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Transient Absorptions Due to Solvated Complexes of [Bis(salicylaldehyde)-o-phenylenediiminato]cobalt(II)

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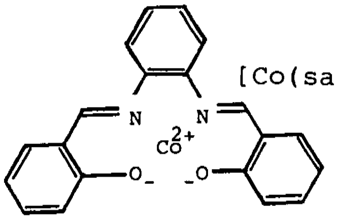
Transient absorptions due to a photo-induced solvation at phenolic oxygen atoms were observed for [Co(saloph)], [Co(saloph)(py)] and [Co(saloph)(py)O_2] in dichloromethane.

Cobalt(II) complexes with Schiff base ligands have been investigated as reversible dioxygen carriers.[1)] The molecular structure of the oxygen adduct of [Co(salen)] was studied by the X-ray analysis,[2)] and analogous coordination of O_2 was confirmed in solutions by ESR studies.[3)] The solvent effects on the oxygen affinities of these Co(II) complexes have been interpreted in terms of coordination of a solvent molecule.[3)] In order to get informations about solvation the author applied the transient spectroscopy for the solutions of the titled complex, [Co(saloph)]. We herein wish to report the transient absorptions due to a solvation.

[Co(saloph)] was prepared following the literature[4)] and stored under nitrogen. The solutions were prepared in a N_2 box by the use of luminescent grade CH_2Cl_2 purged by nitrogen for one hour. The excitations were carried out by a nitrogen laser (Molectron UV14, 4 mJ/pulse) and the transient difference spectra were monitored by a pulsed Xenon lamp and a storagescope(Iwatsu TS-8123). Due to the weak absorptions the values of the lifetimes were preliminary.

Figure 1 shows the difference spectra (ΔOD) of the transient absorptions and the ground-state absorption spectra of [Co(saloph)] and the related complexes in CH_2Cl_2. (1) is the spectrum of [Co(saloph)]. (2) is that of [Co(saloph)(py)].[5)] (3) can be assigned to the spectrum of [Co(saloph)(py)O_2].[4)] The ground-state band at 380 nm is assigned to a locally excited transition of saloph^{2-} in comparison with the band at 390 nm observed for Na_2(saloph) in DMF. The longer-wavelength bands which appeared with complex formation are assigned to charge-transfer transitions



[Co(saloph)]

between Co(II) and saloph^{2-}. The ΔOD scarcely shows a spectral change by coordination of axial ligands. The lifetime of (1) was about 3 ms and unaffected by O_2-bubbling through the solution. The lifetime of (2) was 650 μs. Due to the weak absorbance the lifetime of (3) was only estimated to be similar to that of (2). These long lifetimes insensitive to O_2 indicate that the observed transient species are not the excited states.

Since $[Co(CN)_6]^{3-}$ was reported to form a photo-induced solvated complex with CH_2Cl_2 having a lifetime of 600 μs,$^{6)}$ we examined a possibility of solvated complexes as the transients. Considering that the axial ligands little affected the transient spectra, the equatorial solvation was supposed. Supporting results are: (1) [Co(salen)] monochloroformate was reported to have $CHCl_3$ equatorially solvated to salen in crystal.$^{7)}$ (2) We observed a transient absorption at 400 - 500 nm with the lifetime of more than 3 ms for Na_2(saloph) in air-saturated DMF.

The observed positive peaks of ΔOD show that the strongest peak of the ground-state spectrum at 380 nm shifts to longer-wavelength side by solvation.

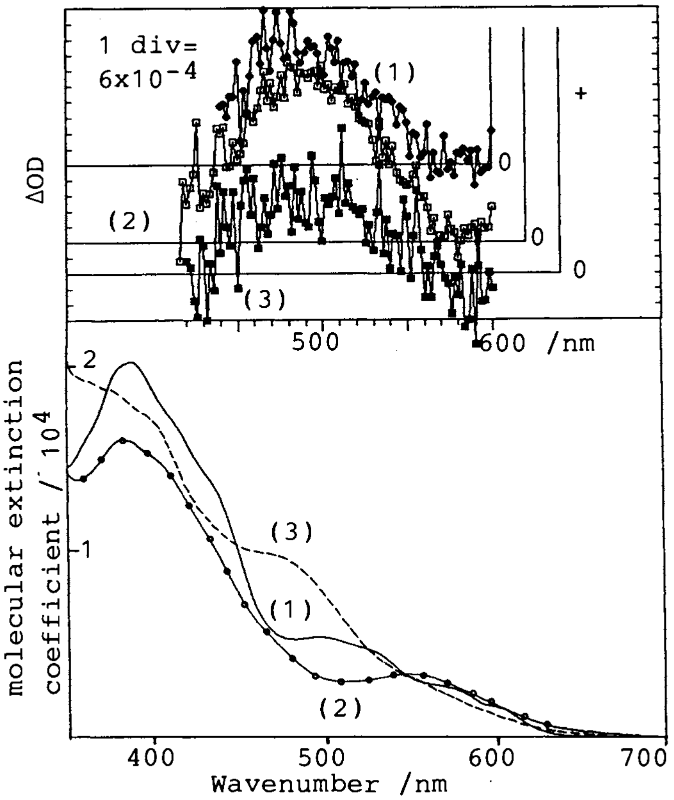


Fig. 1. ΔOD and ground-state absorption spectra in N_2-purged CH_2Cl_2. (1): 5×10^{-4} M (mol dm^{-3}) [Co(saloph)] (●), (2): (1) with 0.1 M pyridine added (□), (3): (2) after O_2-saturation (■).

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