

[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) の溶液における軸配位の機構

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The Mechanism of the Axial Ligation of [Bis (salicylaldehyde) -o- phenylenediiminato] cobalt (II) in Solution

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Introduction

The reversible coordination of molecular oxygen has been widely investigated for the four-coordinated Co (II) complexes with salen and the related Schiff-base¹⁾. The oxygenation was reported to proceed in the five-coordinated species with electron-donating bases at the axial position. The five-coordinated complexes with strong electron-donors such as pyridine were identified by the use of the absorption spectra. Though N, N-dimethylformamide (DMF) was frequently used as a solvent for the oxygenation reactions, the five-coordinated species with DMF has not been confirmed by the absorption spectra. Here, we intended to investigate the interaction between the Co (II) Schiff-base complexes and DMF, a weak electron-donor. In order to eliminate the steric deformation of the complexes by the fifth and the sixth ligation, we used a cobalt (II) complex with Schiff-base of a rigid molecular structure, that is, [bis (salicylaldehyde)-o-phenylenediiminato] cobalt (II) ([Co (saloph)]). In this work, we will report the solvent and temperature dependence of the ultraviolet and visible absorption spectra and specify a five- and six-coordinated complexes in the DMF solution.

Results and Discussions

[Co (saloph)] was prepared²⁾ and stored under nitrogen. DMF and dichloromethane used were of spectroscopic grade. The concentrations of the sample solutions were about 10^{-4} mol dm^{-3} . If necessary, the solutions were bubbled by nitrogen or oxygen for more than one hour.

Solvent dependence of the spectra. Fig. 1 shows the solvent dependence of the absorption spectra of [Co (saloph)]. The spectra shown are normalized by the absorbance of a 385 nm band, which was observed in all solvents. The spectrum in CH_2Cl_2 corresponds to [Co (saloph)] without an axial ligand, that is, the four-coordinated complexes. By adding 0.1 mol dm^{-3} pyridine to the CH_2Cl_2 solution, a new band was observed at 550 nm, showing a forma-

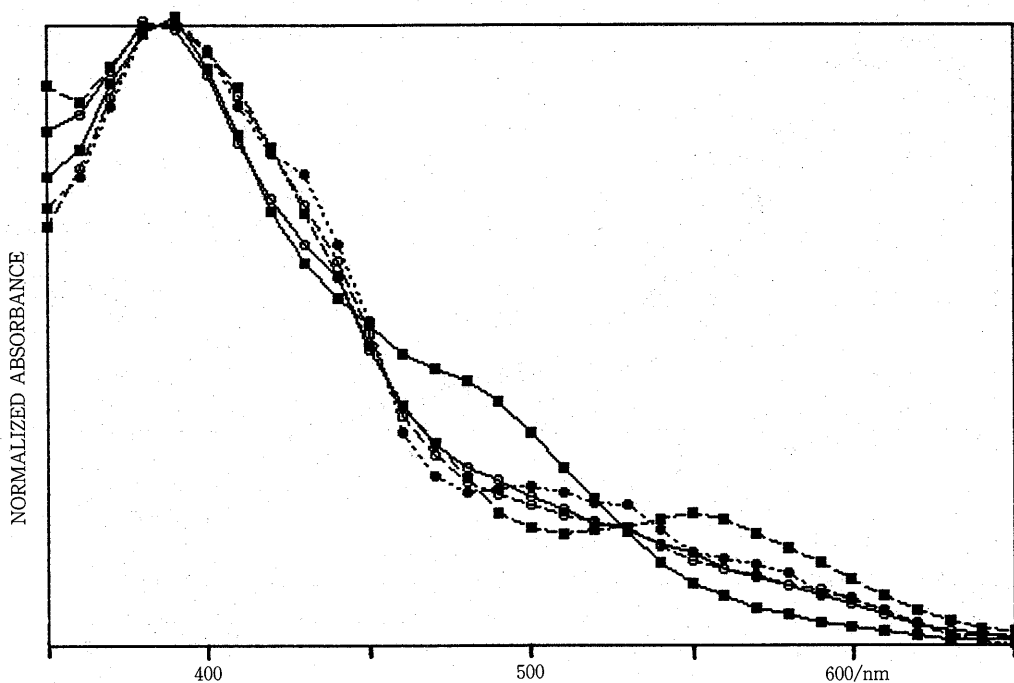


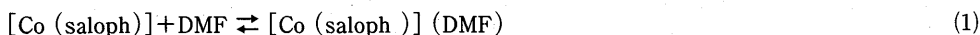
Fig.1

Fig. 1. The absorption spectra of $[\text{Co}(\text{saloph})]$ in DMF at $t = 0$ (\circ —), at $t = \infty$ (\blacksquare —), in CH_2Cl_2 (\bullet —), in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M}$ pyridine (\blacksquare —) and DMA (\circ —).

tion of $[\text{Co}(\text{saloph})](\text{py})$, the five-coordinated complex. In DMA the observed spectrum may be ascribed to $[\text{Co}(\text{saloph})](\text{DMA})$. DMA is a weaker electron-donor than pyridine, so that the small change from the spectrum of the four-coordinated complex is reasonable. In the DMF solution the absorption spectrum exhibited time dependence; $t = 0$ and $t = \infty$ in Fig. 1 describe the conditions just after the sample preparation and under spectral equilibrium. The spectrum at $t = 0$ resembles well the spectrum in DMA, indicating the formation of $[\text{Co}(\text{saloph})](\text{DMF})$.

DMF- CH_2Cl_2 Binary Solutions. In order to clarify the mechanism of the time dependence in DMF, we measured the absorption spectra in DMF- CH_2Cl_2 binary solvents (Fig. 2). In these solutions, the spectra also changed with time, so that we used the spectra under the spectral equilibrium. In the solutions of DMF/ CH_2Cl_2 ratios of less than 1/4 (volume to volume), the isosbestic points were observed at 454 and 509 nm. In the solutions of the higher DMF concentrations, the spectra deviated from the isosbestic points, showing a different process to occur.

The first reaction can be represented by the axial bonding of DMF.



Analyzing the linear relation between the inverse of $A - A_0$ and the inverse of DMF concentration in the region of DMF/ $\text{CH}_2\text{Cl}_2 < 1/4$, the equilibrium constant of the reaction (1) was determined as $K_1 = 1.7 \text{ mol}^{-1} \text{ dm}^3$; A and A_0 describes the absorbance in each binary solvent and

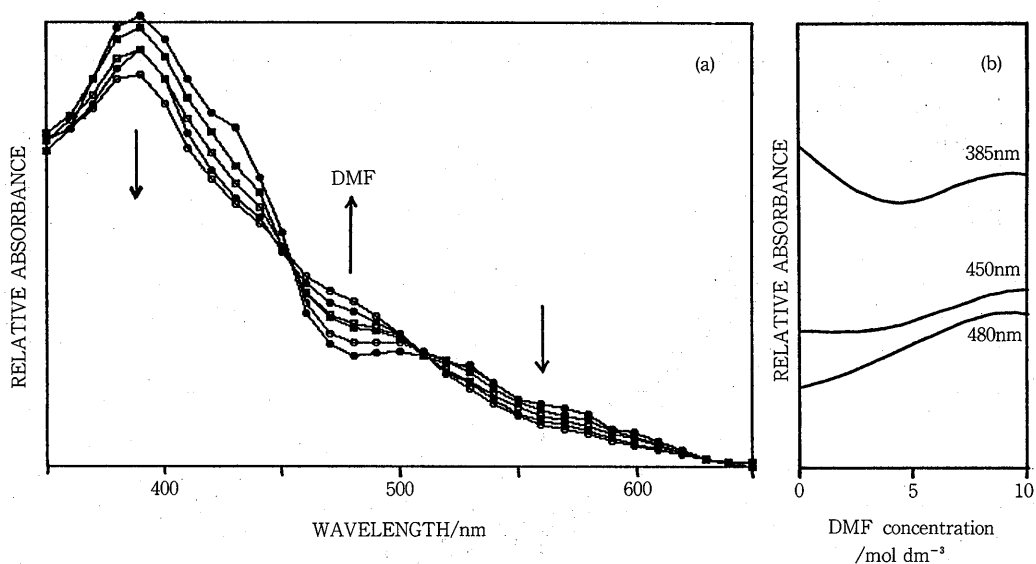


Fig.2

Fig. 2. (a) The absorption spectra of $[\text{Co}(\text{saloph})]$ in $\text{DMF}-\text{CH}_2\text{Cl}_2$: the ratios of $\text{DMF}/\text{CH}_2\text{Cl}_2$ (v/v) are 0/1, 1/100, 1/17, 1/10, 1/7 and 1/4. (b) The absorbance change with DMF concentration at 385, 450 and 480 nm.

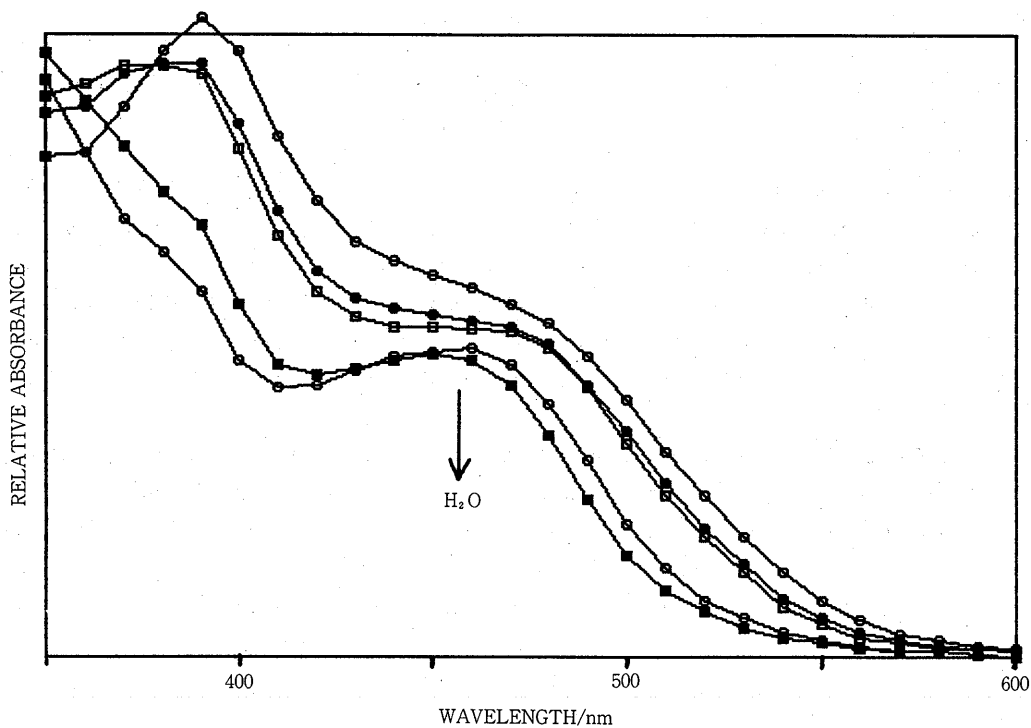
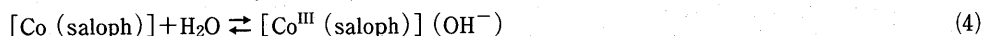
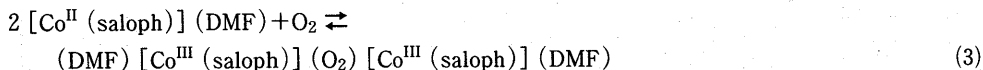
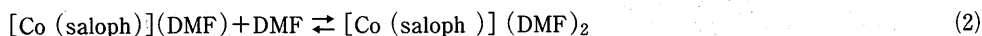


Fig.3

Fig. 3. The absorption spectra of $[\text{Co}(\text{saloph})]$ in $\text{DMF}-\text{H}_2\text{O}$: the ratios of $\text{DMF}/\text{H}_2\text{O}$ (v/v) are 1/0, 9/1, 6/1, 1/1 and 1/3.

in CH_2Cl_2 .

As for the second reaction, the following processes are probable considering the reactions reported for $[\text{Co}(\text{salen})]^{1)}$.



The reaction (3) is denied, because we confirmed no oxygen effect on the spectra by comparing the results in nitrogen- and oxygen-bubbled DMF and because of no concentration dependence of $[\text{Co}(\text{saloph})]$ on the spectra. For the reaction (4) different spectral changes were observed as is seen in Fig. 3. By adding H_2O to the DMF solution of $[\text{Co}(\text{saloph})]$, the 390 nm band became weaker and strong band appeared near 350 nm, those features being the characteristic of the Co (III) complexes of saloph; ^{3, 4)} the bars in Fig. 3 being the reported spectral data of $[\text{Co}(\text{III})(\text{saloph})]^{4)}$. Thus, the observed second step in DMF- CH_2Cl_2 can be assigned to the reaction (2). In the region of $\text{DMF}/\text{CH}_2\text{Cl}_2 > 1/2$, the equilibrium constant of (5) was analyzed as $K_3 = 0.03 \text{ mol}^{-2} \text{ dm}^6$ from the relation between the inverse of $A-A_0$ and the square inverse of DMF concentrations, so that the equilibrium constant of the reaction (2) was calculated as $K_2 = 0.02 \text{ mol}^{-1} \text{ dm}^3$.



Time-Dependence of Spectra in DMF. Fig. 4 (a) shows the time-depending spectra of $[\text{Co}(\text{saloph})]$ in DMF. The spectra resemble those observed in DMF- CH_2Cl_2 with high DMF concentrations, that is, the spectra corresponding to the reaction (2). In order to get an information faster than one scanning of the spectrum (3 min) the absorbance changes per 0.5 min were measured at fixed wavelengths, 385, 450 and 480 nm. At each wavelength, the behavior of the absorbance change with time was very similar to the absorbance change with the increase of DMF concentration (Fig. 2 (b)). This correspondence indicates that in pure DMF the reaction (1) occurs as well as in DMF- CH_2Cl_2 and is completed within several minutes.

Temperature Dependence of Spectra in DMF. Fig. 4 (b) shows the temperature dependence (from 6°C to 46°C) of the DMF solutions of $[\text{Co}(\text{saloph})]$. The temperature change was carried out for the solutions the equilibrium completed. The spectral changes was observed to occur as rapidly as temperature change. Using the values of K_1 and K_2 , the main species in DMF is calculated to be $[\text{Co}(\text{saloph})](\text{DMF})$ and the second as $[\text{Co}(\text{saloph})](\text{DMF})_2$. Therefore, the temperature dependence can be attributed to a dissociation of DMF from the six-coordinated complex with temperature, the reverse reaction of (2). Thus, the quite resemblance between the spectral changes of Figs. 4 (a) and 4 (b) is explainable as resulting from the forwards and reverse reactions of (2).

As is revealed from the above-mentioned experimental results, DMF forms the five- and six-coordinated complexes with $[\text{Co}(\text{saloph})]$. The fact that $[\text{Co}(\text{saloph})]$ is inactive to oxygen in DMF can be interpreted by a formation of the six-coordinated complex with DMF.

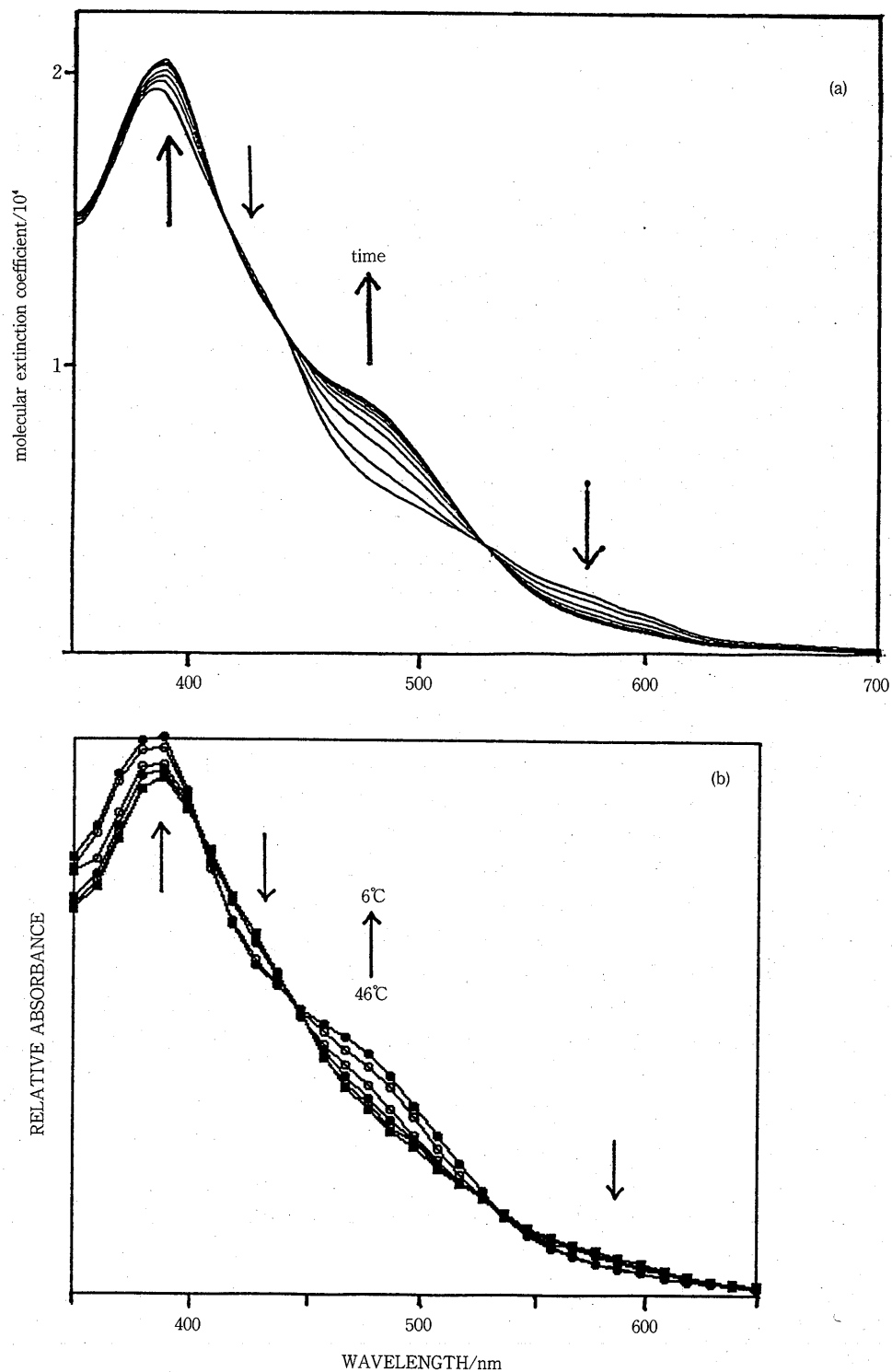


Fig.4

Fig. 4. (a) The time dependence of the absorption spectra of [Co (saloph)] in DMF. (b) The temperature dependence of the absorption spectra of [Co (saloph)] in DMF : at 6, 10, 22, 30, 38 and 46°C.

References

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