Axial Ligation of Oxygen Donors to Tetraphenylporphyrinatocadmium(II)

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Abstract

Axial ligation of a variety of oxygen donors to *meso*-tetraphenylporphyrinatocadmium(II) [Cd(TPP)] was studied in dichloromethane (CH_2Cl_2) by the spectroscopic method. Addition of oxygen donors to Cd(TPP) caused red shifts in the absorption spectrum. The magnitude of the red shift was dependent on the charge of the axial ligands. A weak relationship between the ratio of molar extinction coefficients of alpha bands to that of beta bands and the wavenumber of the Soret band was observed.

Dissociation constants (K_d) were determined for Cd(TPP)–ligand complexes. A 1:1 binding stoichiometry is found in all cases. Increasing affinity for complex formation as a function of increasing basicity is observed among a limited set of structurally similar ligands. Steric constraints also strongly influence ligand binding affinity.

Introduction

Both the important classes of natural metalloporphyrins, the iron porphyrins and magnesium chlorins, have their function associated with axial ligation phenomena: in the former the dioxygen molecule bound to a Fe(II) ion is transported or reduced, and in the latter one chlorophyll molecule is occupying a vacant axial coordination site above the Mg ion of a second chlorophyll molecule. Therefore, a detailed study of axial coordination in metalloporphyrins seems necessary. In fact, the interaction of axial ligands with metalloporphyrins has been an active area of research for many years [1, 2]. A wide variety of spectroscopic techniques have been used to study these interactions in both hemoproteins and model systems [3].

Recently, Nardo and Dawson examined the axial ligation of tetraphenylporphyrinatozinc(II) [Zn(TPP)] with oxygen and nitrogen donors by use of magnetic circular dichroism (MCD) spectroscopy [4]. Further, they investigated the axial ligation of Zn(TPP) with a variety of oxygen donors, and determined the dissociation constant (K_d) and the binding stoichiometries [5]. Such data provide direct evidence for the coordination of oxygen donors to the zinc atom.

Zn(TPP) is often used to study axial ligation because it provides a simple system to observe spectral changes which occur following ligand coordination. Unlike porphyrin complexes with metals such as iron and cobalt, Zn(TPP) will not undergo changes in the metal oxidation state, will accept only one axial ligand [6] and does not undergo changes in spin state. Finally, there are no empty d orbitals to participate in bonding. In fact, spectral changes in the electronic absorption spectrum of Zn(TPP) following axial ligation of a variety of ligands have been well characterized by Nappa and Valentine [7]. Gouterman *et al.* have also studied the effect of axial ligation on the spectra of metalloporphyrins containing Zn(TPP) [8]. Thus, Zn(TPP) is a suitable compound for studying axial ligation.

Since cadmium belongs to the same group IIb as zinc in the periodic table, we expected that Cd(TPP) might also be a good probe for studying the effects of axial ligands on the electronic absorption spectrum. In a previous paper [9] we reported that addition of both neutral and anionic ligands to Cd(TPP) caused red shifts in the absorption spectrum and that the magnitude of the red shift was dependent on the charge but not on the strength of the Cd–ligand bond. We have further investigated axial ligation of a variety of oxygen donors to Cd(TPP) in order to elucidate the coordinating mode of Cd(TPP) in detail.

Experimental

Materials

meso-Tetraphenylporphyrin (TPP) was synthesized by the procedure of Adler *et al.* [10] and was

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freed from the chlorine impurity by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone [11]. Cd(II) ion was inserted by the reported method [12]. Zn(TPP) and Mg(TPP) were prepared and purified by the previously described method [13]. Reagent grade dichloromethane (CH_2Cl_2) was distilled, and passed through a neutral alumina column to remove stabilizers. All oxygen ligands were of reagent grade and were purified by distillation or recrystallization by the usual methods. Perfluoro-1,1-dihydroethanol was used as received.

Procedure

Aliquots of the neat ligand or the solid material in concentrated solution were successively added to 2 ml of Cd(TPP) solution of known concentration in CH_2Cl_2 in a 1-cm capped quartz cell by means of a microsyringe. Absorbance changes were monitored thereafter.

Spectral and Dissociation Constant Measurements

UV–Vis absorption spectra were recorded using a Union Giken SM-401 spectrometer. The temperature of the solution was maintained at 25 °C by use of a thermostated circulator bath.

The dissociation constant (K_d) and binding stoichiometries were estimated by use of the method of Nardo and Dawson [5] with corrections for volume changes and are briefly summarized below.

The dissociation of a ligand, L, from a M(TPP)–ligand complex, M(TPP)L, is defined in eqn. (1) as follows

$$\mathrm{M(TPP)L} \overset{K_d}{\rightleftharpoons} \mathrm{M(TPP)} + \mathrm{L} \quad (1)$$

then

$$K_d = [\mathrm{M(TPP)}][\mathrm{L}]/[\mathrm{M(TPP)L}] \quad (2)$$

where [M(TPP)], [L] and [M(TPP)L] represent the concentrations of the free metalloporphyrin, free ligand and metal–ligand complex, respectively. To evaluate the fraction of the metalloporphyrin which is complexed to the ligand, the term Y (percent saturation) can be defined as follows

$$Y = [\mathrm{M(TPP)L}]/[\mathrm{M(TPP)L} + \mathrm{M(TPP)}] \quad (3)$$

Substituting eqn. (2) into eqn. (3) gives eqn. (4).

$$Y/(1 - Y) = [\mathrm{L}]/(K_d) \quad (4)$$

Y is redefined in terms of an absorbance change. From the conditions in which no ligand is complexed with the metal, A_0, and the ligand is fully complexed to the metal, A_∞, the following equations are estimated (A means absorbance at a chosen wavelength).

$$\Delta A = A_0 - A \quad (5)$$

$$\Delta A_\infty = A_0 - A_\infty \quad (6)$$

From eqns. (4), (5) and (6) we can define Y as follows:

$$Y = \Delta A/(\Delta A_\infty) \quad (7)$$

Substituting eqn. (7) into (3) and rearranging gives eqn. (8) which is represented by a double reciprocal relationship.

$$1/(\Delta A) = K_d/(\Delta A_\infty[\mathrm{L}]) + 1/(\Delta A_\infty) \quad (8)$$

A plot of $(1/\Delta A)$ *versus* $(1/[\mathrm{L}])$ should give a straight line with a slope of $(K_d/\Delta A_\infty)$ and a Y-intercept of $(1/\Delta A_\infty)$. In this mode, K_d and ΔA_∞ can easily be determined from existing data.

Alternatively, taking the logarithm of both sides of eqn. (4) gives the well known Hill equation.

$$\log Y - \log(1 - Y) = \log[\mathrm{L}] - \log K_d \quad (9)$$

Substituting eqn. (9) into eqn. (7) and rearranging gives eqn. (10).

$$\log[\Delta A/(\Delta A_\infty - \Delta A)] = \log[\mathrm{L}] - \log K_d \quad (10)$$

The binding stoichiometry is determined from eqn. (10) by plotting $\log[\Delta A/(\Delta A_\infty - \Delta A)]$ versus $\log[\mathrm{L}]$ and evaluating the slope. Based on the description of the metalloporphyrin–ligand equilibrium presented in eqn. (1), a slope of unity indicates the formation of a 1:1 complex.

Results and Discussion

Spectral Changes of Cd(TPP) on Axial Ligation of Oxygen Donor Ligands

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 and the other two bands, named alpha and beta bands, are observed between 550 and 650 nm (λ_{max} of alpha band > that of beta band) in the same solvents. The Soret band is mainly a result of the transitions $a_{1u}(\pi), a_{2u}(\pi) \rightarrow eg(\pi^*)$ [14].

The oxygen donor ligands were added to Cd(TPP) in CH_2Cl_2. In the almost all ligands the visible absorption spectra of Cd(TPP)L undergo a red shift relative to that of Cd(TPP) itself, accompanied by a decrease in intensity of the beta (550 nm) band and an increase in intensity of the alpha (600 nm) band. But, no spectral changes were observed by the following ligands: triphenyl carbinol, benzhydrol, phenol, *o*-cresol and perfluoro-1,1-dihydroethanol. Representative spectral changes are found in Fig. 1 where the stepwise addition of tetramethylene sulfoxide to a solution of Cd(TPP) in CH_2Cl_2 are displayed. Clear isosbestic points have been observed during the formation of all ligand complexes reported here. Visible absorption spectral data for Cd(TPP)L are listed in Table 1, along with the ratio of the molecu-

lar extinction coefficient of the alpha band (ϵ_α) to that of the beta band (ϵ_β)($\epsilon_\alpha/\epsilon_\beta$).

From Table 1, it is apparent that upon complexation the values of ϵ_{max} (ϵ_{Soret}, ϵ_α and ϵ_β) of these three absorptions are changed. A correlation between the ratio $\epsilon_\alpha/\epsilon_\beta$ and the wavenumber of the Soret band was observed (Fig. 2). Similar correlations have been observed previously for a series of metalloporphyrins [14]. In these cases, $\epsilon_\alpha/\epsilon_\beta$ increases with increase of the wavenumber of all absorption bands in Zn(TPP) complexes. Valentine *et al.* [8] suggested that complexation of a metal with donor groups increases the charge transfer onto the porphyrin ring. Therefore, we think that the red shift and the charges of $\epsilon_\alpha/\epsilon_\beta$ reflect the magnitude of charge transfer to the porphyrin ring via the cadmium atom.

Ligand Binding between Cd(TPP) and Oxygen Donor Ligands

When the reciprocal of the absorbance change, $1/[\Delta A]$, was plotted against the reciprocal of the concentration of added ligands, $1/[L]$, a linear relationship was observed. In Fig. 3, a typical plot for the axial ligation of tetramethylene sulfoxide to Cd(TPP) is shown. From the slope of this straight line, the K_d

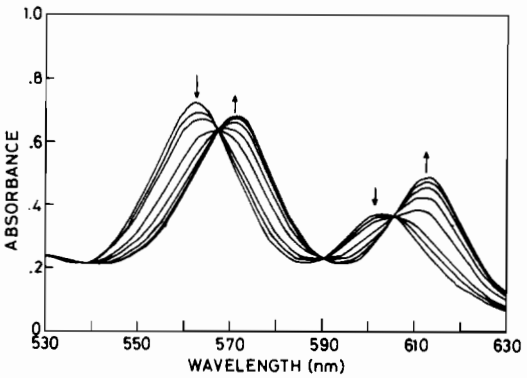

Fig. 1. Visible spectral changes resulting from stepwise addition of tetramethylene sulfoxide to Cd(TTP) in CH_2Cl_2. Starting concentration of Cd(TPP) was 5.14×10^{-5} M, and 1 μl of tetramethylene sulfoxide (neat) was successively added to 2 ml of Cd(TPP) solution.

TABLE 1. Electronic absorption spectra of Cd(TPP) complexes with oxygen donors in CH_2Cl_2

No.	Donor	nm (log ϵ)			
		Soret	β	α	$\epsilon_\alpha/\epsilon_\beta$
	None	429.0(5.33)	562.5(4.30)	603.0(3.93)	0.914
1	Methanol	432.5(5.30)	569.0(3.94)	610.5(3.81)	0.967
2	Ethanol	433.0(5.25)	569.5(3.90)	611.0(3.71)	0.951
3	n-Butanol	430.0(5.27)	569.0(3.88)	611.0(3.66)	0.943
4	n-Pentanol	433.0(5.44)	570.0(4.04)	611.5(3.86)	0.955
5	Perfluoro-1,1-dihydroethanol	–[a]	–	–	–
6	sec-Butanol	432.5(5.38)	569.5(4.00)	611.0(3.79)	0.948
7	tert-Butanol	432.5(5.24)	569.0(3.85)	610.0(3.62)	0.940
8	iso-Butanol	432.0(5.37)	569.5(3.99)	610.5(3.80)	0.952
9	Cyclohexanol	431.0(5.44)	570.0(4.00)	611.5(3.81)	0.960
10	Benzylalcohol	433.0(5.44)	569.0(4.06)	610.5(3.89)	0.958
11	Benzhydrol	–	–	–	–
12	Triphenylcarbinol	–	–	–	–
13	Phenol	–	–	–	–
14	*o*-Cresol	–	–	–	–
15	*m*-Cresol	430.0(5.41)	568.0(4.21)	609.5(4.00)	0.950
16	*p*-Cresol	432.0(5.39)	567.5(4.15)	608.5(3.95)	0.952
17	Diethyl ether	429.0(5.39)	567.5(4.17)	610.0(3.97)	0.952
18	Anisole	431.0(5.32)	565.5(4.03)	606.5(3.76)	0.933
19	Tetrahydrofuran	429.0(5.40)	569.5(4.19)	611.0(4.02)	0.959
20	Ethyl acetate	432.0(5.41)	568.0(4.05)	609.0(3.84)	0.948
21	n-Butyl acetate	432.0(5.37)	567.5(3.98)	609.0(3.76)	0.945
22	4-Butyrolactone	432.0(5.39)	569.0(4.01)	610.5(3.83)	0.955
23	Dimethyl sulfoxide	432.0(5.46)	571.5(4.05)	613.0(3.90)	0.963
24	Tetramethylene sulfoxide	434.0(5.45)	571.5(4.03)	613.0(3.89)	0.965
25	Methyl ethyl ketone	431.0(5.35)	568.0(3.97)	609.5(3.76)	0.947
26	Cyclohexanone	431.0(5.35)	568.5(3.97)	610.0(3.76)	0.947
27	Benzaldehyde	437.0(5.49)	579.0(4.05)	620.5(4.03)	0.995
28	Acetone	432.0(5.45)	568.5(4.05)	610.0(3.85)	0.951
29	Dimethylformamide	432.0(5.45)	571.0(4.04)	613.0(3.89)	0.963

[a]Complex formation was not observed.

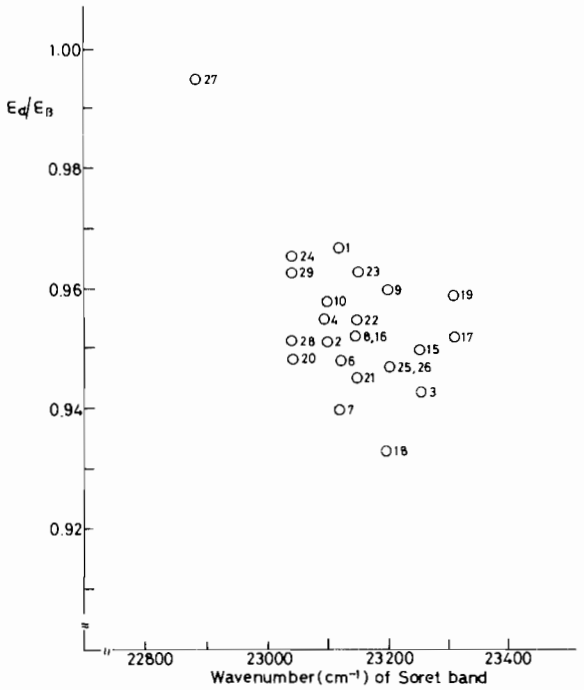

Fig. 2. Plots of $\epsilon_\alpha/\epsilon_\beta$ vs. the wavenumber of the Soret band for Cd(TPP)L complexes. Number represents the same compound as shown in Tables 1 and 2.

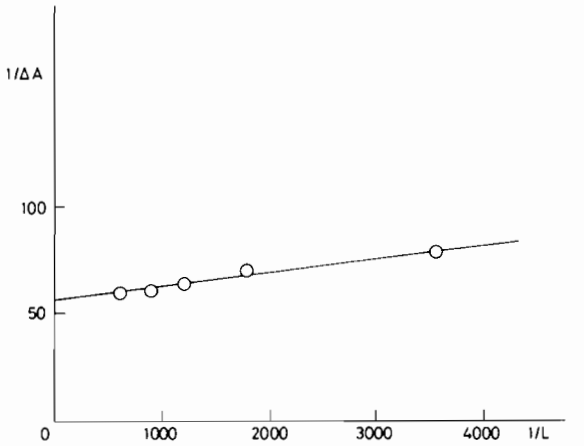

Fig. 3. Plots of $1/[\Delta A]$ vs. $1/[L]$ for the titration of tetramethylene sulfoxide to Cd(TPP).

value was obtained using eqn. (8). Also, the plot of log $\Delta A/(\Delta A_\infty - \Delta A)$ versus log[L] for the axial ligation to Cd(TPP) showed the linear line as shown in Fig. 4. For the slope of this line, the Y value could be obtained by use of eqns. (9) and (10). The K_d values and Y values thus obtained are summarized in Table 2. The fact that the Y value of all the ligands which showed the spectral changes is approximately unity suggest that a 1:1 complex can be formed by the axial ligation of oxygen donor ligands to Cd(TPP). These data show that Cd(TPP) is able to

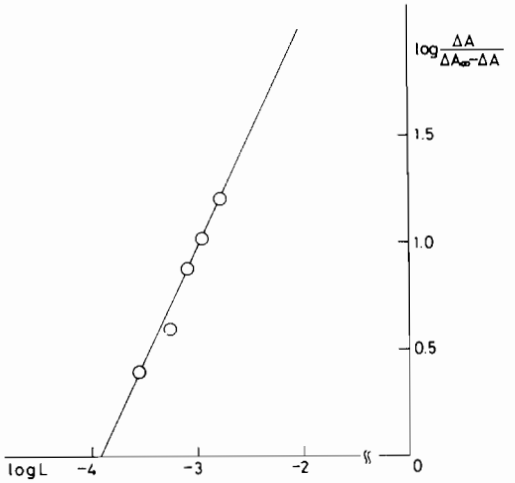

Fig. 4. Plots of log $\Delta A/(\Delta A_\infty - \Delta A)$ vs. log[L] for the titration of tetramethylene sulfoxide to Cd(TPP).

TABLE 2. Dissociation constants for Cd(TPP) complexes with oxygen donors

No.	Donor	pK_a [a]	K_d (M)	Slope (Y)
1	Methanol	15.5	1.73×10^{-1}	0.92
2	Ethanol	15.9	4.37×10^{-2}	1.07
3	n-Butanol	16.1	3.33×10^{-2}	1.04
4	n-Pentanol	16.2	1.87×10^{-2}	0.97
5	Perfluoro-1,1-dihydroethanol	12.4	– [b]	–
6	sec-Butanol	16.1	2.10×10^{-2}	1.05
7	tert-Butanol	18.0	8.40×10^{-3}	0.98
8	iso-Butanol	16.2	3.86×10^{-2}	0.95
9	Cyclohexanol	16.0	8.30×10^{-3}	0.97
10	Benzyl alcohol	14.8	3.17×10^{-2}	1.00
11	Benzhydrol	13.8	–	–
12	Triphenylcarbinol	12.0	–	–
13	Phenol	9.95	–	–
14	*o*-Cresol	10.28	–	–
15	*m*-Cresol	10.08	1.73×10^{-1}	1.00
16	*p*-Cresol	10.19	4.29×10^{-1}	1.01
17	Diethyl ether		4.34×10^{-2}	1.02
18	Anisole		9.14×10^{-1}	0.98
19	Tetrahydrofuran		1.03×10^{-2}	0.99
20	Ethyl acetate		2.34×10^{-1}	0.98
21	n-Butyl acetate		6.66×10^{-2}	1.02
22	4-Butyrolactone		5.07×10^{-2}	0.99
23	Dimethyl sulfoxide		2.40×10^{-4}	0.97
24	Tetramethylene sulfoxide		6.00×10^{-4}	1.05
25	Methyl ethyl ketone		1.43×10^{-2}	1.01
26	Cyclohexanone		4.39×10^{-2}	1.05
27	Benzaldehyde		5.19×10^{-2}	0.97
28	Acetone		6.82×10^{-2}	1.03
29	Dimethylformamide		2.30×10^{-3}	1.02

[a]Ref. 5. [b]Complex formation was not observed.

form ligand complexes with an extensive variety of oxygen donor ligands.

Firstly, we consider the axial ligation of alcoholic oxygen donor ligands in Table 2. It is apparent from Table 2 that K_d values decreased with increase of pK_a in structurally similar ligands. For example, in the normal alcohol from methanol to n-pentanol, the basicity (pK_a) of the alcohol and the binding affinity both increase, as the chain length increases. A similar correlation between the pK_a of a ligand and its affinity for a metalloporphyrin has been observed for some Mg(TPP) complexes with substituted pyridines and imidazoles [15] or some Zn(TPP) complexes with the same group of nitrogen donors [16]. That is, increasing basicity (increasing pK_a) leads to increased affinity (decreasing K_d). However, since steric factors may contribute to the K_d value, only a few comparisons are possible where steric factors are minimized to the point that electronic influences can be accurately revealed. Thus, the structurally similar ethanol (CH_3CH_2OH) and perfluoro-1,1-dihydroethanol (CF_3CH_2OH) can be compared, because C–F bond lengths and the atomic radius of fluorine are sufficiently similar to C–H bond lengths and the atomic radius of hydrogen to rule out steric factors as major influences on the K_d value. As seen in Table 2, normal alcohol is substantially more basic than fluoroalcohol and normal alcohol is a much better ligand than the fluoroalcohol, from the fact that K_d values of normal alcohol are low, whereas no evidence for binding of fluoroalcohol to Cd(TPP) was found. A similar pK_a effect was observed by the axial ligation of cyclohexanol and phenol to Cd(TPP). From Table 2, it is apparent that cyclohexanol is a much better ligand than phenol.

For the series of benzyl alcohols, both steric and electronic factors predict the same trend in binding affinity. The order of basicity is triphenylcarbinol, benzhydrol and benzyl alcohol. However, benzhydrol which has a moderately high pK_a value did not show any binding to Cd(TPP), as well as triphenylcarbinol. Then, these results indicate that both electronic and steric factors are effectively working. Thus, steric factors are not excluded in the binding of aromatic alcohol, but electronic factors are rather effective for the binding of normal alcohol. For example, despite the fact that tert-butanol is considered to show a larger steric hinderance than n-butanol and sec-butanol, the K_d value of tert-butanol is lowest, compared to that of n-butanol, sec-butanol or other normal alcohols. This result indicates that with tert-butanol the electronic effect may overcome the steric effect, because of tert-butanol having a higher pK_a value than other alcohols.

For the series of phenols, both steric and electronic factors predict the same trend in the binding affinity. The phenol has a lower pK_a value than the cresols and as such would be expected to show decreased binding affinity. In fact, no evidence for binding the phenol to Cd(TPP) was observed. On the other hand, in the cresols which have almost the same pK_a values, only *o*-cresol did not bind to Cd(TPP). This is presumably due to steric interference from the *ortho* methyl group.

Steric inferences can also be seen among other functional groups in Table 2. For example, the cyclic ether, tetrahydrofuran, has a higher affinity than the acyclic ether, diethyl ether. With the ketone, cyclohexanone, the cyclic ketone, has a higher affinity than the acyclic ketone, methyl ethyl ketone. Likewise, with esters, the cyclic ester, 4-butyrolactone, has the highest affinity. In all of these cases, the higher affinity is found with the cyclic molecules possibly as a result of less steric hinderance. However, the two sulfoxides examined showed the opposite trend. That is, the acyclic sulfoxide, dimethyl sulfoxide, has a higher affinity than the cyclic sulfoxide, tetramethylene sulfoxide. But, both sulfoxides have the highest affinity among the ligands presented in Table 2. These results suggest that with sulfoxides the binding affinity may not be affected by steric hinderance.

Dimethylformamide (DMF) also shows a higher affinity for Cd(TPP). A possible explanation for the high affinity comes from the fact that a resonance form of DMF exists with a partial negative charge on oxygen, as shown in Fig. 5. Anionic oxygen ligands have a high affinity for Cd(TPP) as has been demonstrated previously [8, 13]. The high affinity of the sulfoxides may result from a similar, charge separated, resonance structure with an anionic oxygen.

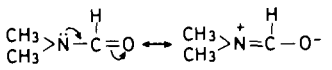

Fig. 5. A resonance form of DMF.

Comparison of Axial Ligations of Cd(TPP) with those of Zn(TPP) and Mg(TPP)

Axial ligations of some oxygen donor ligands to Zn(TPP) and Mg(TPP) which belong to the same group II as cadmium in the periodic table were carried out in order to compare with the ligand binding of Cd(TPP). As a result, Mg(TPP) did not bind the oxygen donor ligands such as tert-butanol, anisole, ethyl acetate, tetramethylene sulfoxide, acetone and *N,N*-dimethylformamide. On the other hand, Zn(TPP) could bind almost all the oxygen donor ligands. In Table 3, representative K_d values of Zn(TPP) are summarized along with those of Cd(TPP). It is apparent from Table 3 that Cd(TPP) has a higher affinity to oxygen donor ligands than Zn(TPP). According to the principles of hard and soft acids and bases (HSAB) [17], Mg^{2+} ion is a hard acid and Cd^{2+} is a soft acid. Further, Zn^{2+} ion is

TABLE 3. Dissociation constants for Cd(TPP) and Zn(TPP) complexes with oxygen donors

Donor	K_d (M)	
	Cd(TPP)	Zn(TPP)
tert-Butanol	8.40×10^{-3}	1.11×10^{-2}
Anisole	9.14×10^{-1}	–[a]
Ethyl acetate	2.34×10^{-1}	1.32
Tetramethylene sulfoxide	6.00×10^{-4}	1.68×10^{-3}
Acetone	6.82×10^{-2}	1.03
Dimethylformamide	2.30×10^{-3}	1.02×10^{-2}

[a]Complex formation was not observed.

intermediate between the soft and hard acid. On the other hand, the oxygen donor ligands are hard bases, and the sulfur donor ligands are soft bases. Thus, Mg(TPP) should have the highest affinity to the oxygen donor ligands and Cd(TPP) should be hard to bind with the oxygen donor ligands. However, our results are opposite. Thus, it is suggested that axial ligation of metalloporphyrins to oxygen donor ligands is not simply explained by HSAB theory. There may be another mechanism.

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