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Spectroscopic Properties of Several Molecular Species of [*N*,*N*′-(*o*-Phenylene)bis(salicylideneaminato)]cobalt(II) in *N*,*N*-Dimethylformamide and CH_2Cl_2 Solutions

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Based on the temperature and concentration dependencies of the UV-vis and ^{1}H NMR spectra of [*N*,*N*′-(*o*-phenylene)bis(salicylideneaminato)] cobalt(II) ([Co(saloph)]), the existence of several species ([Co(saloph)], [Co(saloph)(dmf)], [Co(saloph)(dmf)$_2$], and a dimer [Co(saloph)(dmf)]$_2$) is discussed in *N*,*N*-dimethylformamide (dmf) and CH_2Cl_2. The values of ΔH° and ΔS° were determined to be -3.7 kJ mol^{-1} and -17 J K mol^{-1}, -30 kJ mol^{-1} and -145 J K mol^{-1}, and -39 kJ mol^{-1} and -110 J K^{-1} mol^{-1} for the formation of [Co(saloph)(dmf)], [Co(saloph)(dmf)$_2$] and [Co(saloph)(dmf)]$_2$, respectively. Transient absorptions with lifetimes of 10^{-3} s and 4×10^{-6} s were observed in dmf solution by 337 nm irradiation.

Since Tsumaki recognized reversible oxygenation of four-coordinated cobalt(II) Schiff-base complexes (CoL) in the solid state,[1] the properties of these complexes have been widely investigated.[2,3] The formation of five molecular species has been reported in solutions and in the solid state based on EPR and NMR spectra, magnetic susceptibility, and X-ray analysis.[2,4] The species are, (1) a four-coordinated low-spin complex in the solid state and in non-coordinating solvents, (2) a five-coordinated low-spin or high-spin complex with one axial ligand in the solid state and in coordinating solvents, (3) a six-coordinated complex with two axial ligands in coordinating solvents, (4) a complex with a molecule weakly bonding to the phenolic oxygen atoms of the Schiff-base ligand in the solid state,[5,6] and (5) a diamagnetic dimer in the solid state.[7] It is generally accepted for these complexes that the oxygenation reaction in solution starts from a five-coordinated base adduct ([CoL(B)]), where B is an electron-donating molecule and frequently a solvent molecule. In dmf solutions, the oxygenation reactions occurred effectively, but the formation of [CoL(dmf)] was not observed.[8]

We then intended to investigate the molecular species of these complexes in solutions.[9] In order to avoid the structural complexity of the species, we selected [Co(saloph)] with a planar structure instead of [*N*,*N*′-ethylenebis(salicylideneaminato)]cobalt(II) [Co(salen)], the widely-investigated Schiff-base complex, with a more flexible structure. Recently, for CH_2Cl_2 and dmf solutions of [Co(saloph)], we reported evidence of the four-coordinated and the five-coordinated paramagnetic species and the diamagnetic dimer on the basis of the temperature dependence of the ^{1}H NMR spectra and the solution magnetic moments.[10] In this paper, we wish to report a UV-vis study with respect to the species existing in solutions of [Co(saloph)]. Although the d–d absorptions of the Schiff-base cobalt(II) complexes have been studied with respect to the orbital assignment of an unpaired electron, the UV-vis absorption spectra have been rarely utilized to characterize the species.[11]

Experimental

[Co(saloph)] was prepared following the literature[12] and stored under nitrogen atmosphere. Dmf and CH_2Cl_2 were of luminescent grade and dmf was treated with molecular sieves 4A 1/16. The solutions were prepared under nitrogen atmosphere using solvents purged with nitrogen gas for more than one hour. The absorption spectra of the dmf solutions thus prepared showed a slow time dependent change but this change was suppressed by the use of dried nitrogen gas; the nitrogen gas was purged through concentrated sulfuric acid before use. Measurements of the absorption spectra in the temperature range from 0 to 100 °C were carried out using a thermoelectric cell holder. For measurements from -55 to 25 °C, a copper cell holder controlled with a dry ice–acetone bath and a nitrogen-gas flow was used. The molar absorption coefficients shown in the figures are the calibrated values for solutions at 20 °C in consideration of the thermal expansion of the solvents. The concentrations of [Co(saloph)] used for the absorption measurements were in the range 10^{-4} to 10^{-2} mol dm^{-3}. A cell with a 0.1 mm optical length was used for the 10^{-2} mol dm^{-3} solutions. The difference spectra of the transient absorptions were measured by a system consisting of a nitrogen laser (Molectron UV14, 4 mJ/pulse), a pulsed xenon lamp, and a computer-controlled storage scope (Iwatsu TS-8123). Simultaneous measurements of the absorption spectra under cyclic voltammetry were carried out in the dmf solutions containing 0.5 mol dm^{-3} tetraethylammonium perchlorate with the system reported in the literature;[13] a working electrode of a platinum net made with 80 mesh wire, a silver wire reference electrode, and a platinum wire counter electrode were used.

Results and Discussion

Formation of [Co(saloph)(dmf)] in CH_2Cl_2-dmf Solutions. Figure 1 shows the UV-vis absorption spectra of [Co(saloph)] measured in various ratios of dmf to CH_2Cl_2, keeping the concentration of [Co(saloph)] constant. The concentration of [Co(saloph)] did not affect the spectra in the range 10^{-4} to 10^{-2} mol dm^{-3}. In the CH_2Cl_2–dmf solutions containing dmf

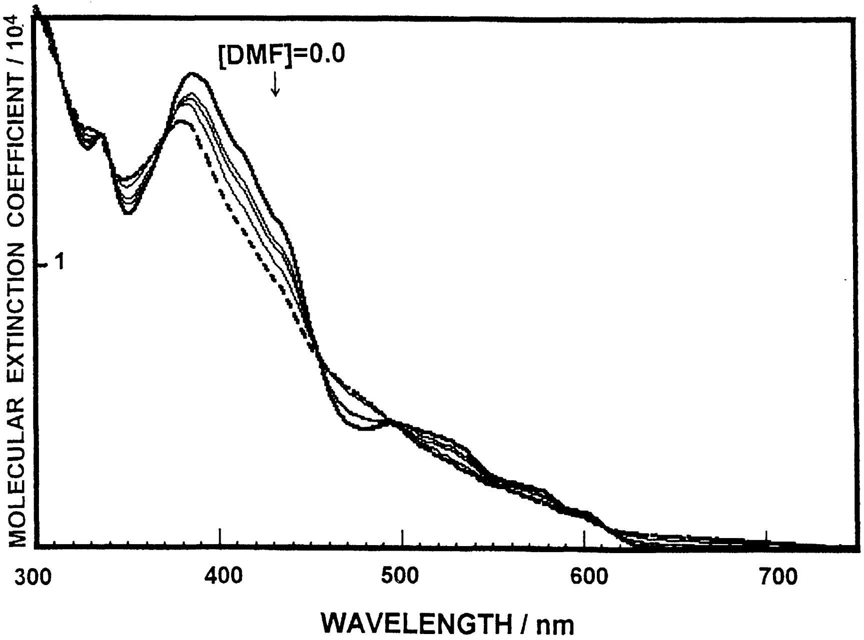

Fig. 1. Solvent dependence of the absorption spectrum of [Co(saloph)] in CH_2Cl_2–dmf binary solvent at 20 °C. [dmf]: 0.0 (the bold line), 0.8, 1.0, and 1.2 mol dm^{-3}. The broken line: the calculated spectrum of [Co(saloph)(dmf)].

of less than 2 mol dm^{-3}, isosbestic points were observed. We previously proposed equilibrium (1) on the basis of the ^{1}H NMR and magnetic measurements in CH_2Cl_2–dmf binary solutions;[10]

$$[\mathrm{Co(saloph)}] + \mathrm{dmf} \rightleftarrows [\mathrm{Co(saloph)(dmf)}]. \qquad (1)$$

In our study, the complex was attributed to a four-coordinated low-spin ($S=1/2$) complex, [Co(saloph)], in CH_2Cl_2 based on the typical Curie behavior of the proton signals and the value of the magnetic moment (1.4 B. M.). With an increase in the dmf concentration in the binary solvents, a large change in the chemical shifts of the proton signals was observed (Fig. 2), which indicated the formation of a new paramagnetic species, [Co(saloph)(dmf)]. From the solvent dependence of the absorption spectra in Fig. 1, the equilibrium constant of equilibrium (1) was determined using the linear relation of $(A-A_0)^{-1}$ to [dmf]$^{-1}$, where A_0 and A are the absorbances in CH_2Cl_2 and in each CH_2Cl_2–dmf solvent, respectively. The spectrum of the five-coordinated complex [Co(saloph)(dmf)] (the broken line in Fig. 1) was obtained based on the equilibrium constant determined.

The temperature dependence of the equilibrium constant was obtained from the absorption spectra in the temperature range 6 to 35 °C. As a result, the values of $\Delta H°$ and $\Delta S°$ for equilibrium (1) were obtained as -3.7 ± 1.0 kJ mol^{-1} and -17 ± 4 J K^{-1} mol^{-1}, respectively. In the case of [Co^{II}L] where L is salen, salen derivatives, or saloph derivatives, the values for the binding reaction of the axial ligand were reported as $\Delta H°=-20$ to -40 kJ mol^{-1} and $\Delta S°=-60$ to -120 J K^{-1} mol^{-1} for imidazole and pyridine,[14] and as $\Delta H°=-10.8$ kJ mol^{-1} and $\Delta S°=-31$ J K^{-1} mol^{-1} for dimethylsulfoxide.[2] In comparison with the reported values, the present small values of $\Delta H°$ and $\Delta S°$ reveal very weak dmf-cobalt binding in [Co(saloph)(dmf)]. This is partly due to the small donor ability of dmf; the donor numbers of pyridine, dimethylsulfoxide, and dmf are reported to be 33.1, 29.8, and 26.6, respectively.

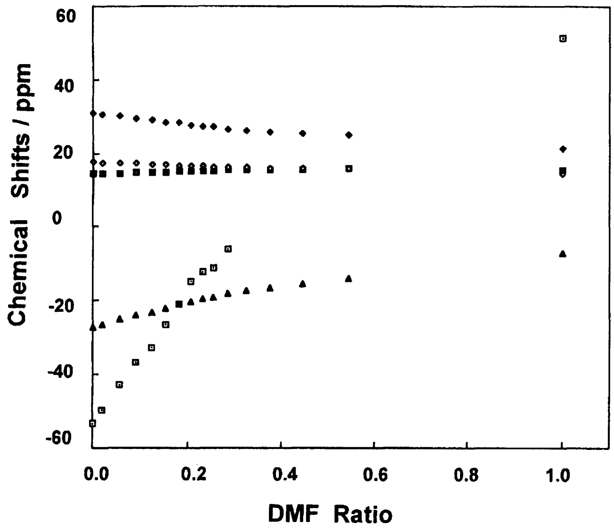

Fig. 2. Solvent dependence of the proton chemical shifts of the proton signals of [Co(saloph)] in CD_2Cl_2–dmf-d_7 binary solvent at 24 °C (2.4×10^{-3} mol dm^{-3}).

Formation of Dimer of 10^{-2} mol dm^{-3} dmf Solution. On the basis of the previous NMR and magnetic study of [Co(saloph)] in 7×10^{-2} mol dm^{-3} dmf solution, we proposed equilibrium (2) between the five-coordinated paramagnetic species and the diamagnetic dimer;[10)]

$$2[\mathrm{Co(saloph)(dmf)}] \rightleftarrows [\mathrm{Co(saloph)(dmf)}]_2. \quad (2)$$

At temperatures above 60 °C, the Curie plot shown in Fig. 3 gave a linear line for each proton signal, suggesting that the monomeric species [Co(saloph)(dmf)] predominates over the dimeric one $[\mathrm{Co(saloph)(dmf)}]_2$. At temperatures below 60 °C, each Curie line showed a curvature and moved to the diamagnetic position. Correspondingly, the magnetic moment determined by the Evans method decreased to nearly 0 B.M. below −35 °C.[10)] Anti-Curie behavior was observed at higher temperatures with an increase of the concentration of [Co(saloph)] (60 and 20 °C for 7×10^{-2} and 4×10^{-2} mol dm^{-3}, respectively), which suggested that the major species at low temperatures was the antiferromagnetically-coupled dimer.

Thermodynamic analysis of the dimer formation was carried out based on the temperature dependence of the chemical shifts (Fig. 3). The equilibrium constant of equilibrium (2) was expressed as;

$$K = x/2a(1-x)^2, \quad (3)$$

where a is the initial concentration of [Co(saloph)], and $a(1-x)$ and $ax/2$ are the concentrations of [Co(saloph)(dmf)] and $[\mathrm{Co(saloph)(dmf)}]_2$, respectively, in the equilibrium state. The ratio x was calculated from the observed chemical shifts δ_{obsd} according to Eq. 4 ,

$$x = (\delta_{\mathrm{para}} - \delta_{\mathrm{obsd}})/(\delta_{\mathrm{para}} - \delta_{\mathrm{dia}}), \quad (4)$$

where δ_{para} denotes the chemical shift of the paramagnetic [Co(saloph)(dmf)] at the temperature in question which was obtained by the extrapolation of the Curie line in Fig. 3 from higher temperatures, 60 to 151 °C. δ_{dia} denotes the chemical shift of the diamagnetic dimer and the value of diamagnetic [Co(saloph)] I was used for δ_{dia}. Thus, from the observed chemical shift, the equilibrium constant was determined at each temperature and the values of ΔH° and ΔS° were calculated to be -39 ± 3 kJ mol^{-1} and -110 ± 5 J K^{-1} mol^{-1} with the linear relation of ln K to $1/T$.

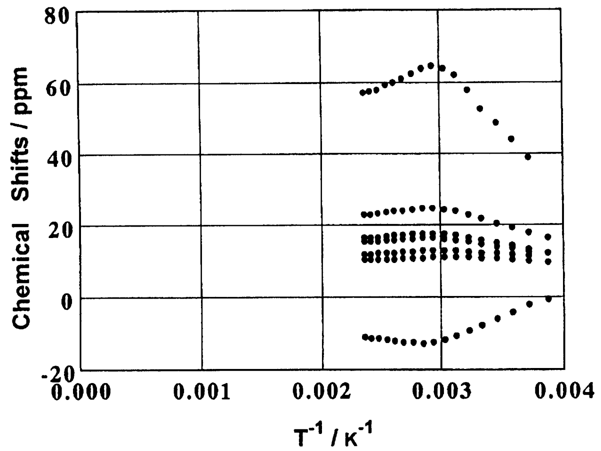

Fig. 3. Temperature dependence of the proton chemical shifts of [Co(saloph)] in dmf-d_7 (7×10^{-2} mol dm^{-3}) from −35 to 150 °C.

Figure 4 shows the absorption spectra of [Co(saloph)] in dmf (1×10^{-2} mol dm^{-3}) in the temperature range −50 to 90 °C. The molar absorption coefficient of the spectra was the calibrated value for the solution at 20 °C in consideration of the solvent expansion. The absorption spectrum at 90 °C was almost identical to the spectrum of [Co(saloph)(dmf)] in Fig. 1, which is consistent with the calculated value of $x = 0.01$ obtained from Eq. 3 based on $a = 0.01$ mol dm^{-3} and $K = 0.73$ mol^{-1} dm^3 (the determined value at 90 °C). The spectrum of the dimer was given as the dotted line in Fig. 4, by taking the equilibrium constant and the spectrum of [Co(saloph)(dmf)] into consideration. The dimer spectrum has a peak at 380 nm compared with the 385 nm peak of [Co(saloph)(dmf)] and a new broad band in the 500—700 nm region. Since the reported dimeric unit in the crystal has a short intermolecular distance (2.25 Å) for [Co(saloph)],[7)] the broad absorption at 500—700 nm might be attributed to charge transfer bands between the two halves of the dimer.[15)]

Formation of $[\mathrm{Co(saloph)(dmf)_2}]$ in dmf Solution. Figure 5 shows the absorption spectra of the dmf solution of [Co(saloph)] (5×10^{-4} mol dm^{-3}) in the temperature range −55 to 90 °C. The molar extinction coefficients are the calibrated values for the 20 °C solution. The spectrum at 90 °C was identical to that of [Co(saloph)(dmf)] in Fig. 1. On the other hand, the spectrum at −55 °C is quite different from that of the dimer in Fig. 4, suggesting the formation of a new species in this concentration region. In the solutions of the cobalt(II) Schiff-base complexes $[\mathrm{Co^{II}L}]$, several species have been reported. In the presence of oxygen, the cobalt(II) complexes in coordinating solvents (B) were frequently oxidized according to Eq. 5;[2,3)]

$$[\mathrm{Co^{II}L(B)}] + \mathrm{O_2} \rightleftarrows [\mathrm{Co^{III}L(B)(O_2{}^{-\bullet})}]. \quad (5)$$

In alcoholic and aqueous solutions, the formation of $[\mathrm{Co^{III}L(OR)}]$ and $[\mathrm{Co^{III}L(OH)}]$ was also reported in the presence of oxygen.[11)] We measured the spectral change of $\mathrm{Co^{II}} \rightarrow \mathrm{Co^{III}}$ for the dmf solution of [Co(saloph)] by in-situ spectrocyclic voltammetry (Fig. 6). Repeated measurements gave reversible results. Being consistent with the reported spectral change for the process of $[\mathrm{Co^{II}(salen)}] \rightarrow [\mathrm{Co^{III}(salen)(OH)}]$,[11)] Fig. 6 shows that the intensity at 380 nm became weaker for the cobalt(III) species than for the cobalt(II) species. The cobalt(III) species has a very different spectrum from that observed at low temperature (Fig. 5). In the absence of oxygen, the formation of the six-coordinated cobalt(II) complexes was reported in 4-picoline,[16)] pyridine,[17,18)] and 1-methylimidazole,[17)] and dimethylsulfoxide[18)] so-

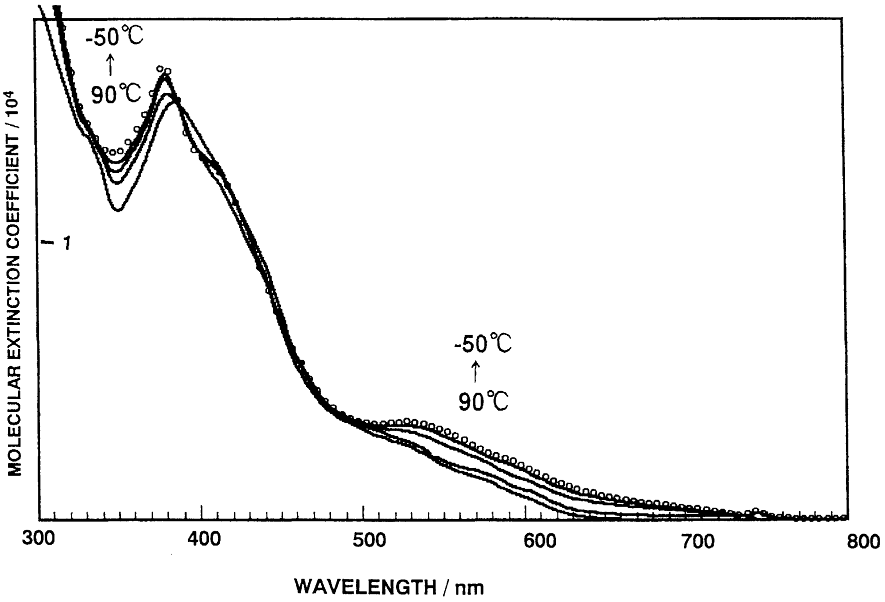

Fig. 4. Temperature dependence of the absorption spectrum of [Co(saloph)] in dmf (10^{-2} mol dm^{-3}) from −50 to 90 °C. The dotted line: the analyzed spectrum of the dimer.

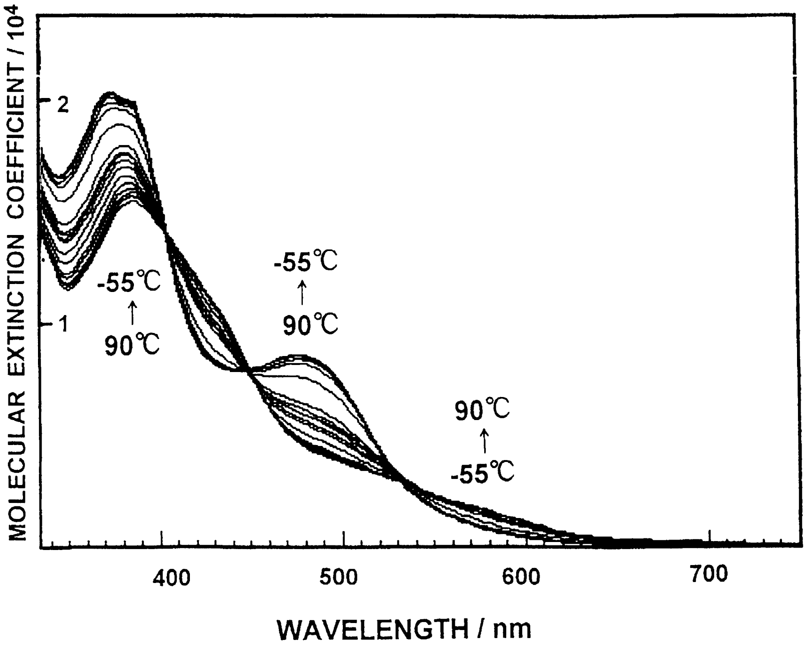

Fig. 5. Temperature dependence of the absorption spectrum of [Co(saloph)] in dmf (5×10^{-4} mol dm^{-3}) from −55 to 90 °C.

lutions;

$$[\mathrm{Co^{II}L(B)}] + \mathrm{B} \rightleftarrows [\mathrm{Co^{II}L(B)_2}]. \qquad (6)$$

Since dmf also is a donating molecule, we assumed that spectral equilibrium in Fig. 5 corresponds to equilibrium (6) between the five-coordinated complex [Co(saloph)(dmf)] and the six-coordinated complex [Co(saloph)(dmf)$_2$]. The equilibrium constant of equilibrium (6) was determined at each temperature, by using the spectrum of [Co(saloph)(dmf)] in Fig. 1 and by assuming that the spectrum at −55 °C in Fig. 5 represents the spectrum of [Co(saloph)(dmf)$_2$]; the assumption is supported by the fact that no spectral change was observed below −40 °C. From the temperature dependence of the equilibrium constants, the values of $\Delta H°$ and $\Delta S°$ were calculated as -30 ± 3 kJ mol^{-1} and -145 ± 5 J K^{-1} mol^{-1}, respectively. The values are about eight times those determined for the formation of [Co(saloph)(dmf)].

Species under Equilibria in dmf. From the above-mentioned results, it is concluded that three species are under equilibria in the dmf solutions of [Co-

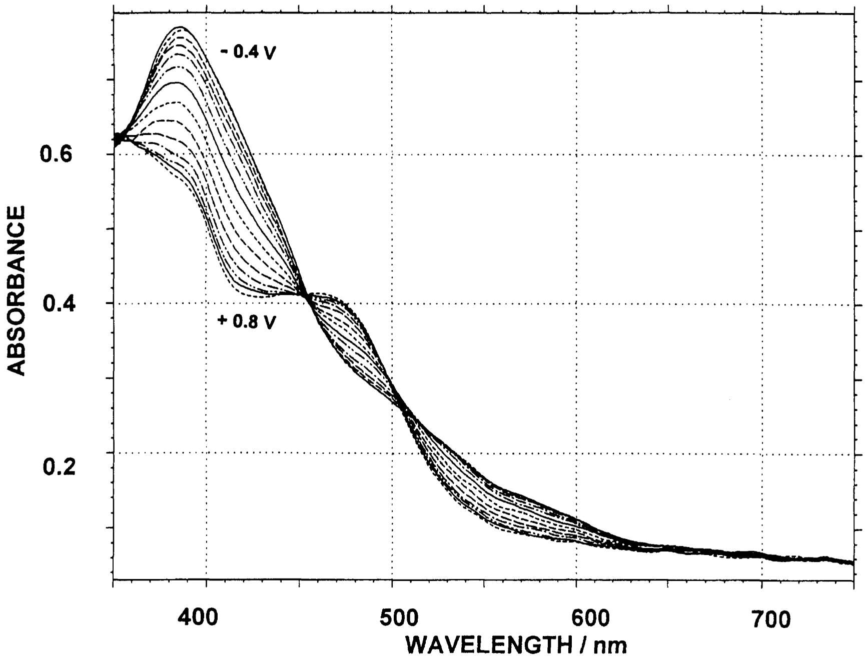

Fig. 6. Spectra of the $Co^{II} \rightarrow Co^{III}$ process in the dmf solution of 2×10^{-3} mol dm^{-3} [Co(saloph)] and 0.5 mol dm^{-3} tetraethylammonium perchlorate for the potentials from −0.4, 0, 0.2, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, and 0.80 V.

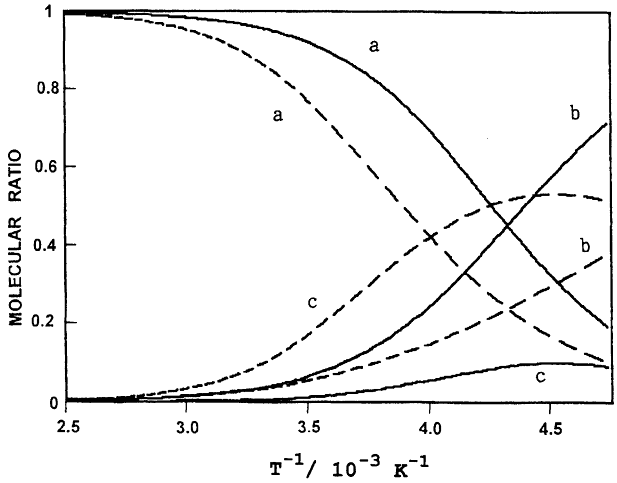

Fig. 7. Temperature dependence of molecular ratios of a: [Co(saloph)(dmf)], b: [Co(saloph)(dmf)$_2$], and c: 1/2[Co(saloph)(dmf)]$_2$. The broken line: 1×10^{-2} mol dm^{-3} and the solid line: 5×10^{-4} mol dm^{-3}.

(saloph)];

$$\begin{aligned}[\mathrm{Co(saloph)(dmf)_2}] &\rightleftharpoons [\mathrm{Co(saloph)(dmf)}] + \mathrm{dmf} \\ &\rightleftharpoons 1/2[\mathrm{Co(saloph)(dmf)}]_2 + \mathrm{dmf}.\end{aligned}$$

By using the thermodynamic parameters of equilibria (2) and (6), the molecular ratios of the three species were calculated in the temperature range −60 to 120 °C as shown in Fig. 7. The broken and solid curves correspond to [Co(saloph)] concentrations of 1×10^{-2} mol dm^{-3}and 5×10^{-4} mol dm^{-3}, respectively. Figure 7 shows that [Co(saloph)(dmf)] (a) is the major component at higher temperatures regardless of the concentration, and that at lower temperatures the complex exists either as the six-coordinated monomer (b) or as the antiferromagnetically-coupled dimer (c), depending upon the concentration of [Co(saloph)].

Transient Species Induced by Laser Irradiation. Figures 8a and 8b show the difference spectra of the transient absorptions of a dmf solution of [Co(saloph)] (5×10^{-4} mol dm^{-3}) at 24 and −5 °C, respectively, induced by 337 nm laser irradiation. Oxygen or photodecomposition effects were not found in repeated measurements. At 24 °C (Fig. 8(b)) a broad absorption with a lifetime of 10^{-3} s was observed. From the curves shown in Fig. 7, the main species in the 5×10^{-4} mol dm^{-3} solution at 24 °C was assigned to [Co(saloph)(dmf)]. Similar transient absorptions were reported in the CH_2Cl_2 solutions of [Co(saloph)] and [Co(saloph)(pyridine)]; broad bands appeared near 480 nm with lifetimes of 10^{-3} s.[9] Since the four-coordinated complex ([Co(saloph)] in CH_2Cl_2) and the five-coordinated complexes ([Co(saloph)(pyridine)] and [Co(saloph)(dmf)]) showed analogous transient absorptions, one of the plausible structures for the transient species is the solvated one which has a solvent molecule weakly bonded to the phenolic oxygen atoms of saloph; such solvated complexes were reported in the crystals of an ethanol adduct and a chloroform adduct of the salen-type cobalt(II) complex.[5,6] At −5 °C (Fig. 8(a)), the transient absorption exhibited two-exponential decay with lifetimes of 4×10^{-6} s and about 1×10^{-3} s. The long-lived absorption was similar to that observed at 24 °C. The spectrum at $t=0.0$ is in good accord

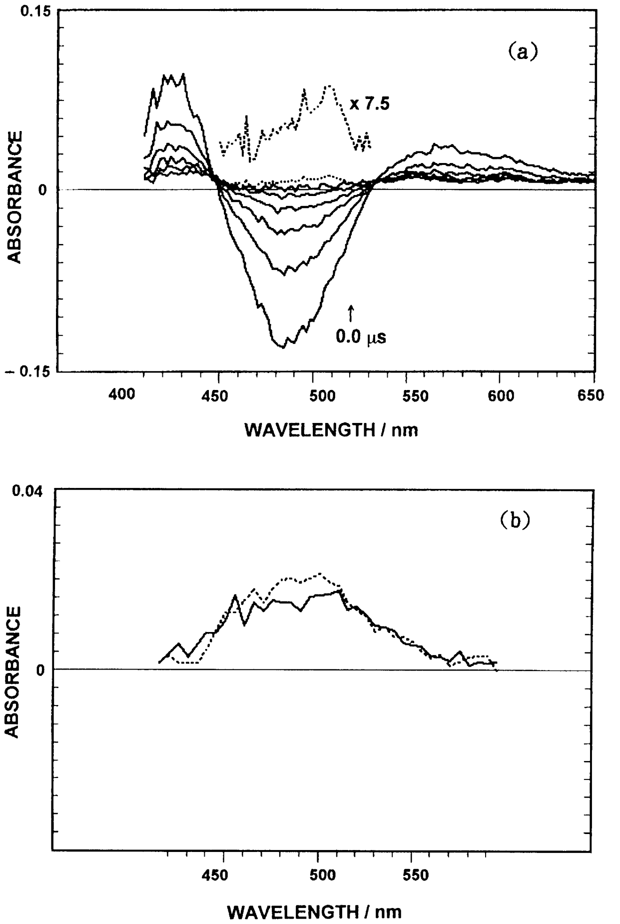

Fig. 8. Time-resolved difference spectrum of the transient absorption of [Co(saloph)] in dmf (5×10^{-4} mol dm^{-3}) in 2 mm cell. (a) the solid line: t=0, 2, 4, 6, 8 and 10 μs, and the dotted line: 30 μs after an excitation at −5 °C. (b) the solid line: t=0 and the dotted line: 8 μs at 24 °C.

with the difference spectrum obtained by subtracting the spectrum of [Co(saloph)(dmf)$_2$] from that of [Co(saloph)(dmf)]. It indicates that the observed process at t=0.0 corresponds to the photodecomposition reaction of [Co(saloph)(dmf)$_2$]→[Co(saloph)(dmf)]+dmf. The observed time-dependence of the transient absorption may be attributed to a recombination process of [Co(saloph)(dmf)]+dmf→[Co(saloph)(dmf)$_2$] with a rate constant of 2.5×10^5 s^{-1}. A similar recombination process was reported at −92 °C for the pyridine adduct of tetraphenylporphrin nickel(II) ([NiTPP(py)$_2$]) with the rate constant of 3×10^4 s^{-1}.[19] The fact that the short-lived component became clearer at −5 °C than at 24 °C is consistent with the increase of the population of [Co(saloph)(dmf)$_2$] as shown in Fig. 7.

Conclusion. In this UV-vis and ^{1}H NMR study of [Co(saloph)] in dmf, we found that three species containing coordinated dmf molecules existed in the solutions; [Co(saloph)(dmf)], [Co(saloph)(dmf)$_2$], and [Co(saloph)(dmf)]$_2$. The population ratios of these species varied depending on the temperature and the concentration of [Co(saloph)]. We also observed a fourth species by 337 nm laser excitation, which was ascribed to a transient solvated species. Although the relative stability of these species is expected to change if the structurally rigid saloph ligand is replaced by a more flexible ligand such as salen, these spectra can be utilized to identify the species of the cobalt(II) Schiff-base complexes in solution.

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