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The Influence of Axial Ligands on Metalloporphyrin Visible Absorption Spectra. Complexes of Tetraphenylporphinatozinc

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Abstract: Electronic absorption spectra for a number of Zn(TPP)L and Zn(TPP)X$^-$ (TPP = tetraphenylporphinato) complexes in benzene or toluene are reported as well as spectra of ZnTPP in several noncoordinating solvents. Two principal effects are seen upon addition of axial ligands to ZnTPP: a red shift of the entire spectrum relative to that of ZnTPP and an increase in $\epsilon_\alpha/\epsilon_\beta$ that is correlated with the magnitude of the red shift. The magnitude of the red shift is shown to depend on the charge and polarizability of the axial ligand and not on the strength of the Zn–ligand bond. Equilibrium constants for complexation of the halides to ZnTPP increase in the order I < Br < Cl < F but the opposite order of red shifts is observed. IR spectra of Zn(TPP)(NCS)$^-$ show it to be N bound. Complexes of ZnTPP with crown ethers and imidazolate are observed. The spectra of the superoxide and imidazolate complexes are similar and fall between those of the hydroxide and cyanide complexes. The spectrum of the *n*-butylthiolate complex resembles that of carboxycytochrome P-450 in that the Soret band is abnormally red shifted and a new "hyper" band appears on the short-wavelength side of the Soret band.

The dependence of the electronic spectra of metalloporphyrins on the nature of their axial ligands makes heme a natural reporter of its immediate environment in hemoproteins. Thus considerable effort has been expended in cataloguing and interpreting the spectra of iron and other metalloporphyrins and the effects of varying axial ligation.[1-3] A particularly interesting example is the observation of the unusually long wavelength Soret band of the carbonyl complex of cytochrome P-450,[4,5] the successful synthesis of carboxy ferrous porphyrin thiolate complexes that reproduce the essential features of its spectrum,[6-9] and the theoretical analysis of this spectrum as an example of a "hyper" spectrum.[10]

Understanding the effects of axial ligands on the electronic spectra of iron porphyrins as opposed to other metalloporphyrins is the ultimate goal in this field because of its biological relevance. Unfortunately such interpretation has not been straightforward because of complications introduced by partially filled d orbitals and ambiguities in coordination numbers, spin states, and oxidation states. In the course of our recent studies of complexes of zinc porphyrins, we observed substantial spectral shifts of the electronic absorption spectrum as a function of the nature of axial ligands. Although such effects have been observed previously for a limited range of ligands,[11-17] we have extended the range of ligands and studied

these spectra in some depth for three reasons. First, zinc porphyrin complexes provide a simpler system than those of iron in which to study a wide range of different ligands. This is because the metal is unambiguously in the 2+ oxidation state; the four-coordinate zinc porphyrin will accept one and only one axial ligand to form five-coordinate complexes;[12,13,18] and, since the electronic configuration is d^{10}, there are no empty d orbitals involved in the bonding. Secondly, we have made a number of complexes of zinc porphyrins with the relatively uncommon ligands superoxide,[19] imidazolate, crown ethers, and *n*-butylthiolate. Interpretation of the visible absorption spectra of these complexes allows us to compare some of the properties of these ligands with those of several more thoroughly studied ligands. Finally, examination of the visible spectra of other metalloporphyrins with different axial ligands has shown that the effects we see in the relatively straightforward zinc system can be seen in more complicated systems as well.

Experimental Section

Materials. Tetraphenylporphinatozinc (ZnTPP) was synthesized and purified from the chlorin impurity by literature methods.[20] It was recrystallized from toluene and dried in vacuo at 100 °C for 2 days. (Mesoporphinato IX dimethyl ester)zinc (Zn(MesoIXDME)) was

Table I. Electronic Absorption Spectra of ZnTPP in Neat Solvents

solvent[a]	Soret[b]	ϵ_{rel}	β[b]	ϵ_{rel}	α[b]	ϵ_{rel}
1. cyclohexane	24 000	221	18 340	10.0	17 120	0.935
2. CHCl$_3$	23 890	258	18 320	10.0	17 140	1.39
3. CH$_2$Cl$_2$	23 880	217	18 260	10.0	17 080	2.27
4. benzene	23 670	223	18 200	10.0	17 000	1.68
5. toluene	23 650	208	18 200	10.0	16 980	1.69
6. C$_6$H$_5$Br	23 600	222	18 200	10.0	17 020	1.69
7. CS$_2$	23 260	163	18 130	10.0	16 940	1.59
8. MeOH	23 800	269	18 000	10.0	16 800	3.53
9. CH$_3$CN	23 700	253	17 940	10.0	16 720	4.39
10. Et$_2$O	23 790	241	18 060	10.0	16 850	2.71
11. DME	23 770	240	18 070	10.0	16 880	2.98
12. THF	23 720	192	17 990	10.0	16 800	3.14
13. Bu$_2$NH	23 350	252	17 770	10.0	16 600	4.72
14. DMF	23 530	263	17 900	10.0	16 700	4.39
15. HMPA	23 360	281	17 760	10.0	16 590	5.18
16. Me$_2$SO	23 390	234	17 830	10.0	16 660	4.72
17. py	23 250	220	17 730	10.0	16 660	5.10

[a] Abbreviations used in this table: DME, dimethoxyethane; THF, tetrahydrofuran; DMF, dimethylformamide; HMPA, hexamethylphosphoramide; py, pyridine. [b] cm^{-1}.
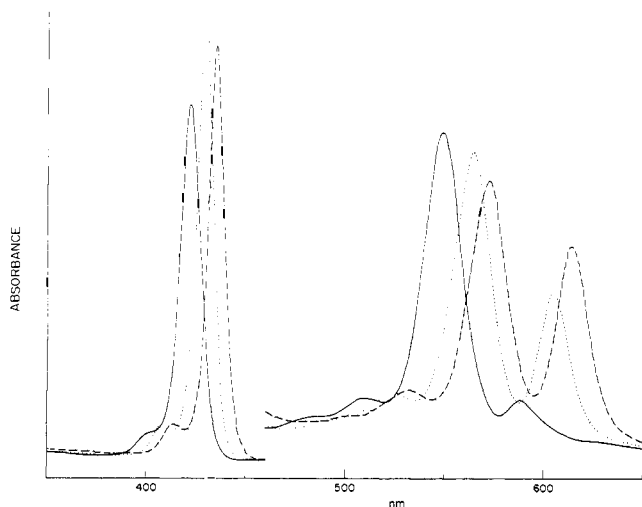

Figure 1. Visible absorption spectra in toluene of (a) ZnTPP (—); (b) Zn(TPP)ImH (···); (c) Zn(TPP)Im$^-$ (- - -).

used as purchased from Porphyrin Products. Tetrabutylammonium chloride, bromide, iodide, and tetrafluoroborate, tetraethylammonium fluoride (all Eastman), and tetraphenylarsonium chloride (Fluka) and bromide (Eastern Chemicals) were dried in vacuo over P$_2$O$_5$ overnight and stored in an inert atmosphere box. Tetramethylammonium hydroxide was purchased from Baker. Dicyclohexyl-18-crown-6 (DC18C6) was purchased from PCR; 18-crown-6 (18C6) was synthesized by literature methods[21] and further purified by precipitation from dimethoxyethane by addition of a double volume of hexane followed by cooling in dry ice–acetone with vigorous stirring, all under argon (mp 39.5–40.0 °C, lit. 38.0–38.5 °C). Chloroform was passed through an alumina column to remove ethanol. Other solvents were spectrograde and/or were distilled immediately prior to use. Benzene and toluene were distilled from sodium.

Preparations. Potassium imidazolate was prepared by the reaction of potassium with imidazole in refluxing dry benzene.[22] The white powder was filtered under argon and washed with hot benzene to remove excess imidazole.

Potassium butylthiolate was prepared by dropwise addition of a benzene solution of the distilled thiol (25% excess) to a solution of KH in benzene followed by stirring for 6 h. The white solid product was filtered under argon, washed with two portions of dry benzene, and dried in vacuo overnight.

Spectra of Zn(TPP)L and Zn(TPP)X$^-$ Derivatives. Solutions of Zn(TPP)L and Zn(TPP)X$^-$ derivatives were prepared in benzene or toluene by addition of the minimum amount of ligand needed to

completely convert ZnTPP to the liganded derivative. In the case of some ligands for which binding constants are small, such as Me$_2$S, large amounts were added in order to cause complete conversion. For all of the anion complexes except the halides, anions were introduced by addition of the DC18C6 solubilized potassium salts. For the halide complexes, tetraalkylammonium salts were used because DC18C6 interfered with the binding of the halides. The unsubstituted crown ether 18C6 could not be used at all because it interfered with the binding of all but a few anions.

The thiolate complexes were prepared by addition of solutions of DC18C6 solubilized KSBu or by titrating the thiol complexes with 2 M Me$_4$NOH in ethanol. Complete conversion to the zinc porphyrin thiolate complex was observed by the former but not the latter method, similar to results observed with Fe(II) porphyrins.[8]

Spectral and Equilibrium Constant Measurements. Vis–UV absorption spectra were obtained at 25.0 ± 0.1 °C using a Cary 118C spectrophotometer, 1.0-cm quartz cells, and a porphyrin concentration of approximately 4×10^{-6} M. The equilibrium constants were determined using Ph$_4$AsBr, Ph$_4$AsCl, and Et$_4$NF in CH$_2$Cl$_2$ rather than toluene because of greater solubility of the anion salts. The method of Miller and Dorough[12] was used with corrections made for volume changes and with the ionic strength adjusted using Bu$_4$NBF$_4$. The K_{eq} for Zn(TPP)Br$^-$ is approximate; because it is low, large amounts of Br$^-$ had to be added and the ionic strength could not be held constant.

Infrared spectra were obtained on a Perkin-Elmer 225 grating spectrophotometer. The 0.1-mm sample cell held 3×10^{-2} M ZnTPP and 0.5 M KSCN in acetone while the variable path length reference cell held the same concentration of KSCN and was adjusted to blank out the uncomplexed ligand.

Results

The visible absorption spectrum of ZnTPP is strongly solvent dependent. Table I lists spectroscopic data for ZnTPP in a variety of neat solvents. An additional visible spectrum was obtained of 8.8×10^{-3} M ZnTPP in toluene freshly distilled from sodium with all transfers carried out in an inert atmosphere box in order to assess the possibility of ZnTPP scavenging water from noncoordinating solvents. The resulting spectrum was identical with that obtained in more dilute solutions (see Table II).

Addition of ligands to ZnTPP was carried out in benzene and toluene. Complexes of ZnTPP with neutral or anionic ligands give visible absorption spectra that are red shifted relative to those of ZnTPP itself. Visible absorption spectra of the Zn(TPP)L and Zn(TPP)X$^-$ complexes formed are tabulated in Table II. Representative spectra are given in Figure 1.

Equilibrium constants were determined in CH$_2$Cl$_2$. The low solubility of the salts of the anionic ligands in benzene or tol-

Table II. Electronic Absorption Spectra of ZnTPP Derivatives

complex[a]	solvent[a]	Soret	ϵ_{rel}	β	ϵ_{rel}	α	ϵ_{rel}
Zn(TPP)(DC18C6)*[b]	b	23 580		18 160		16 860	
18. Zn(TPP)THF	t	23 560	272	18 000	10.0	16 800	2.83
19. Zn(TPP)DMF	t	23 460	280	17 910	10.0	16 710	3.46
20. Zn(TPP)Me₂SO	t	23 420	278	17 900	10.0	16 700	3.60
21. Zn(TPP)BuSH	b	23 420	241	17 960	10.0	16 690	3.30
22. Zn(TPP)(CH₃CN)	t	23 410	295	17 860	10.0	16 630	4.00
23. Zn(TPP)(2-Mepy)	t	23 380	141	17 840	10.0	16 640	3.88
24. Zn(TPP)(18C6)	b	23 350	273	17 870	10.0	16 670	4.15
25. Zn(TPP)py	t	23 350	298	17 790	10.0	16 610	4.33
26. Zn(TPP)Me₂S	t	23 320	256	17 800	10.0	16 600	4.78
27. Zn(TPP)(Bu₂NH)	t	23 290	294	17 770	10.0	16 600	4.95
28. Zn(TPP)(2-MeImH)	t	23 250	198	17 710	10.0	16 530	4.87
29. Zn(TPP)ImH	b	23 200	242	17 660	10.0	16 490	5.43
30. Zn(TPP)(N-MeIm)	b	23 190	232	17 660	10.0	16 480	5.81
31. Zn(TPP)PPh₃	b	23 180	198	17 770	10.0	16 530	4.37
32. Zn(TPP)F⁻	b	23 170	195	17 610	10.0	16 440	5.85
Zn(TPP)NCS⁻ *	b	23 120		17 660		16 460	
33. Zn(TPP)NCO⁻	b	23 020	289	17 540	10.0	16 320	6.17
34. Zn(TPP)OMe⁻	b	22 980	264	17 500	10.0	16 320	6.80
35. Zn(TPP)OH⁻	b	22 980	263	17 480	10.0	16 310	7.41
36. Zn(TPP)OtBu⁻	b	22 970	286	17 490	10.0	16 320	7.52
Zn(TPP)Cl⁻ *	b	22 910		17 470		16 290	
37. Zn(TPP)O₂⁻	b	22 900	258	17 420	10.0	16 240	7.09
38. Zn(TPP)Im⁻	b	22 890	224	17 390	10.0	16 220	7.46
Zn(TPP)Br⁻ *	b	22 810		17 450		16 260	
39. Zn(TPP)CN⁻	b	22 800	313	17 340	10.0	16 170	8.40
40. Zn(TPP)SBu⁻ c,d	b	22 260	257	17 040	10.0	15 810	11.3
Zn(Meso-IX-DME)	t	24 780	200	18 800	10.0	17 580	16.4
Zn(Meso-IX-DME)SBu⁻ e	t	22 820	103	17 800	10.0	16 790	2.36
Zn(TPP)Cl⁻	CH₂Cl₂	23 110	240	17 570	10.0	16 400	5.59
Zn(TPP)Br⁻	CH₂Cl₂	23 030	295	17 560	10.0	16 370	6.21
Zn(TPP)NCS⁻	acetone	23 390	119	17 680	10.0	16 500	5.95

[a] Abbreviations used in this table: DC18C6, dicyclohexyl-18-crown-6; THF, tetrahydrofuran; DMF, dimethylformamide; 2-Mepy, 2-methylpyridine; 18C6, 18-crown-6; py, pyridine; ImH, imidazole; N-MeIm, N-methylimidazole; Im⁻, imidazolate; 2-MeImH, 2-methylimidazole; b, benzene; t, toluene. [b] Asterisk indicates that complex was not fully formed. [c] Potassium salt. [d] Additional band at 26 480 cm⁻¹, ϵ_{rel} 28.6. [e] Additional band at 28 260 cm⁻¹, ϵ_{rel} 33.7.

Table III. Equilibrium Constants[a]

ligand	solvent	K_{eq}, M⁻¹	μ (ionic strength), M (Bu₄NBF₄)
F⁻	CH₂Cl₂	>10 000[b]	0.0124
Cl⁻	CH₂Cl₂	290 ± 30	0.0124
Br⁻	CH₂Cl₂	17 ± 2	0.0124-0.0238[c]
I⁻	CH₂Cl₂	d	
pyridine	CH₂Cl₂	6900 ± 350	0
pyridine	CH₂Cl₂	4740 ± 370	0.0124
pyridine[e]	cyclohexane	25 100	0
pyridine[f]	benzene	5300	0
pyridine[g]	benzene	6030	0

[a] Temperature 298 K. [b] Low solubility precluded a more accurate measurement. [c] Ionic strength was not held constant; see Experimental Section. [d] No evidence for complex formation. [e] Data from ref 17. [f] Data from ref 16. [g] Data from ref 13.

uene precluded their use as solvents for these determinations. The results are tabulated in Table III.

The infrared spectrum of Zn(TPP)(NCS)⁻ in acetone showed a strong peak at 2095 cm⁻¹. Free SCN⁻ showed a peak at 2064 cm⁻¹ in the same solvent.

Discussion

Normal metalloporphyrin electronic absorption spectra show three prominent bands in the visible region.[1,2] The most intense is the B or Soret band, which usually occurs near 420 nm for benzene solutions of metallo-TPP derivatives. The other two intense bands are the Q or α and β bands which are usually found between 500 and 600 nm in the same solvent.

According to Gouterman's four-orbital model,[23] the transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ are largely responsible for the Soret and α, β bands. The spectrum of four-coordinate ZnTPP in a noncoordinating solvent such as benzene (see Figure 1a) is a representative example of a normal metalloporphyrin spectrum. Three effects are seen upon addition of axial ligands: (1) a red shift of the entire spectrum, (2) a change in the relative intensities of the α and β bands, and (3) in the case where the axial ligand is a thiolate, the appearance of a new band on the high-energy side of the Soret (see Figure 2).

Red Shift and Change in α, β Intensity Ratio. The red shift of the visible absorption spectrum upon complexation of anionic[11] or neutral[12-17] ligands to ZnTPP has been reported by several investigators. In the case of a limited number of N and O donor ligands, it has been reported that the red shift of the Soret band of ZnTPP upon complexation is correlated with the pK_a of the ligand or with $-\Delta H$ calculated from E and C parameters for the reaction ZnTPP + L $\rightleftarrows$ Zn(TPP)L.[14,17] The latter correlation was reported not to hold for S donor ligands.[17]

The correlation of red shift with ligand pK_a or with $-\Delta H$ for complexation reported in ref 14 and 17 might be interpreted to imply that the red shift is correlated with the strength of the zinc–ligand bond. The data presented in the present work, however, contradict such an interpretation. Numerous studies have demonstrated that ZnTPP is a class a (or high E/C ratio) acid.[15,17] In other words, it is clear that there is a large electrostatic contribution to the binding of ligands to ZnTPP.
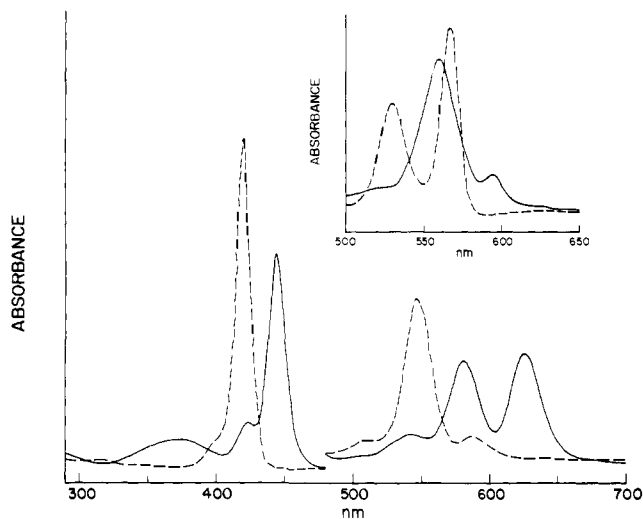
Figure 2. Visible absorption spectra in toluene of zinc porphyrin *n*-butyl-thiolate complexes. Main spectrum: (a) ZnTPP (- - -); (b) Zn(TPP)SR⁻ (—) (peak at 423 nm is unreacted ZnTPP). Inset: (a) Zn(Meso-IX-DME) (- - -); (b) Zn(Meso-IX-DME)SR⁻ (—).

Figure 3. Plot of $\epsilon_\alpha/\epsilon_\beta$ vs. the α band frequency (ν_α) for Zn(TPP)L and Zn(TPP)X⁻ derivatives. Numbers refer to complexes in Table II.

Vogel and Searby[15] have shown furthermore that the enthalpies of adduct formation for different donor atom types increase, i.e., become less negative, in the order N < P < O < S. As can be seen from Table II, in which ligands are listed in order of increasing red shift of the Soret band, the magnitude of the red shift does not follow the order N > P > O > S expected if the red shift is correlated with bond strength.

The lack of correlation of the red shift with $-\Delta H$ is seen most dramatically in the ordering of the anions. We have determined equilibrium constants for anion binding for the halides (Table III). These clearly fall in the order F > Cl > Br > I. If we assume that ΔS does not vary greatly in this series, as is the case for the neutral ligands,[17] the ordering of K_{eq} is also the ordering of bond strengths for Zn(TPP)X⁻. This is completely in accord with the class a character of ZnTPP. Note, however, that the red shift of the visible absorption bands is in exactly the opposite order, Br > Cl > F. We conclude, therefore, that the red shift is not in general correlated with $-\Delta H$. The equilibrium constant for binding of pyridine in a number of solvents is included in Table III for comparison but conclusions concerning bond strengths cannot be made without knowledge of ΔS for the reaction with anionic vs. neutral ligands.

In looking elsewhere for the origin of the red shifts, we note that a similar red shift as well as a changing ratio of the α and β band intensities is observed for Sn^{IV}(Etio)X$_2$ (X = F, Cl, Br, I).[24] The order of increasing red shift is F < Cl < Br < I for all three major bands and the intensity ratio $\epsilon_\alpha/\epsilon_\beta$ decreases in that order (F, 1.1; Cl, 0.94; Br, 0.94; I, 0.57). As can be seen in Table II and Figure 3, we see the same order of red shifts for the halides and an inverse correlation with $\epsilon_\alpha/\epsilon_\beta$, i.e., in the case of ZnTPP, $\epsilon_\alpha/\epsilon_\beta$ increases with red shift. Correlation of the magnitude of red shifts with $\epsilon_\alpha/\epsilon_\beta$ has been observed previously for series of metalloporphyrins where the metal is changed.[1,23] In those cases also, $\epsilon_\alpha/\epsilon_\beta$ *decreases* with red shift for etioporphinato, octaethylporphinato, mesoporphinato IX, and protoporphinato IX complexes but *increases* for TPP complexes.

In analyzing the Sn(Etio)X$_2$ spectra, Gouterman et al.[24] carried out extended Hückel calculations in order to estimate the electron densities on the metal, halide, and porphyrin ring in the series Sn(porph)X$_2$, X = F, Cl, Br, I. Their results show the charge on the metal remaining relatively constant while increasing amounts of negative charge are transferred to the
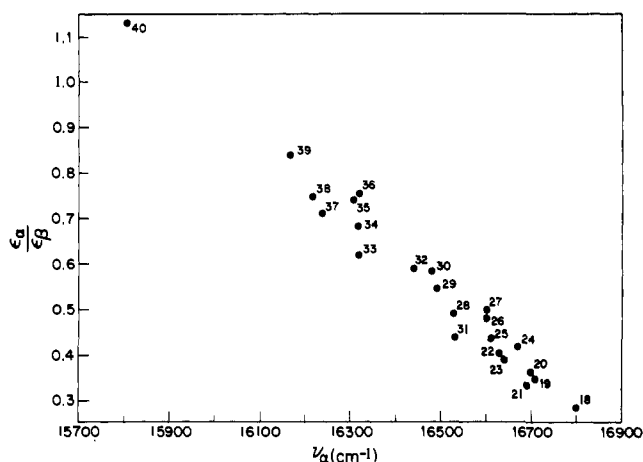
porphyrin ring in the order F < Cl < Br < I. They conclude that the effect on the spectrum of changing axial halides is similar to that observed upon changing metals in a series of closed-shell metalloporphyrins. In such series it is observed that red shifts and α,β intensity ratio changes are correlated with the electronegativity of the metal; for TPP derivatives, the spectrum red shifts and $\epsilon_\alpha/\epsilon_\beta$ increases with decreasing electronegativity. Thus, it is suggested, decreasing electronegativity of the metal results in a shift of electron density from the metal toward the porphyrin ring. Complexation of ligands that donate charge to the metal is believed to have the same effect, i.e., increased transfer of charge out onto the ring.

The results shown in Table II clearly implicate charge as a factor in the red shift as all of the anion complexes are more red shifted than the neutral ligand complexes. We believe therefore that the red shift and α,β intensity ratio changes derive from the amount of negative charge transferred from the ligand to the porphyrin ring via the zinc atom. Thus ZnTPP preferentially binds "hard" ligands with donor atoms that have relatively high electronegativities and low polarizabilities such as N or O donor ligands while the ligands with less electronegative, more polarizable donor atoms such as S, P, or unsaturated N cause a larger red shift because they allow more negative charge to be transferred to the porphyrin ring.

Thiocyanate is a particularly good example of the two separate effects. Because ZnTPP is a class a acid, we predicted that thiocyanate would bind preferentially through the N atom. We confirmed this prediction by the observation that the C–N stretch of Zn(TPP)(NCS)⁻ occurs at 2095 cm⁻¹, which is typical for N but not S bound thiocyanate ligands.[25] The red shift caused by thiocyanate binding is less than that of any other anion except fluoride. If it were S bound, we would predict a much greater red shift, based on comparisons with other ligands. The preference of ZnTPP for the atom that causes a smaller red shift illustrates the lack of correlation of $-\Delta H$ of binding with the red shift.

One other possible explanation for the red shift and change in α,β intensity ratio is that different ligands draw the zinc ion out of the porphyrin plane by differing amounts. It is known that the zinc atom in Zn(TPP)L complexes is out of the plane in those complexes for which structures are known.[18] We cannot exclude this possibility as a source of the effects we observe. We consider, however, that such an effect is unlikely to be the major source of the spectral changes because the shifts we see are comparable in magnitude to those observed by Gouterman et al. for the Sn(porph)X$_2$ systems in which the tin atom is in the plane of the porphyrin ring.[26]

A similar effect of changing axial anions has also been observed in a Mn(III) system.[27] Changing the axial ligand X^- in $Mn(Etio)XH_2O$ produces red shifts of all the bands in the order $X = F < OAc < NCO < NO_2 < OH \sim Cl < N_3 \sim NCS \sim Br < I$. Because of the possibility of changing coordination number, it was not possible to compare the effects of neutral ligands with those of anions.

Solvent Effects. It should be noted that the shifts in band positions recorded in Table II are caused by *ligation* and not merely *solvation*. This is nicely illustrated by analysis of the positions of the α bands in Table I using the method of Bayliss[28,29] and the function $(n^2 - 1)/(2n^2 + 1)$ (see Figure 4). The positions of the α bands in noncoordinating solvents show a linear dependence on this function, as predicted. Coordinating solvents, on the other hand, cause substantially greater shifts. A similar analysis of the position of the Soret band gives a similar result except that the slope is more negative. Thus the Soret band shifts more than the α band as a function of solvent, i.e., the difference in energy between the α and Soret bands is markedly solvent dependent. For this reason, the spectra described in Table II were all carried out in one solvent. The splitting between the α and Soret bands is very nearly constant, 6700 ± 150 cm^{-1} (except for thiolate described below), indicating that the effect of solvation is very similar for all of these complexes.

An alternative explanation of these results is that our spectra in noncoordinating solvents are those of $Zn(TPP)H_2O$ where water has been scavenged from the solvent. We do not believe this to be the case for a number of reasons. First, spectra of concentrated solutions of ZnTPP in toluene prepared under rigorously dry conditions are identical with those obtained in more dilute solutions (see Results). Secondly, spectra of $Zn(TPP)L$ where L is a neutral O donor ligand have $\epsilon_\alpha/\epsilon_\beta >$ 0.27 (see Tables I and II). It is difficult to understand why $Zn(TPP)H_2O$ would have $\epsilon_\alpha/\epsilon_\beta < 0.23$ as would be the case if entries 1–7 in Table I were due to this species. Finally, the spectra of ZnP (P = porphine), $Zn(P)D_2O$, $Zn(P)EtOH$, $Zn(P)Et_2O$, and $Zn(P)py$ in n-octane matrix at 4.2 K are known.[30] The 0–0 transitions in the absorption spectra of the EtOH, D_2O, Et_2O, and py complexes are all >300 cm^{-1} red shifted from the ZnP spectrum. Our spectra of ZnTPP in MeOH, Et_2O, and py are all red shifted from that of ZnTPP in cyclohexane by comparable amounts. We conclude, therefore, that the spectra that we see in noncoordinating solvents are due to uncomplexed ZnTPP and not to $Zn(TPP)H_2O$.

Uncommon Ligands. Table II includes ZnTPP complexes of several relatively uncommon ligands: superoxide, imidazolate, two crown ethers, and butylthiolate. The existence of the superoxide complex of ZnTPP has been reported earlier.[19] If we accept the premise that the red shift and α,β intensity ratio are correlated with the amount of charge transferred by a ligand to the porphyrin ring upon complexation, we can draw some conclusions about some properties of these ligands.

In Table II it can be seen that spectra of the ZnTPP complexes of superoxide and imidazolate fall between those of the chloride, hydroxide, and alkoxide complexes and that of the cyanide complex. We believe that this may indicate the relative polarizabilities of these novel anionic ligands. Since superoxide and imidazolate ligands have N and O donor atoms that are part of unsaturated systems, it is not surprising that they fall on the more polarizable side of saturated O donor ligands such as OH^- and OR^-. Imidazolate complexes of tetraphenylporphinatoiron(III) have recently been reported.[31] It is interesting to note that sequential deprotonation of the two imidazoles of $Fe(TPP)(ImH)_2^+$ results in a red shifting of the Soret band and an increase in $\epsilon_\alpha/\epsilon_\beta$ analogous to that seen for deprotonation of $Zn(TPP)ImH$ to give $Zn(TPP)(Im)^-$ (see Figure 1b and 1c).

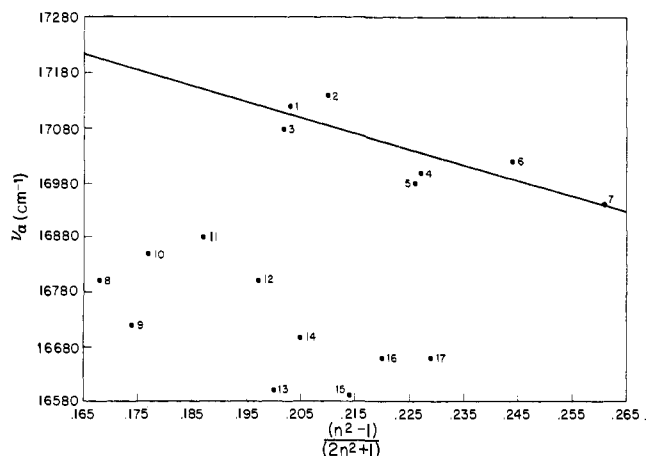The spectra of ZnTPP in the presence of the crown ethers

Figure 4. Plot of the α band frequency (ν_α) of ZnTPP in neat solvents vs. $(n^2 - 1)/(2n^2 + 1)$, where n is the refractive index of the neat solvent. Numbers refer to solvents in Table I. The line represents a least-squares regression through points 1–7.

Table IV.[a] Electronic Absorption Spectra of Cytochrome P-450 and Related Systems

	"hyper band", nm	Soret, nm	β, nm	α, nm
cytochrome P-450 CO	363	450	558	none
cytochrome P-420 CO		421	538	565
hemoglobin CO		420	541	568
cytochrome P-450 EtNC				
(low pH)		429	530	557
(high pH)	not reported	454	551	none
$Zn(TPP)(SBu)^-$	377.6	449.2	586.9	632.5
$Zn(Meso-1X-DME)-(SBu)^-$	353.9	438.2	561.8	595.6

[a] Data for proteins taken from ref 4 and 5.

dicyclohexyl-18-crown-6 and 18-crown-6 (Table II) show that these molecules are coordinating to ZnTPP. The red shifts are in the right range for O ligands. It is interesting to note further that the shifts are not identical and that 18C6 has been observed to bind more strongly to ZnTPP based on studies of the interference by crown ethers of anion binding (see Experimental Section). We interpret this to mean that the more flexible 18C6 ligand binds more strongly than DC18C6 which may mean that more than one O atom is involved in bonding.

The spectrum of the n-butylthiolate complex $Zn(TPP)-(SBu)^-$ (Figure 2) shows three distinct differences from the spectra of the other complexes. First, the Soret band is more red shifted than those of all the other complexes. Secondly, the magnitude of the red shift of the Soret band is greater than that of the α band, unlike what is observed for the other complexes. Finally, there is a new broad band centered at 378 nm on the high-energy side of the Soret band. The appearance of a new band along with an abnormally red-shifted Soret band makes this spectrum similar to those observed for carboxy ferrous porphyrin thiolate complexes synthesized as models for carboxycytochrome P-450[6–9] (see Table IV). Hanson et al.[10] have interpreted the spectra of these complexes as examples of "hyper" metalloporphyrin spectra. Thus it is believed that a sulfur p $\rightarrow$ porphyrin $e_g(\pi^*)$ charge transfer transition is of low enough energy to mix with the Soret resulting in two bands in the Soret region, one of which is abnormally red shifted relative to Soret bands in normal metalloporphyrin spectra.

A similar interpretation of the spectrum of Zn(TPP)(SR)⁻ would explain all three unusual features of its spectrum.

It is also possible that further analysis of this spectrum can help to explain the anomalous α,β region in carboxycytochrome P-450 and the model systems which essentially duplicate its spectrum. In the cytochrome and model systems, only one band is seen in the α,β region appearing at 558 nm.[4,5] This is unusual compared to the spectrum of carboxyhemoglobin and carboxycytochrome P-420 (a slightly denatured form of P-450).[4] These spectra are summarized in Table IV. In the case of Zn(TPP)(RS)⁻ we see not only that the Soret band is strongly red shifted, but also that $\epsilon_\alpha/\epsilon_\beta$ is the highest of any of the ligands examined. Remembering that the correlation of red shift with $\epsilon_\alpha/\epsilon_\beta$ should be reversed for protoporphyrin compared to TPP, we would predict that a thiolate ligand in OCFe-(porph)SR⁻, being both anionic *and* highly polarizable, should produce an $\epsilon_\alpha/\epsilon_\beta$ ratio much lower than that for an imidazole ligand from histidine in hemoglobin, i.e., OCFe(porph)ImH. A similar effect can be seen in the low- and high-pH forms of the isonitrile complexes of cytochrome P-450 (see Table IV) where presumably the equilibrium is between thiol and thiolate as ligands.[32] Thus we believe that the band observed is the β band and that the α band is weak owing to the low $\epsilon_\alpha/\epsilon_\beta$ ratio and that this high ratio is normal for a metalloporphyrin complex of a highly polarizable anionic ligand.

Other Metalloporphyrin Systems. A recent publication[33] describing cobalt-substituted horseradish peroxidase (CoHRP) provides an illustration of effects similar to those described above in zinc porphyrin systems. For Co³⁺HRP(L) derivatives, the α, β, and Soret bands red shift in the order L = H₂O < F⁻ < O₂⁻ < OH⁻ < N₃⁻ < CN⁻, a series similar to that which is observed in zinc porphyrins. Moreover, a correlation of the magnitude of the red shift with decreasing $\epsilon_\alpha/\epsilon_\beta$ (as expected for a protoporphyrin derivative) is seen in Figure 3 of ref 33 for the series L = H₂O < O₂⁻ < CN⁻.

Summary

Care must be exercised in interpreting the effects caused by changing axial ligands on many metalloporphyrin spectra because of the complications introduced by changing geometries and/or spin states. Nevertheless, the conclusions drawn from the present study of Zn(TPP)L and Zn(TPP)X⁻ systems can, we believe, aid in the analysis of other metalloporphyrin spectra. These conclusions are (1) that the red shifts and α,β intensity ratio changes are principally correlated with the charge and polarizability of the axial ligands and their resulting ability to transfer charge to the porphyrin ring and (2) that "ligand-type" hyper spectra may be a general phenomenon in metalloporphyrin spectra when a ligand to porphyrin charge transfer transition is of appropriate energy and symmetry.

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