

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

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

for the red shift

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

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

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

the plot of the regression through the origin (correlation coefficient 0.99) is shown in Figure 1. The data of Nappa and Valentine² 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

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Chemistry Department
Southwestern College
Winfield, Kansas 67156

Orland W. Kolling

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Additions and Corrections

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Claude Musikas, Christine Cuillerdier, and Claude Chachaty*: ¹³C, ¹⁴N, and ¹⁵N 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 ($H_0 \approx 23.5$ kG) and 5.8×10^{10} rad s⁻¹ ($H_0 \approx 3.3$ kG) in NMR and ESR experiments, respectively. The T_{1c}^{-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 $K = 1.18 \times 10^{20} \text{ s}^{-2}$ ($D = 0.33 \text{ cm}^{-1}$).—Claude Chachaty