## Notes

Chem. Pharm. Bull.
31(6)2110—2113(1983)

# Absorption Spectral Shift of *meso*-Tetraphenylporphinatocadmium on Axial Ligation

TOSHIHIKO OZAWA* and AKIRA HANAKI

*National Institute of Radiological Sciences, 9-1, Anagawa-4-chome, Chiba, 260, Japan*

(Received November 19, 1982)

The effects of axial ligation to *meso*-tetraphenylporphinatocadmium (CdTPP) were studied in dimethyl sulfoxide (DMSO) or dichloromethane ($CH_2Cl_2$). Addition of neutral (L) or anionic ligands ($X^-$) to CdTPP caused red shifts in the absorption spectrum. The magnitude of the red shift depended on the charge but not on the strength of the Cd-ligand bond. Further, a relationship between the ratio $\varepsilon_\alpha/\varepsilon_\beta$ and the wavenumber of the Soret band was observed.

**Keywords**——*meso*-tetraphenylporphinatocadmium; CdTPP; visible absorption spectrum; metalloporphyrin; Soret band; $\alpha$ band; $\beta$ band; axial ligand; red shift

Valentine *et al.* have shown that the red shifts of the visible absorption bands observed in a series of tetraphenylporphinato zinc (ZnTPP) complexes with axial ligands (Zn(TPP)L and Zn(TPP)$X^-$, where L and $X^-$ represent neutral and anionic ligands, respectively) are correlated with the charge and the polarizability of the ligands.[1]

In the course of studies on the reactions of superoxide ion ($O_2^-$) with some non-redox metalloporphyrins, we observed that the electronic absorption spectrum of CdTPP undergoes shifts in wavenumber upon addition of axial ligands. Since cadmium belongs to the same group IIb as zinc in the periodic table, we expected that CdTPP might also be a good model for studying the effects of axial ligands on the electronic absorption spectrum. In this paper, we report some spectral effects of changing the axial ligands.

## Experimental

**Materials**——CdTPP was prepared by the reported method.[2] Potassium superoxide ($KO_2$) was purchased from Alfa Products, Inc. Potassium chloride (E. Merck), potassium bromide and iodide (Wako Pure Chemical Ind. Ltd.) and dicyclohexyl-18-crown-6 (Nisso Chemical Co.) were used without further purification. Imidazole (Im), 2-methylimidazole (2-MeIm) and 4-methylimidazole (4-MeIm) were recrystallized from benzene. Other reagents were commercial products and were used without further purification. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure from $CaH_2$ and stored over freshly activated 4 A molecular sieves under dry argon. Dichloromethane ($CH_2Cl_2$) was distilled, and passed through a neutral alumina column.

**Preparation of Solutions of Anionic and Neutral Ligands**——Anionic ligands ($X^-$) were prepared as follows. Potassium superoxide, hydroxide and halides were each ground to a fine powder with a motar and pestle in a dry atmosphere. Powdered compounds and 2—3 mol equivalent of dicyclohexyl-18-crown-6 were dissolved in dry DMSO by stirring for a few hours under argon. Neutral ligands (L) were dissolved in $CH_2Cl_2$.

**Reactions of CdTPP with Axial Ligands**——Aliquots of $\sim 10^{-2}$ M solutions of the ligands were successively added to 2 ml of $CH_2Cl_2$ or DMSO solution of CdTPP ($10^{-5}$—$10^{-6}$ M) in a 1-cm capped quartz cell by means of a microsyringe. The visible spectra were recorded thereafter.

**Spectral and Equilibrium Constant Measurements**——Ultraviolet (UV)/visible absorption spectra were obtained at 25.0°C using a Union Giken SM-401 spectrophotometer. The equilibrium constants ($K_{eq}$) in DMSO were estimated by use of the method of Miller and Dorough[3] with corrections for volume changes. In this case, dicyclohexyl-18-crown-6 had no influence on the equilibrium constant, because its addition to DMSO solution of CdTPP did not affect the spectrum of CdTPP itself even when the mixture was allowed to stand for 3 d in the dark.[4]

## Results and Discussion

The ligands were added to CdTPP in DMSO or in $CH_2Cl_2$. The visible absorption spectra of Cd(TPP)L and Cd(TPP)$X^-$ undergo a red shift relative to that of CdTPP itself. Representative spectral changes are shown in Fig. 1. Visible absorption spectral data for Cd(TPP)L and Cd(TPP)$X^-$ are listed in Table I, along with the ratio of the molecular extinction coefficient of the $\alpha$ band ($\varepsilon_\alpha$) to that of the $\beta$ band ($\varepsilon_\beta$) ($\varepsilon_\alpha/\varepsilon_\beta$).

Usually the absorption spectra of metalloporphyrins consist of three intense bands in the visible region. The most intense absorption band, the Soret band, is observed around 430—445 nm in $CH_2Cl_2$ or DMSO and the other two bands, named $\alpha$ and $\beta$ bands, are observed between 550 and 650 nm ($\lambda_{max}$ of $\alpha$ band>that of $\beta$ band) in the same solvents. The Soret band is largely a result of the transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \longrightarrow e_g(\pi^*)$.[5]

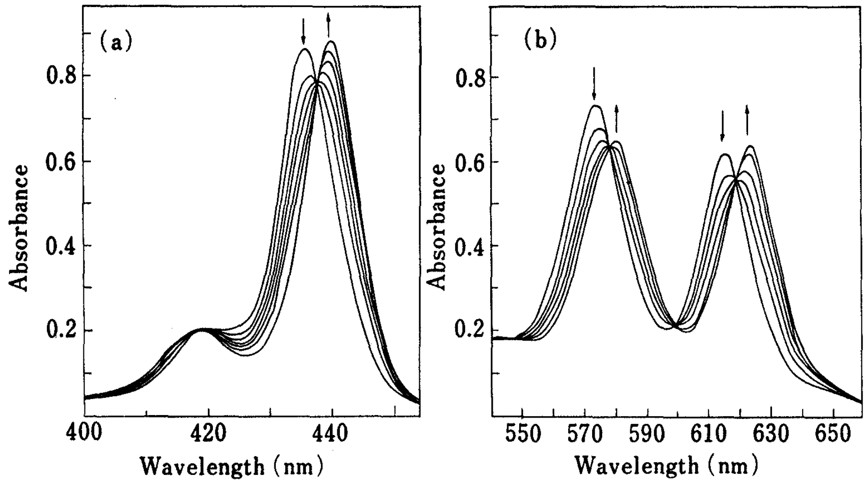

Fig. 1. Visible Spectral Change Resulting from Successive Additions of $Cl^-$ Solution to CdTPP in DMSO

Starting concentration of CdTPP was $3.12 \times 10^{-5}$ M, and 5 μl aliquots of $Cl^-$ solution ($2.64 \times 10^{-2}$ M) were successively added to 2 ml of CdTPP solution. (a) Change of Soret band (×1/10); (b) Change of $\alpha$ and $\beta$ bands.

TABLE I. Electronic Absorption Spectra of CdTPP Derivatives

| Complex | Solvent | $\lambda_{max}$/nm (log $\epsilon$) | | | |
|---|---|---|---|---|---|
| | | Soret | $\beta$ | $\alpha$ | $\epsilon_\alpha/\epsilon_\beta$ |
| CdTPP | $CH_2Cl_2$ | 430.5 (5.18) | 564.0 (4.05) | 604.5 (3.77) | 0.526 |
| Cd (TPP) THF | $CH_2Cl_2$ | 433.0 (5.38) | 569.0 (3.97) | 610.0 (3.83) | 0.715 |
| Cd (TPP) $CH_3CN$ | $CH_2Cl_2$ | 433.0 (5.39) | 570.0 (3.95) | 612.0 (3.78) | 0.666 |
| Cd (TPP) DMSO | $CH_2Cl_2$ | 434.5 (5.42) | 571.5 (3.97) | 613.0 (3.83) | 0.728 |
| Cd (TPP) DMF | $CH_2Cl_2$ | 433.5 (5.42) | 572.0 (3.96) | 613.0 (3.81) | 0.709 |
| Cd (TPP) py[a] | $CH_2Cl_2$ | 436.0 (5.44) | 575.0 (3.95) | 617.0 (3.83) | 0.767 |
| Cd (TPP) Im | $CH_2Cl_2$ | 436.5 (5.35) | 576.5 (4.01) | 618.5 (3.91) | 0.797 |
| Cd (TPP) 2-MeIm | $CH_2Cl_2$ | 437.0 (5.36) | 577.0 (4.03) | 619.0 (3.98) | 0.886 |
| Cd (TPP) 4-MeIm | $CH_2Cl_2$ | 437.0 (5.35) | 576.5 (3.96) | 618.5 (3.90) | 0.885 |
| Cd (TPP) $PPh_3$[b] | $CH_2Cl_2$ | 442.0 (5.29) | 581.0 (3.97) | 623.5 (3.97) | 0.986 |
| Cd (TPP) $Br^-$ | DMSO | 439.0 (5.40) | 577.0 (4.00) | 621.0 (3.95) | 0.881 |
| Cd (TPP) $Cl^-$ | DMSO | 440.5 (5.47) | 581.0 (4.03) | 624.0 (4.02) | 0.991 |
| Cd (TPP) $O_2^-$ | DMSO | 441.0 (5.27) | 584.5 (3.99) | 628.0 (4.01) | 1.043 |
| Cd (TPP) $OH^-$ | DMSO | 445.0 (5.41) | 587.0 (4.02) | 631.0 (4.11) | 1.226 |

[a] py, Pyridine. [b] $PPh_3$, Triphenyl phosphine.

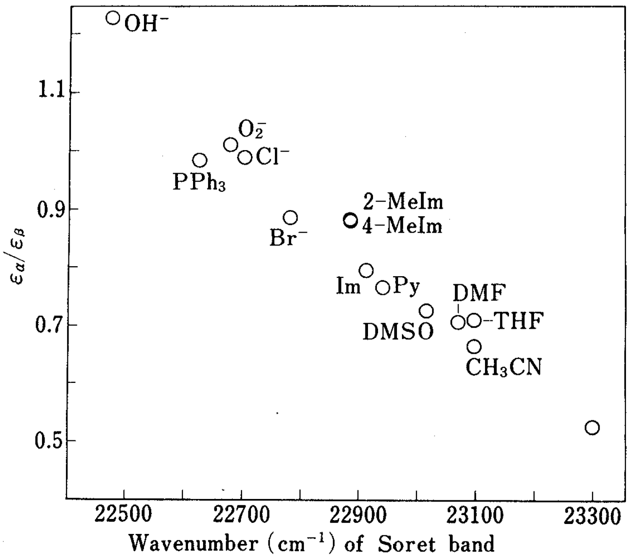

Fig. 2. Plots of $\varepsilon_\alpha/\varepsilon_\beta$ *vs.* the Frequency ($\nu_{Soret}$) of the Soret Band for Cd(TPP)L and Cd(TPP)X⁻ Derivatives

The red shift of the Soret band was accompanied with red shifts of the $\alpha$ and $\beta$ bands. From Table I, it is apparent that upon complexation the values of $\varepsilon_{max}$ ($\varepsilon_{Soret}$, $\varepsilon_\alpha$ and $\varepsilon_\beta$) of these three absorptions are changed. A correlation between the ratio $\varepsilon_\alpha/\varepsilon_\beta$ and the wavenumber of the Soret band was observed (Fig. 2). Similar correlations have been observed previously for a series of metalloporphyrins.[5,6] In those cases, $\varepsilon_\alpha/\varepsilon_\beta$ increases with increase of the wavenumber of all absorption bands in ZnTPP complexes. However, the $\varepsilon_\alpha/\varepsilon_\beta$ *vs.* wavenumber plot for CdTPP complexed with halides shows an opposite tendency (Table II). This may be explained by the difference of electronegativity of the metals.[7]

We have determined the equilibrium constants for anionic binding of halide and hydroxide (Table III). The order of $K_{eq}$ is $Cl^- > Br^- > OH^-$. This order is different from the order of the red shift of the visible bands ($OH^- > Cl^- > Br^-$). These results suggest that the magnitude of red shift ($\Delta\lambda^{-1}$) does not depend on the strength of the CdTPP-ligand bond, because $K_{eq}$ is related to bond strength for the metalloporphyrins.[8]

Table II. The Order of the Red Shift and of the $\epsilon_\alpha/\epsilon_\beta$ Ratio in the Visible Absorption Spectra of Metalloporphyrins Complexed with Halides

| Complex | Wavenumber | $\epsilon_\alpha/\epsilon_\beta$ | Ref |
|---|---|---|---|
| Zn (TPP)X⁻ | F <Cl<Br | F <Cl<Br | 1 |
| Cd (TPP)X⁻ | Br<Cl | Br<Cl | This work[a)] |

*a)* KF did not dissolve in DMSO-crown ether and I⁻ did not appear to form a complex.

Table III. Equilibrium Constants in DMSO at 25 °C

| Ligand | $K_{eq}$, $M^{-1}$ |
|---|---|
| OH⁻ | $4.94\times10^2$ |
| Br⁻ | $3.11\times10^3$ |
| Cl⁻ | $1.21\times10^4$ |

Valentine *et al.*[1] suggested that complexation of a metal with donor groups increases the charge transfer onto the porphyrin ring. The results shown in Table I clearly indicate that charge is a main factor determining $\Delta\lambda^{-1}$, because all of the anion complexes are more red-shifted than the neutral ligand complexes, except in the case of ligation of triphenyl phosphine which has a different nature from the other neutral ligands. Therefore, we think that the red shift and the changes of $\varepsilon_\alpha/\varepsilon_\beta$ reflect the magnitude of negative charge transfer from the ligand to the porphyrin ring *via* the cadmium atom.

## References

1) M. Nappa and J.S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).
2) A.D. Adler, F.R. Rongo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
3) J.R. Miller and G.D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).

4) T. Ozawa and A. Hanaki, *Inorg. Chim. Acta*, **80**, 33 (1983).
5) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).
6) M. Gouterman, "The Porphyrins," Vol. III, ed by D. Dolphin, Academic Press, New York, N.Y., 1978, Part A, Chap. 2.
7) M. Gouterman, F.P. Schwarz, P.D. Smith and D. Dolphin, *J. Chem. Phys.*, **59**, 676 (1973).
8) G.C. Vogel and J.R. Stahlbush, *Inorg. Chem.*, **16**, 950 (1977).