Correspondence

Soret Red Shift for Zinc Tetraphenylporphine in the Presence of Uncharged Lewis Bases

Sir:

As with other metalloporphyrins, the band positions in the electronic spectrum of (tetraphenylporphine)zinc(II) exhibit a pronounced dependence upon the solvent and donor environment. The intense Soret absorption peak at approximately 416 nm is red-shifted by as much as 14 nm in the presence of strong Lewis bases, and recent investigators have compared the magnitude of the red shift to several chemical characteristics of the base.[1,2] Experimental evidence supports the fundamental description of the Lewis acid–base interaction as the equilibrium in eq 1 in which zinc(II) has fourfold

$$\mathrm{Zn(TPP)} + \mathrm{L} \rightleftharpoons \mathrm{Zn(TPP)L} \qquad (1)$$

coordination with the porphyrin ring and can accept only a single additional axial ligand, L, to yield a 1:1 complex. Attempts have been made to correlate various *separate* empirical parameters related to bond strength, ligand polarity, and ligand base strength with the Soret shift. For example, free energy changes for the reaction relate linearly to the pK_a of the donor, but only if the ligands are closely related structurally;[3] no general relationship between the red shift and the E_B or C_B values (Drago parameters) is observed,[1] nor to dielectric constant functions for the donor[2] or to the Gutmann donor numbers. Although an approximately linear correlation exists between ΔH_f for adduct formation in eq 1 and the Soret shift,[1] scattered points occur for a variety of donors (benzene, triethylamine, tetrahydrothiophene) so that a resolution of the general from steric influences among the donors is clouded, and the scattering of points in the correlation exceeds the experimental uncertainty in the data base.

This brief communication summarizes the results of a multiple-regression treatment of the data for the Soret shift of ZnTPP induced by a wide range of aprotic ligands, with both literature and new experimental values. Rather than using a single parameter to describe the ligand characteristics as a donor, we now assume that the contribution of the Lewis base to the reaction in eq 1 arises from a *minimum* of two sources: (a) the empirical base strength of L as an electron pair donor toward a structurally simple reference acid for which specific ligand effects usually are not dominant; (b) the polarity–polarizability property of the donor reflecting its structural asymmetry. For the latter, the recently proposed π^* scale of Kamlet and Taft was selected since it is directly related to the molecular dipole moments of aprotic donors.[4]

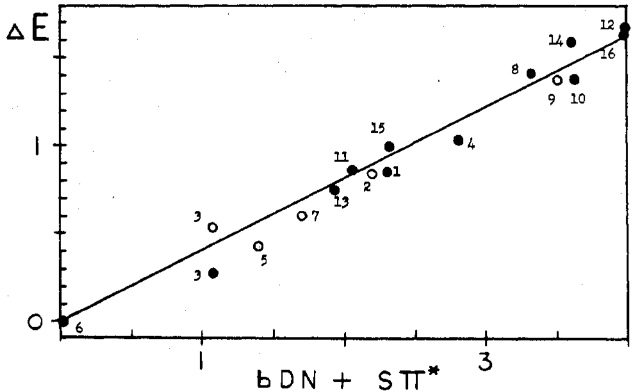

Figure 1. Regression plot of the Soret shift (ΔE) for ZnTPP as a function of the ligand parameters DN and π^* (All units kcal/mol): literature data[1] (●); new experimental values (○). Numbered points refer to bases in Table I.

Decisions on what experimental parameters can be used reliably for the fundamental measures of electron pair donor strengths of uncharged ligands have been strongly debated. Frequently applied thermodynamic scales of Lewis basicity include: (a) the enthalpy changes for donor–acceptor interactions derived from the E–C numbers of Drago et al.[5] (with respect to iodine as the reference acid); (b) the donor number (DN)–acceptor number (AN) system of Gutmann for Lewis acid–base reactions in which $SbCl_5$ is the reference acid;[6] and (c) Gibbs free energy changes related to macroscopic parameters for the donor.[7] Lim and Drago have demonstrated conclusively that DN and E–C data are not compatible as quantitative predictors of reaction enthalpies.[8] Limitations of the E–C numbers and other thermodynamic parameters have been examined experimentally by Arnett, Mitchell, and Murty (parts C and D)[9] for hydrogen-bonding systems. The significance of the enthalpy and entropy changes for adduct formation by ZnTPP has been discussed by Vogel and Stahlbush.[1]

Table I. Soret Shifts for ZnTPP:Donor Complexes and Donor Parameters at 25 °C

	Lewis base[f]	$-\Delta H_f$, kcal/mol	Soret $\Delta\lambda_{max}$, nm[a]	ΔE_{TR}, kcal/mol	Gutmann DN[c]	Kamlet-Taft π^*, kcal/mol[d]
1	acetone	6.5	5.2	0.848	17.0	1.953
2	acetonitrile		5.2[b]	0.850	14.1	2.039
3	benzene	1.4	1.6 (3.3)[b]	0.26 (0.54)	0.1	1.682
4	bridge ether[e]	7.1	6.3	1.02	19.6	2.497
5	chloroform		2.5[b]	0.41	0.0	2.174
6	cyclohexane		0.0	0.0	0.0	0.000
7	diethyl ether		3.7[b]	0.61	19.2	0.781
8	dimethylacetamide	8.4	8.8	1.42	27.8	2.522
9	dimethylformamide		8.6[b]	1.39	30.9	2.502
10	dimethyl sulfoxide	8.7	8.5	1.38	29.8	2.859
11	ethyl acetate	6.1	5.3	0.864	17.1	1.559
12	hexamethylphosphoramide	9.9	10.4	1.68	38.8	2.491
13	methyl acetate	5.7	4.6	0.75	16.5	1.438
14	pyridine	10.0	9.9	1.60	33.1	2.500
15	tetrahydrofuran	7.6	6.2	1.01	20.0	1.647
16	triethylamine	12.0	10.1	1.63	61.0	0.400

[a] Soret shifts reported by Vogel and Stahlbush,[1] relative to cyclohexane. [b] New experimental values, with the same method as Vogel and Stahlbush.[1] [c] Recent DN values given by Gutmann (ref 6, Table 2). [d] Converted to thermal units from π^* data of Kamlet, Abboud, and Taft,[4] Table I. [e] 7-Oxabicyclo[2.2.1]heptane. DN value estimated from C_B vs. DN trend for other ethers. [f] Numbers refer to numbered points in Figure 1.

0020-1669/79/1318-1175$01.00/0

Early trial correlations in this study comparing the ΔH_f or the E_B–C_B values for L with the Soret shift by use of both single and multiple linear regression functions either failed or had correlation coefficients inferior to the Vogel–Stahlbush data.[1] On the other hand, empirical correlations using the Gutmann donor numbers as composite measures of electron-pair activity were more successful in multiple regressions based upon the assumed model as stated above. Attempted correlations with the use of other empirical scales and free energy functions (Fowler et al.[7]) with the Soret red shift of ZnTPP generally were less satisfactory than the results obtained by Vogel and Stahlbush.[1]

If the Soret transition energy for ZnTPP with a given donor is designated E_{TR} and that for a specified reference donor (cyclohexane) is $(E_{TR})_0$, then the model linear regression function has the form of eq 2. Or, stated as the energy change

$$E_{TR} = (E_{TR})_0 + b'(DN) + s'\pi^* \qquad (2)$$

for the red shift

$$\Delta E_{TR} = E_{TR} - (E_{TR})_0 = b'(DN) + s'\pi^* \qquad (3)$$

An iterative procedure was then applied to the data in Table I, expressing all variables in units of kcal/mol. A survey of the uncertainties in the parameters established the limiting quantity in the convergence routine to be π^* at ± 0.31 (SD). The final derived function based upon all 16 donors is given by eq 4 in which the uncertainty in ΔE_{TR} is ± 0.05 (SD), and

$$\Delta E_{TR} = 0.0249(DN) + 0.265\pi^* \qquad (4)$$

the plot of the regression through the origin (correlation coefficient 0.99) is shown in Figure 1. The data of Nappa and Valentine[2] for the shift of ZnTPP in the pure solvents are not included in Figure 1, although conforming approximately to the linear function in eq 3. The degree of scattering for their data points is considerably greater than for those in Table I and appears to reflect a greater overall experimental uncertainty in the measured Soret wavelength.

It should be noted that the improved correlation provided by the multiple regression model is consistent with one major conclusion of Nappa and Valentine, namely, that the magnitude of the Soret shift is determined by the polarizability of the axial ligand and is not a simple response to changes in solvation. As one compares the relative arithmetic contributions of the two terms in eq 4 to the size of the red shift, it is clear that DN dominates for the interaction of the strongly coordinating bases (DMF, pyridine, HMPA, etc.) with ZnTPP, and at the lower end of the regression the polarizability term in π^* is the greater factor determining the smaller red shifts with such donors as chloroform and benzene.

The general form of the regression in eq 2 is equivalent mathematically to the Krygowski–Fawcett function for Lewis acid–base interactions.[10] From the data in Table I, it is apparent that the trend in the ΔH_f and DN of the ligand follows nearly the same qualitative order for adduct formation by the bases with respect to ZnTPP as the acceptor. However, even though DN exhibits a continuous positive correlation to $-\Delta H_f$ for this specific donor–acceptor system, the nonlinearity of that empirical correlation excludes the direct substitution of ΔH_f for DN in a linear regression function like eq 2.

Registry No. ZnTPP·1, 61483-54-3; ZnTPP·2, 67820-00-2; 3, 71-43-2; ZnTPP·4, 69204-48-4; 5, 67-66-3; ZnTPP·7, 69204-47-3; ZnTPP·8, 61477-54-1; ZnTPP·9, 67820-01-3; ZnTPP·10, 61483-89-4; ZnTPP·11, 61477-51-8; ZnTPP·12, 61477-56-3; ZnTPP·13, 61483-53-2; ZnTPP·14, 24389-79-5; ZnTPP·15, 61477-52-9; ZnTPP·16, 61484-36-4; ZnTPP, 14074-80-7.

References and Notes

(1) G. Vogel and J. Stahlbush, *Inorg. Chem.*, **16**, 950 (1977).
(2) M. Nappa and J. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).
(3) S. Cole et al., *Inorg. Chem.*, **11**, 1024 (1972).
(4) J. Abboud, M. Kamlet, and R. Taft, *J. Am. Chem. Soc.*, **99**, 8325 (1977).
(5) R Drago, G. Vogel, and T. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971); R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973).
(6) V. Gutmann, *CHEMTECH*, **7**, 255 (1977).
(7) F. Fowler et al., *J. Chem. Soc. B*, 460 (1971).
(8) Y. Lim and R. Drago, *Inorg. Chem.*, **11**, 202 (1972).
(9) E. Arnett, E. Mitchell, and T. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).
(10) T. Krygowski and W. Fawcett, *J. Am. Chem. Soc.*, **97**, 2143 (1975).

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Received January 18, 1978

Additions and Corrections

1978, Volume 17

Claude Musikas, Christine Cuillerdier, and Claude Chachaty*: ^{13}C, ^{14}N, and ^{15}N Nuclear Magnetic Resonance and Relaxation Study of the Binding of Thiocyanate to Trivalent Lanthanide Ions.

Page 3612. The two sentences following eq 16 and 17 should be read: In these equations $K = (1/50)D^2[4S(S + 1) - 3]$, D being the zero field splitting parameter and ω_s the electron Larmor frequency equal to 4.13×10^{11} rad s^{-1} ($H_0 \simeq 23.5$ kG) and 5.8×10^{10} rad s^{-1} ($H_0 \simeq 3.3$ kG) in NMR and ESR experiments, respectively. The T_{1e}^{-1} and T_{2e}^{-1} vs. T^{-1} curves given in Figure 3 have been fitted to experimental data by taking $\tau_v = 1.76 \times 10^{-14} \exp(3590/RT)$ s and $K = 1.18 \times 10^{20}$ s^{-2} ($D = 0.33$ cm^{-1}).—Claude Chachaty