Table IV. Comparison between $SnPc_2$ and UPc_2 [a]

		Sn	U
Metal Coordination–Square Antiprism Dimensions			
Metal-N, Å		2.347 ± 7	2.43
Metal-square nitrogen planes, Å		1.35 ± 2	1.40_5
N-N in square, Å		2.756 ± 6	2.80
N-N between squares, Å		2.95 ± 2	
		3.08 ± 2	
Rotation of the rings, deg		42	37
Phthalocyanine Rings			
Pyrrole ring	N-C, Å	1.375 ± 6	1.38
	C-C, Å	1.467 ± 9	1.46
Pyrrole-pyrrole link	C-N, Å	1.321 ± 7	1.32
Phenyl-pyrrole	C-C, Å	1.387 ± 8	1.40
Phenyl	C-C, Å	1.409 ± 9	1.40
	C-C, Å	1.410 ± 9	1.39
	C-C, Å	1.42 ± 2	1.41
Pyrrole ring	C-N-C, deg	108.1 ± 7	107.9
	N-C-C, deg	109.2 ± 4	109.4
	C-C-C, deg	106.6 ± 5	106.6
Pyrrole-pyrrole′	N-C-N′, deg	128.7 ± 5	127.6
	C-C-N′, deg	121.8 ± 6	123.0
	C-N′-C, deg	121.3 ± 10	123.9
Pyrrole-phenyl	C-C-C, deg	130.5 ± 5	131.8
	C-C-C, deg	122.7 ± 4	121.6
Phenyl	C-C-C, deg	115.3 ± 6	116.8
	C-C-C, deg	121.8 ± 7	121.5

[a] Deviations given are standard deviations in the mean.

Registry No. $Sn(C_{32}H_{16}N_8)_2$, 12581-75-8.

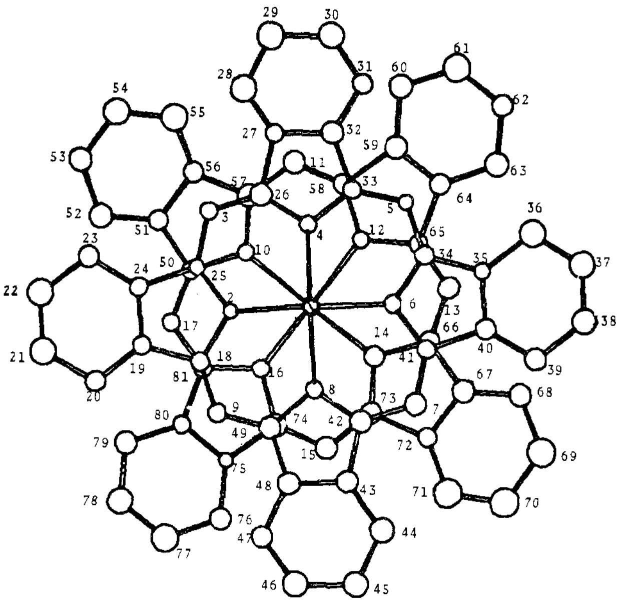

Figure 3. Plan view of the Pc_2Sn molecule.

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Lewis Acid-Base Interactions of Zinc α,β,γ,δ-Tetraphenylporphine with Several Neutral Donors

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The thermodynamic parameters for the formation of a 1:1 adduct between zinc α, β, γ, δ-tetraphenylporphine and several neutral Lewis bases are reported. For the bases studied, the enthalpies of adduct formation increase in the order S < O < P < N. The effect of change in extinction coefficient of the adduct on the determination of the equilibrium constant is discussed in terms of the Rose-Drago equation.

Introduction

Much work has been done in recent years on the structure and reactivity of porphyrins and metalloporphyrins.[2,3] One area of interest has been the Lewis acid-base interaction between metalloporphyrins and neutral ligands whose donor atom is nitrogen. The literature contains essentially no thermodynamic data describing the interaction of metalloporphyrins with Lewis bases other than nitrogen donors and, in many cases involving the nitrogen donors, these studies are limited to the determination of stability constants.[3]

In addition to iron-porphyrin systems, considerable work has been done on the Lewis acid-base interaction between nitrogen donors (pyridines) and zinc α, β, γ, δ-tetraphenylporphine (ZnTPP).[4-6] Miller and Dorough[4] have determined the equilibrium constant and enthalpy and entropy for the formation of the adduct between ZnTPP and pyridine in the solvent benzene. Their data indicate that ZnTPP forms a 1:1 adduct with pyridine. In order to obtain information concerning the Lewis acidity of ZnTPP, we have extended the study of the Lewis acid-base interaction of ZnTPP in benzene to oxygen, sulfur, and phosphorus donors.

Experimental Section

Materials and Apparatus. Tetraphenylporphine and zinc tetraphenylporphine were synthesized by literature methods.[7,8] The

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ZnTPP was purified using dry column chromatography.[8] The column was packed with Fisher adsorption alumina, 80-200 mesh. Eastman 1,1,3,3-tetramethylthiourea (TMTU) was recrystallized once from water and twice from *n*-hexane. Eastman GLC grade 1,1,3,3-tetramethylurea (TMU) was dried over Linde 4A molecular sieves and used without further purification. Aldrich triphenylphosphine (TPPP) was recrystallized three times from ethanol and dried under vacuum. Baker analyzed reagent benzene was treated as reported.[9]

The absorbance measurements were made on a Cary Model 14 uv-visible spectrophotometer with a thermostated cell compartment. Quartz cells with 1.000-cm path length were used.

Procedure. The absorbances were measured using a difference method of spectroscopy with the ZnTPP in the reference cell and ZnTPP and donor in the sample cell. The equilibrium constants were measured at approximately 5° intervals between 15 and 35°.

Treatment of Data. The equations which have been normally used to calculate the equilibrium constant for the formation of the 1:1 complex between ZnTPP and various substituent pyridines are given by Miller and Dorough (method I).[4] In the situation where the equilibrium constant is large and the absorbance of the complex A_C can be measured, their equations are applicable. However, inherent in these equations is the assumption that the extinction coefficient is independent of medium effects introduced by changing the donor concentration. In the case of small equilibrium constants, A_C cannot be measured directly and a graphical method has been used.[4] However, it has been pointed out[10] that such graphical treatments may lead to uncertainty in the equilibrium constant as large as a factor of 10. A procedure which allows one to obtain equilibrium constants without measuring the extinction coefficient of the complex ϵ_C directly and enables one graphically to analyze the data has been reported (method II).[11]

The equilibrium constant for the formation of a 1:1 adduct between ZnTPP and a donor is given by

$$K = \frac{C}{(A_0 - C)(B_0 - C)} \tag{1}$$

where A_0 and B_0 are the initial concentration of the metalloporphyrin and donor, respectively, and C is the equilibrium concentration of the metalloporphyrin complex. Since both the metalloporphyrin and the complex absorb in the same region, the total absorbance at a given wavelength is given by

$$a = \epsilon_C C + \epsilon_A A \tag{2}$$

where A is the concentration of free metalloporphyrin at equilibrium and ϵ_C and ϵ_A are the extinction coefficients of the complex and free metalloporphyrin, respectively. Combining eq 1 and 2 with $A_0 - C = A$ and $a_0 = \epsilon_A A_0$ yields the Rose-Drago equation

$$K^{-1} = \frac{a - a_0}{\epsilon_C - \epsilon_A} - A_0 - B_0 + A_0 B_0 \frac{\epsilon_C - \epsilon_A}{a - a_0} \tag{3}$$

This equation contains two unknowns, K and ϵ_C, and can be solved graphically.[11]

In order to remove the arbitrariness associated with the graphical solution of eq 3, it may be recast into a form more applicable to solution by a computer

$$a - a_0 = \frac{\epsilon_C - \epsilon_A\,[\beta - (\beta^2 - 4K^2 A_0 B_0)^{1/2}]}{2K} \tag{4}$$

where $\beta = K(A_0 + B_0) + 1$. A computer program utilizing a general minimization routine, SIMPLEX,[12] has been used to obtain K and ϵ_C by minimizing the difference between the experimentally obtained $a - a_0$ and that calculated by eq 4. A plot of $1/K$ *vs.* ϵ_C (or $\epsilon_C - \epsilon_A$) allows one to examine the precision of that data and to identify any trends in ϵ_C with increasing concentration of the donor.[13]

The enthalpy and entropy for the complex formation were determined from the temperature dependence of the equilibrium constant using a least-squares fit.

Table I. Plotting Data for Determination of Enthalpies and Entropies of ZnTPP-Base Systems

Base	Temp, °C	K_{eq}, l./mol
TMTU	15.4	18.2
	19.6	14.3
	25.0	11.8
	34.6	8.85
	44.4	6.79
TMU	15.1	105.2
	19.8	82.1
	25.0	70.2
	29.9	60.7
	34.4	52.0
TPPP	15.3	40.8
	20.2	33.8
	25.4	24.9
	29.3	23.5
	35.1	16.9

Table II. Thermodynamic Results for ZnTPP-Base Systems[a]

Base	K_a, l./mol	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol K
TMTU[c]	12.0 ± 0.1	5.6 ± 0.1[b]	13.8 ± 0.3
TMU[d]	72.1 ± 0.1	6.5 ± 0.2	13.3 ± 0.6
TPPP	26.6 ± 0.1	7.7 ± 0.6	19.4 ± 2.0
py[e]	6030	9.2 ± 0.1	14.0 ± 0.4

[a] Temperature 298 K. [b] Standard deviations; "National Bureau of Standards Handbook 91," U. S. Government Printing Office, Washington, D. C., 1963, Chapter 5. [c] Evidence that supports sulfur coordination is given by R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Amer. Chem. Soc.*, 86, 1694 (1964). [d] Evidence that the donor site is the carbonyl oxygen is given by R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *J. Amer. Chem. Soc.*, 86, 388 (1964). [e] Pyridine data reported by Miller and Dorough[4] subjected to our least-squares analysis.

Results

Spectroscopic data for the ZnTPP-base systems at various temperatures are available.[14] The equilibrium constants calculated from these data by method II are given in Table I. Figure 1 contains the Arrhenius plots of the data reported in Table I. The thermodynamic parameters resulting from a least-squares analysis are listed in Table II.

Discussion

Determination of *K*. Figure 2 is a plot of K^{-1} *vs.* $\Delta\epsilon$ ($\Delta\epsilon = \epsilon_C - \epsilon_A$) for the ZnTPP-tetramethylurea (TMU) system at 25.0° using eq 3. Each line in Figure 2 represents one of the pairs of acid and base concentrations for 25°. The coordinates for the intersection of curves gives the common solution for K and $\Delta\epsilon$. The computer-minimized solution is $K = 70.25$ and $\Delta\epsilon = -1.29 \times 10^4$ (or $\epsilon_C = 0.95 \times 10^4$). The fact that the intersections occur over a small area indicates that the precision of the measurements is very good, that the ϵ_C is independent of donor concentration range employed, and that a 1:1 complex is formed.[11]

Since the equilibrium constants for the systems reported in this work are relatively small ($100 > K > 1$), the extinction coefficient for the complex ϵ_C cannot be measured directly except in the case of TMU and then only if the concentration of the base is greater than 4 *M*. The ϵ_C measured when concentration of TMU is greater than 4 *M* does not agree with that obtained by method II in the dilute solu-

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(14) Tables of spectroscopic data for ZnTPP-base systems will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-936.

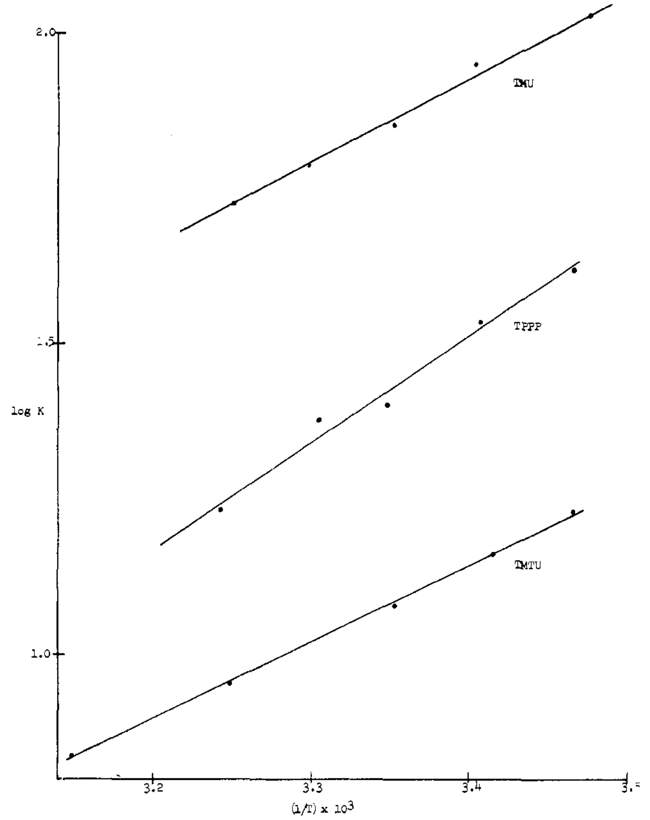

Figure 1. Plot of log K *vs.* $1/T$ for the ZnTPP-base systems. Correlation coefficients: TMTU, 0.9995; TMU, 0.9986; TPPP, 0.9911.

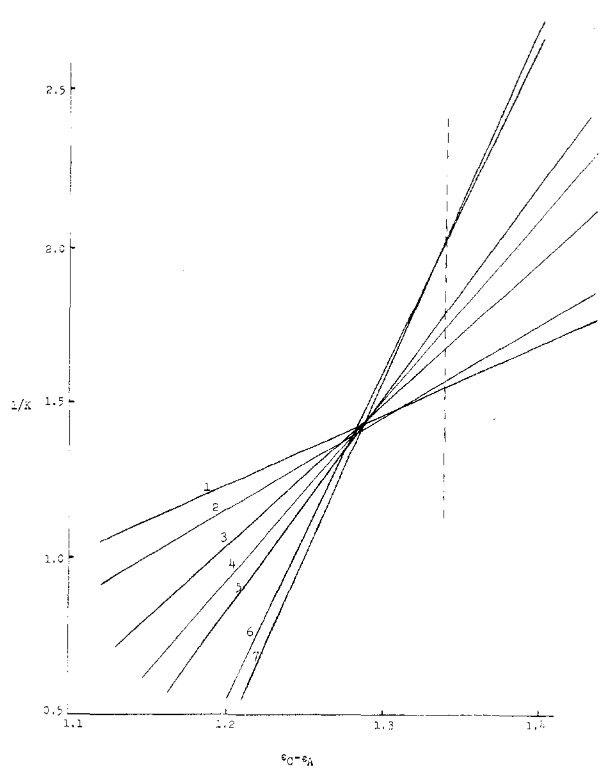

Figure 2. Plot of $1/K \times 10^2$ *vs.* $-\Delta\epsilon \times 10^{-4}$ for ZnTPP + TMU in benzene at 25.0°.

	10^5[ZnTPP], M	[TMU], M	$-(a - a_0)$
1	3.80	0.01482	0.249
2	3.55	0.02420	0.288
3	3.80	0.04446	0.370
4	3.55	0.06060	0.370
5	3.80	0.07410	0.410
6	3.55	0.12120	0.408
7	3.80	0.13238	0.442

Table III. Calculation of Equilibrium Constants by Method I

[TMU], M	K, l./mol	[TMU], M	K, l./mol
0.01482	64.6	0.07410	55.8
0.02420	63.4	0.12120	49.7
0.04446	59.8	0.13238	49.7
0.06060	57.8		Av 57.3

tions, *i.e.*, the concentration range given in Figure 2. The values for ϵ_C are 9.50×10^3 and 9.05×10^3 l./mol cm for the dilute solutions and the concentrated solutions, respectively.

Much has been written concerning the many pitfalls in the procedure for determining the equilibrium constants of weak molecule complexes;[15-19] however, little has been written concerning the reliability of equilibrium constants obtained when K is large enough to enable ϵ_C to be determined experimentally.[20] It is of interest to calculate the equilibrium constant using method I in which ϵ_C is measured in concentrated donor solution and to compare these results with those obtained by method II. The equilibrium constants calculated from the data given in Figure 2 for 25.0° by assuming ϵ_C is independent of donor concentration are listed in Table III. These results indicate an apparent dependence of the equilibrium constant on the donor concentration. The average value of the equilibrium constant is 57.3 which is drastically different from the value 70.2 calculated by method II. Graphically, this value of K determined by method I is the average of those values obtained from the intersections of the dotted line and solid lines in Figure 2. The dotted line indicates the value of $\Delta\epsilon$ calculated from the experimentally determined ϵ_C, 9.05×10^3. As can be seen graphically, the two methods differ greatly. Methods I and II will only give the same value for the equilibrium constants when data are very precise and the ϵ_C is independent of the donor concentration. Inspection of Figure 2 indicates that a small difference between the ϵ_C measured in concentrated solution and that determined for dilute solution will cause an incorrect value of the equilibrium constant to be calculated by method I. In fact, method I does not use all the information contained in the data, as seen graphically in Figure 2. Method I calculates the equilibrium constant from seven intersections while ignoring the others; that is, method I assigns a zero weighting factor to all intersections except those with the dotted line. On the other hand, method II utilizes $(n - 1)!$ intersections where n is the number of acid-base pairs and is not dependent on a measured ϵ_C. Thus the results of method II are independent of any error in the measurement of ϵ_C and/or any dependence of ϵ_C on medium effects introduced by changing the donor concentration. Unless it can be shown that ϵ_C is independent of the concentration of the donor and unless ϵ_C can be measured very accurately, method I should not be used to calculate equilibrium constants since an incorrect value for K is obtained.

It should be noted that the concentration of the donor need not be as high as that used to measure ϵ_C for the TMU system (4 M) to affect the determination of K. In the

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pyridine complexes the equilibrium constants are ~5000[4,5] and in the particular case of pyridine only a 1.24 *M* solution of pyridine is needed to determine ϵ_C experimentally. However, analysis of the pyridine data[4] by eq 3 shows that method II yields more precise results and that ϵ_C measured in 1.24 *M* pyridine solution is different from that determined from the data measured in very dilute solution. This change in ϵ_C accounts for the apparent dependence of the equilibrium constant on the base concentration.[4]

Thermodynamic Parameters. The previous work on the py–ZnTPP system in benzene[4] and chloroform[6] showed that a 1:1 complex was formed. The results for the three donors reported here also are consistent with the formation of a 1:1 adduct indicating that the stoichiometry of the ZnTPP adducts is independent of the type of donor atom binding the ZnTPP. The formation of 1:1 adducts is reasonable in light of the crystal structure work of Hoard and coworkers that shows the Zn^{2+} ion lies out of the plane of the porphine skeleton making square-pyramidal coordination favorable.[21] Inspection of Table II shows that the equilibrium constant for the ZnTPP-py interaction is substantially larger than those found for tetramethylthiourea, tetramethylurea, or triphenylphosphine interactions. However, entropy change accompanying the adduct formation is essentially constant within the error limits except when triphenylphosphine is the base. It is tempting to speculate that the larger entropy change accompanying the triphenylphosphine interaction is due to loss of some rotational freedom along Zn–P bond due to steric interaction between the phenyl rings of triphenylphosphine and the porphyrin.

The enthalpy of adduct formation measured in the gas phase or poorly solvating media is a measure of the strength of the bond formed between a Lewis acid and base. However, due to limited solubility (in hydrocarbons) and decomposition (in CCl_4) in poorly solvating solvents, benzene was employed as the solvent. Since benzene is a basic solvent,[9] the interpretation of enthalpies measured in benzene is more complex than those measured in poorly solvating media due to the specific interaction between ZnTPP and benzene. However, the sequence of various donors toward ZnTPP can be established as long as only enthalpies measured in the same solvent are compared and the solvation energies of the reactants and products cancel. The results reported for several Lewis acid–base systems in benzene and *o*-dichlorobenzene indicate that the assumption that solvation contributions cancel is reasonable.[9,22] For the donors studied with ZnTPP, the enthalpies increase in the order $S < O < P < N$.

Using this sequence of donor strength toward ZnTPP, one can attempt to determine the relative importance of electrostatic and covalent contribution to the bonding in its adducts. For comparison, a hydrogen bonding acid, such as an alcohol or phenol, interacts with Lewis base in the order $S < O < N$.[23] A more polarizable acid, I_2, interacts with Lewis bases in the order $O < S \leqslant N$.[23] On this limited basis, ZnTPP can be tentatively classified with H-bonding acids.

Recently the enthalpies of adduct formation of trimethylalane, $Al(CH_3)_3$, toward a series of nitrogen, oxygen, phosphorus, and sulfur donors have been measured.[24] The general sequence of donor strength toward trimethylalane, $S < O < P < N$, has been established, which is the same sequence found to hold for ZnTPP. Since $Al(CH_3)_3$ has been classified as an acid with a small *C*:*E* ratio,[23] that is, as an acid with a relatively large electrostatic contribution to the bonding, the tentative classification of ZnTPP as an acid in which the electrostatic contribution to the bonding is dominant appears reasonable.

Registry No. ZnTPP–TMTU, 38560-50-8; ZnTPP–TMU, 38536-02-6; ZnTPP–TPPP, 38560-51-9.

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