dimethylformamide (DMF)³⁾ and in dichloromethane⁴⁾ and attributed them to short-lived solvated complexes. In the present paper we study spectroscopic properties of the methanol solution of [Co(saloph)] and compared them with those observed in DMF and dichloromethane.

Results and Discussions

[Co(saloph)] was synthesized and stored under nitrogen. Methanol used is of luminescent grade. The concentrations of the sample solutions are about 10^{-4} mol dm⁻³. The experimental method was described in references 3 and 4.

In the previous paper,³⁾ we reported a slow time-dependence of the ground-state absorption of [Co(saloph)] in DMF and assigned it to an axial solvation of a DMF molecule to the cobalt(II) ion of the planar complex. For the related Co(II) Schiff base complexes, slow oxidative reactions of Co(II) to Co(III) were frequently observed but such a slow solvation was not reported before. In order to support our discussion about the axial solvation, we measured the ground-state absorptions of [Co(saloph)] in methanol. In alcohols the oxidations of Co(II) to

Co (III) were reported to produce the corresponding alcoholatocobalt (III) complexes.⁵⁾

Figures 1, 2 and 3 show the time dependence of the absorption spectra in methanol after oxygen bubbling for 30 min, of air-saturated condition and after nitrogen bubbling for 30 min, respectively. In methanol bubbled by oxygen the absorbance increases its intensity with time in the region of 300-530 nm and the peak at 380 nm becomes obscure. The final spectrum resembles the spectra of the Co (III) complexes such as [Co (saloph) (py)₂] I and [Co (saloph) (py) (CH₂C₆H₅CN)] which show only shoulders near 400 nm superposed on strong tails of shorter-wavelength bands.⁶⁾

With respect to the three methanol solutions, the formation rate constants of the spectroscopic equilibria were determined on the basis of the absorbances at 480 nm as 5.6×10^{-4} , 1.7×10^{-4} and $1.4 \times 10^{-4} \text{ s}^{-1}$. The rate constants increased with oxygen concentration. On these basis the reaction observed in oxygen-bubbled methanol can be assigned to an oxidation of [Co (saloph)].

In methanol bubbled by nitrogen two equilibria were observed. The first one with three isobestic points resembles that observed in DMF and may correspond to an axial solvation to the Co (II) complex. The succeeding slow change is mainly an intensity decrease of the band at 380 nm. The spectral change of the air-saturated methanol solution is an intermediate of Figs. 1 and 3.

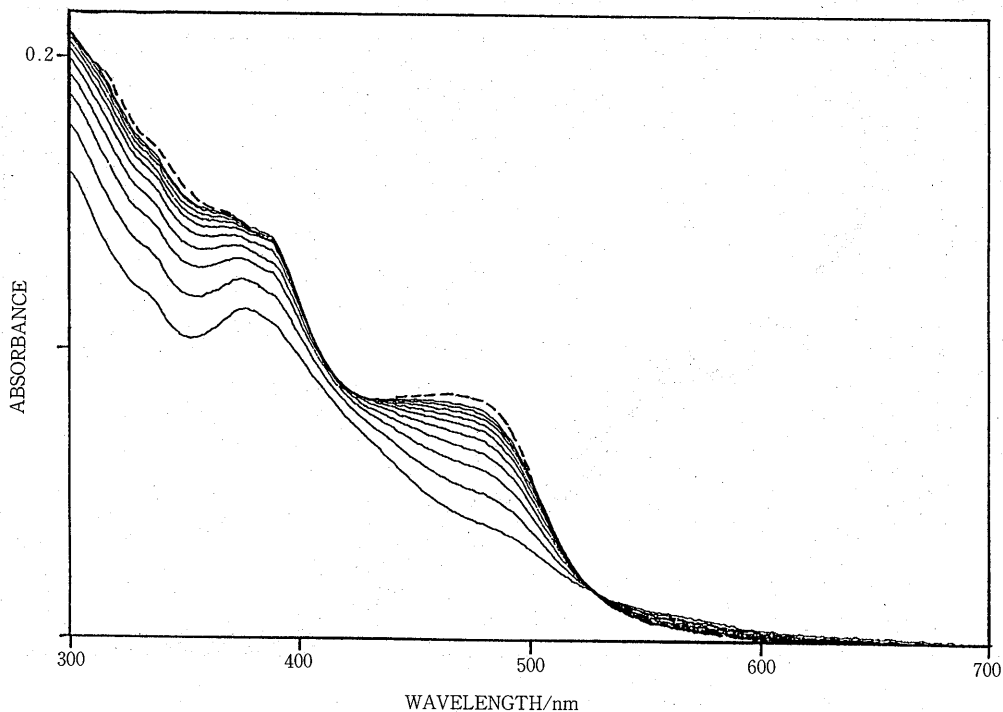


Fig. 1. Time dependence of the absorption spectrum of [Co (saloph)] in oxygen-bubbled methanol by ten minutes. The dashed line shows the final spectrum.

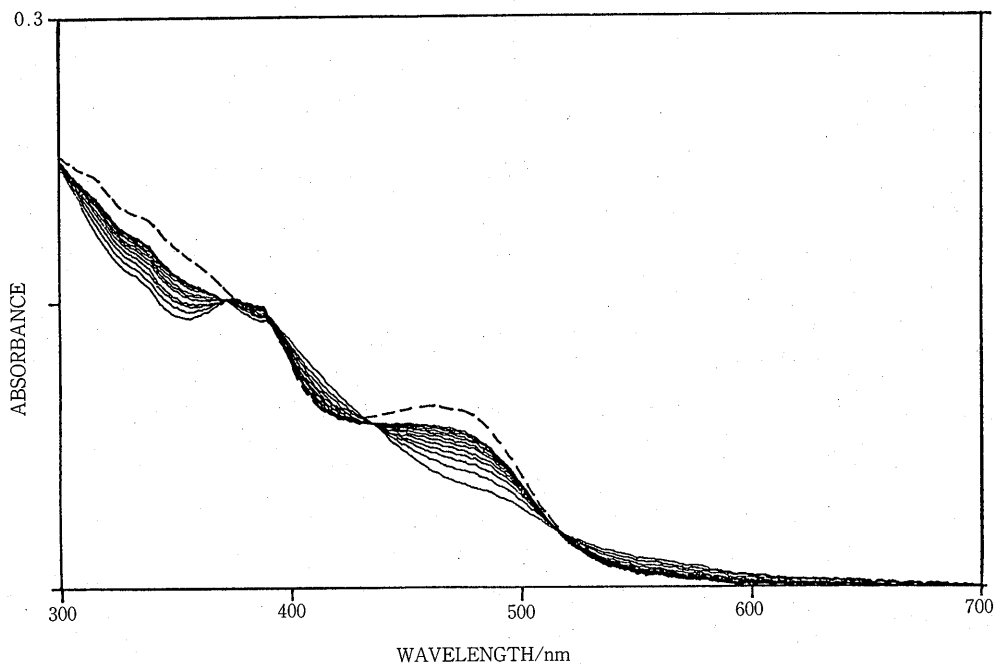


Fig. 2. Time dependence of the absorption spectrum of [Co (saloph)] in air-saturated methanol by ten minutes. The dashed line shows the final spectrum.

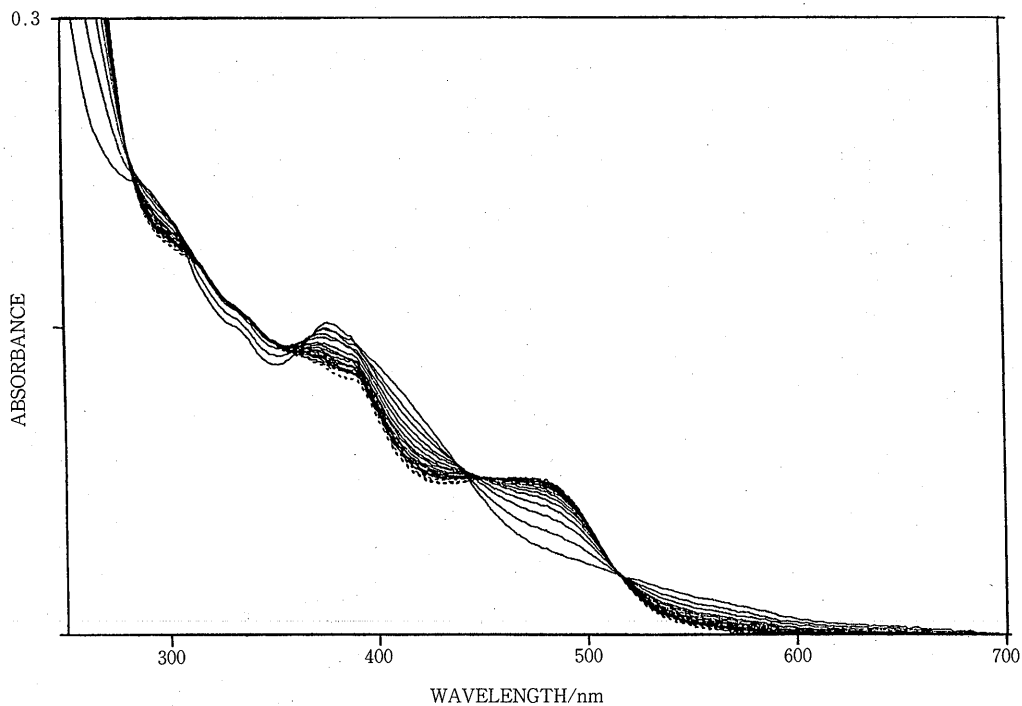


Fig. 3. Time dependence of the absorption spectrum of [Co (saloph)] in nitrogen-bubbled methanol by ten minutes. The dashed line shows the final spectrum.

Table 1 Rate Constants of Formation of Equilibrium

solvent	N ₂ -bubbled	air-saturated	O ₂ -bubbled
DMF	$6.7 \times 10^{-4} \text{s}^{-1}$	$4.2 \times 10^{-4} \text{s}^{-1}$	$6.7 \times 10^{-4} \text{s}^{-1}$
methanol	1.4×10^{-4}	1.7×10^{-4}	5.6×10^{-4}

In the DMF solutions of [Co (saloph)], the change of the spectral pattern was not influenced by oxygen bubbling.³⁾ The formation constants of the equilibria in DMF were summarized in Table 1. The rate constant is the smallest in the air-saturated DMF and has the same value in DMF bubbled by oxygen or nitrogen. A plausible interpretation is that the reactions observed in the three DMF solutions are same and that a trace of volatile impurities such as formic acid⁷⁾ catalyzes the reaction. The characteristics of the time dependence in DMF are quite different from those in methanol, so that a possibility of the oxidative reaction in the DMF solutions can be denied.

Since the oxidative products of the Co (II) complexes with Schiff base ligands analogous to

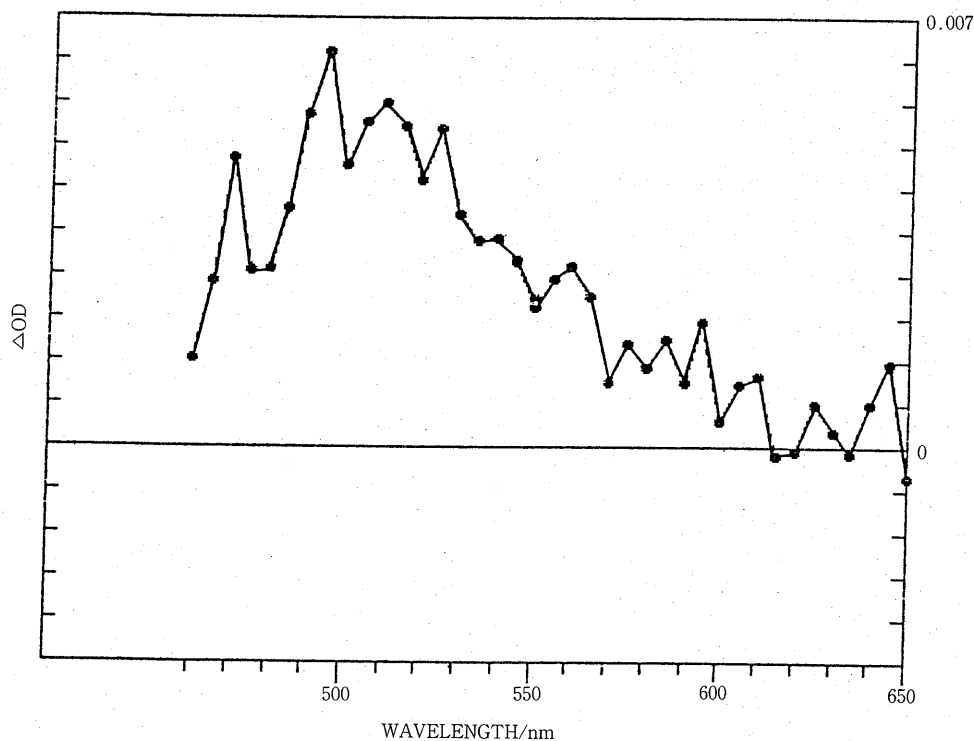


Fig. 4. The difference spectrum of the transient absorption of [Co (saloph)] in nitrogen-bubbled methanol.

saloph were precipitated by bubbling of oxygen through the suspensions in methanol,⁵⁾ the same procedure was applied to [Co (saloph)]. Being different from the results in reference 5, no clear solution was formed by oxygen bubbling for 3 hours. After an evaporation of methanol, a filtration and an addition of water to the solution, no precipitation was found.

The difference spectrum (ΔOD) of the transient absorptions of [Co (saloph)] in methanol was observed and shown in Fig. 4. The lifetime was longer than 10 μ s. Oxygen bubbling gave little influence on the absorption spectrum and the lifetime. The spectrum resembles that observed in dichloromethane⁴⁾ but the intensity is about half of its intensity. It is concluded that also in methanol a photo-induced solvation at phenolic oxygen atoms of [Co (saloph)] is considered to occur.

References

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