12.560(1), $\alpha = 118.82(1)$, $\beta = 114.63(1)$, $\gamma = 77.68(1)$; U = 1134.1 Å$^3$, Z = 1; $F_{000} = 542$; $d_{calc} = 1.587$, $d_{obs} = 1.56 \pm 0.02$ g.cm$^{-3}$; space group P1 (N° 1); CuK$\alpha$ (1.54184 Å) radiation for cell dimensions and intensity measurements; $\mu = 71.52$ cm$^{-1}$.

Preliminary X-ray examination established a one-molecule triclinic unit cell. Precise lattice constants and diffracted intensities were derived from measurements carried out on a Enraf-Nonius CAD4F automatic diffractometer using a crystal of dimensions 0.20 × 0.16 × 0.08 mm. The setting angles of 25 reflections with $\theta$ values in the range 9–20° were determined. Least-squares refinement of these reflections led to the lattice constants reported above. The measured density reported was obtained by flotation in aqueous zinc chloride solution.

Intensity data were collected by using the $\theta/2\theta$ scan technique and graphite-monochromated Cu K$\alpha$ radiation. The intensities of 4058 unique reflections were measured within $0.045 < (\sin\theta)/\lambda < 0.587$. the prescan speed was 2° min$^{-1}$, and all reflections having $I < \sigma(I)$ during the prescan were flagged unobserved and not measured. The final scan speed was adjusted to have at least $\sigma(I)/I < 0.4$. The total $\omega$ scan angle was 1.20 + (Cu K$\alpha_1\alpha_2$ splitting)°.

The intensities of three standard reflections were monitored throughout the data collection period and measured every 2 h; no significant trend appeared. The intensity data were reduced to relative square amplitudes by application of the standard Lorentz and polarization factors. Absorption factors were computed by using the numerical integration method of Busing Levy.[21] For each reflection, a standard deviation was attached as $\sigma^2(F_o^2) = \sigma_{count}^2 + (pI)^2$ with a $p$ value of 0.08.

For all computations, the Enraf-Nonius SDP/V17 package[22] was used.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique using the 3569 reflections having $F^2 \geq 3\sigma(F^2)$. All nonhydrogen atoms were refined by assuming anisotropic thermal motion. Hydrogen atoms were introduced in structure factor calculations with their computed coordinates (C-H = 0.95 Å) and isotropic thermal factors ($B_H = 7$ Å$^2$) but not refined. The final values of $R_1(F)$ and $R_2(F)$ are 0.051 and 0.067, respectively, after determination of the absolute configuration. The estimated standard deviation of a unit weight observation is 1.33. A final difference map showed no significant peaks.

Tables IV and V list the final atomic positional and thermal parameters.[23]

**Acknowledgment.** We wish to thank Louis Ricard[2] for useful discussions and André Mitschler[2] for X-ray data collection.

**Supplementary Material Available:** Tables of positional and thermal parameters and general temperature factor expressions and a listing of structure factors (21 pages). Ordering information is given on any current masthead page.

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[21] Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–182.

[22] Frenz, B. A. "The Enraf-Nonius CAD4-SDP". Computing in Crystallography: Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds., Delft University Press: Delft, Holland, 1978, 64–71.

[23] See paragraph at end of paper regarding supplementary material.

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# The Effects of Solvent on Axial Ligation Constants of a Cobalt(II) Porphyrin

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**Abstract:** Axial ligation constants for the reaction of Co(T($p$-CH$_3$O)PP) with pyridine, piperidine, and $N$-methylimidazole in several solvents, 1,2 dichloroethane, methylene chloride, chlorobenzene, chloroform, toluene, dimethylformamide, and $o$-nitrotoluene/toluene mixtures, were found to be nearly constant at room temperature. This was attributed to the fact that reactions were carried out near the isoequilibrium temperature (320 ± 24 K) as determined from plots of $\Delta H$ vs. $\Delta S$. The solvent was found to affect the enthalpy and entropy changes of the ligation reaction in three ways. In low dielectric constant media, the change of $\Delta H$ and $\Delta S$ with the dielectric constants of the solvents was linear and "gas-phase" enthalpy and entropy changes for the reactions were obtained by extrapolation. The values of $\Delta H$(g) and $\Delta S$(g) for pyridine, piperidine, and $N$-methylimidazole reactions were respectively $-5.5 \pm 0.8$ kcal/mol and $-7 \pm 2$ eu, $-8.0 \pm 0.3$ kcal/mol and $-13 \pm 1$ eu, and $-7.5 \pm 0.6$ kcal/mol and $-12 \pm 2$ eu. The difference between $\Delta H$(g) and $\Delta H$ was related to the enthalpy of solvation which had the effect of stabilizing the adduct linearly with respect to the dielectric constant of the solvent. Reactions in the higher dielectric medium of dimethylformamide required the displacement of coordinated solvent prior to reaction of the complex with base, and this resulted in near constant and more positive values of $\Delta H$ ($-7 \pm 0.5$ kcal/mol) and $\Delta S$ ($-11 \pm 1$ eu) than expected on the basis of the linear relationship found in low dielectric media. The enthalpy and entropy change for reactions in solvent mixtures of $o$-nitrotoluene and toluene were nearly constant, and this was attributed to the ability of the solvent to form $\pi$ complexes with the cobalt porphyrin adduct.

The importance of solvent in affecting the stability of dioxygen adducts of cobalt and iron porphyrin complexes has appeared in several reports in the literature[1] but a systematic study regarding the fundamental properties causing the effect has not been published. We decided to carry out an investigation of this type by first defining the solvent interactions occurring in the forming of the precursor complex. The particular system chosen was (5,10,15,20-tetrakis($p$-methoxyphenyl)porphinato)cobalt(II) (Co(T($p$-CH$_3$O)PP). The electronic, axial ligation, and reversible oxygenation properties were previously studied by Walker[2] and her reports were used as a basis for this study.

Thermodynamic values for the axial ligation of cobalt porphyrin complexes were also determined in other studies. Most of these were concerned with protoporphyrin IX dimethyl ester (PP(IX)DME) compounds,[3-5] picket fence porphyrins,[6] and capped

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[1] (a) Stynes, H. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 5125–5127. (b) Molinaro, F. S.; Little, R. G.; Ibers, J. A. *Ibid.* **1977**, *99*, 5628–5632. (c) Brinigar, W. S.; Chang, C. K.; Geibel, J.; Traylor, T. G. *Ibid.* **1974**, *96*, 5597–5599.

[2] (a) Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235–4244. (b) *Ibid.* **1973**, *95*, 1150–1153; (c) *Ibid.* **1973**, *95*, 1154–1159. (d) Walker, F. A.; Beroiz, D.; Kadish, K. M. *Ibid.* **1976**, *98*, 3484–3489.

[3] (a) Stynes, D. V.; Stynes, H. C.; James, B. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 1796–1801. (b) Stynes, D. V.; Stynes, H. C.; Ibers, J. A.; James, B. R. *Ibid.* **1973**, *95*, 1142–1149.

[4] Drago, R. S.; Beugelsdjk, T.; Breese, J. A.; Cannady, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5374–5382.

[5] Takayanagi, T.; Yamamoto, H.; Kwan, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2618–2622.

porphyrin systems.[7] Recently, the *E* and *C* parameter concept has been extended to the reaction of CoPP(IX)DME with pyridine (py), *N*-methylimidazole (N-MeIM), piperidine (pip), and tetrahydrothiophene (THTP) in toluene.[4] Several literature ΔH values were redetermined in order for them to fit the empirical equation

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

It was assumed that solvent interactions were minimal (or at least similar) for the reactions studied.

Such interactions have proven to be quite large in studies with $SbCl_5$ and have given rise to the donor number concept referenced to reactions in 1,2-dichloroethane.[8] The process involves direct interaction of the "donor solvent" with $SbCl_5$ in dichloroethane according to reaction 2. Donor numbers were assigned as the

$$\mathrm{D(soln)} + \mathrm{SbCl_5(soln)} \overset{\Delta H_D}{\rightleftharpoons} \mathrm{D{\cdot}SbCl_5(soln)} \qquad (2)$$

values of $-\Delta H_D$ for reaction 2 and range from 0.1 for sulfuryl chloride to 38.8 for hexamethylphosphoramide. The range of solvents for which donor numbers are assigned does not include solvents of low dielectric constants used in this study such as toluene, chloroform, chlorobenzene, or methylene chloride, although one might expect that the principles used in developing donor numbers could also be applied to these solvents as well.

Two extreme limits could be anticipated for the formation of the "five-coordinate" precursor complex as summarized by eq 3 and 4. One would expect that the product in (3) would be

$$\mathrm{Co{\cdot}P(soln)} + \mathrm{B(soln)} \overset{K}{\rightleftharpoons} \mathrm{Co{\cdot}P{\cdot}B(soln)} \qquad (3)$$

$$\mathrm{Co{\cdot}P(soln)} + x\mathrm{S} \overset{K_s}{\rightleftharpoons} \mathrm{CoPS}_x\mathrm{(soln)} \overset{K'}{\rightleftharpoons} \mathrm{CoPBS}_{x-1} + \mathrm{S} \qquad (4)$$

stabilized as the donor number or dielectric constant of the solvent increases if charge separation is produced in the product and that this would be reflected in more negative Δ*H* values. The opposite trend in the enthalpy change would be predicted for reaction 4. In this case displacement of the more rigorously bound solvent by the base would depend inversely on the donor number or dielectric constant of the medium. Both of these cases are considered in this paper.

## Experimental Section

**Preparation of Co(T(*p*-$CH_3O$)PP).** The free base porphyrin, $H_2T$(*p*-$CH_3O$)PP, was prepared by the method of Adler et al.,[9] and the methods of Walker[2a] were used for inserting cobalt into the porphyrin and purification of the product. Recrystallization of the product from benzene resulted in the nonsolvated compound.

Anal. Calcd for $CoC_{48}H_{36}N_4O_4$: C, 72.8; H, 4.5; N, 7.1. Found: C, 72.1; H, 4.6; N, 7.1.

**Purification of Reagents.** Purchased chemicals were reagent grade but required special handling and purification procedures.

Pyridine and piperidine were purified by distillation from KOH pellets under dry nitrogen; *N*-methylimidazole was dried by vacuum distillation from KOH pellets. The three amines were stored under dry nitrogen for several weeks after distillation without any difficulty.

The solvents chlorobenzene, chloroform, dimethylformamide, methylene chloride and *o*-nitrotoluene were dried by storing them under dry nitrogen and over freshly dried molecular sieves (Davidson, 4–8 mesh beads, 4 Å) for at least 1 week prior to use. In order to ensure that these solvents were free of oxygen, 100–300-mL volumes of the solvents were degassed by bubbling nitrogen through them for 15 min before use.

Toluene was dried by refluxing it over $CaH_2$ for a minumum of 3 days prior to use and then gently distilling it under a steady flow of dry nitrogen, discarding the first 60% of distillate. The collected distillate was used immediately.

**Electronic Absorption Spectra.** Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. The wavelength scale was calibrated with a holmium oxide crystal.[10]

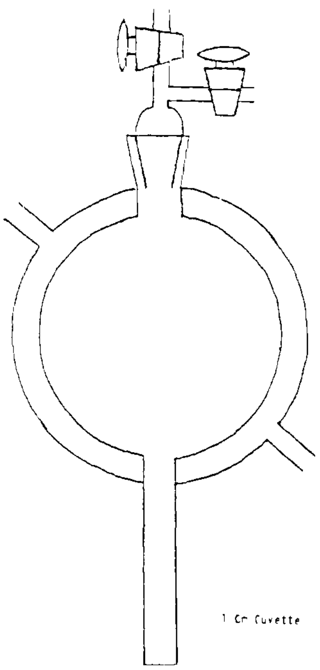

Figure 1. Water-jacketed tonometer for use as a titration cell above 0 °C.

**Measurement of Equilibrium Constants.** A solution of Co(T(*p*-$CH_3O$)PP) was prepared under nitrogen by dissolving a small amount of the complex in a solvent and adjusting the concentration by dilution techniques until the absorbance of the 532-nm band was approximately 1.0 in a 1-cm cuvette. The concentration of the complex in this solution was approximately $6 \times 10^{-5}$ M, depending on the solvent.

A solution having a known concentration of base was prepared in the same solvent as the complex. The base concentration was then adjusted by dilution until it was such that the first increment of base solution added in the titration would cause a decrease in the absorbance of the 532-nm band of 0.05 absorbance unit. This assured a base solution of such a concentration that the titration could be completed without adding enough base solution to cause a significant change in the volume of the solution being titrated.

While care was taken to maintain a nitrogen atmosphere in the titration vessel and all glassware, a 25.00-mL aliquot of the complex solution was added to the cell (Figure 1). The cell was attached to a vacuum manifold, degassed by the freeze–thaw–pump method, a septum was installed over the glass tubing of the vertical stopcock, and the cell was refilled with a positive pressure of nitrogen. The cell was then mounted in the cell compartment of the Cary 14, and the water jacket was connected by tygon tubing to the pump of a Haake FK-2 water bath. Water of the desired temperature (measured by using an iron–constatan thermocouple and a Honeywell potentiometer referenced to 0 °C) was circulated through the water jacket of the cell and cell block holder of the Cary 14 for 20 min to allow the solution to come to thermal equilibrium. After thermal equilibrium was reached, a spectrum of the solution was recorded between 700 and 450 nm. Between 0.1 and 0.50 mL of base solution was added in small increments via either a 0.10 or a 1.0-mL gas-tight syringe mounted on the cell for the duration of the experiment. After each base addition, the cell was removed from the cell compartment, and the solution was mixed by shaking. A spectrum of the solution was recorded again immediately after mixing. At the end of the titration, 0.1 mL of neat base was added to the solution to ensure complete reaction of the complex.

**Dielectric Constant Measurements.** The dielectric constant of a mixture of two solvents, toluene and *o*-nitrotoluene (ONTOL), in their various proportions was measured at 25 °C by using the resonance method[11] and benzene as a reference solvent. The results were in agreement with literature values[12] for the neat solvents. Measured values were as follows: toluene, 2.38 (lit. 2.397) and ONTOL, 25.5 (lit. 27.4 at 20 °C). A mixture of 25% (by volume) ONTOL in toluene had a dielectric

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(6) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Hayes, S. E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2761–2766.

(7) Ellis, P. E., Jr.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889–1896.

(8) Gutmann, V. "Coordination Chemistry in Nonaqueous Solutions"; Springer-Verlag: New York, 1968; pp 12–20.

(9) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(10) Jurgenson, C. K.; Brenen, J. S. *Mol. Phys.* **1963**, *6*, 629.

(11) Daniels, F.; Williams, J. W.; Bender, P.; Alberty, R. A.; Cornwell, C. D. "Experimental Physical Chemistry", 6th ed.; McGraw-Hill: New York, 1962; pp 223–230.

(12) "Handbook of Chemistry and Physics", 42nd ed.; CRC Press: Cleveland, 1961; pp 2513–2522.

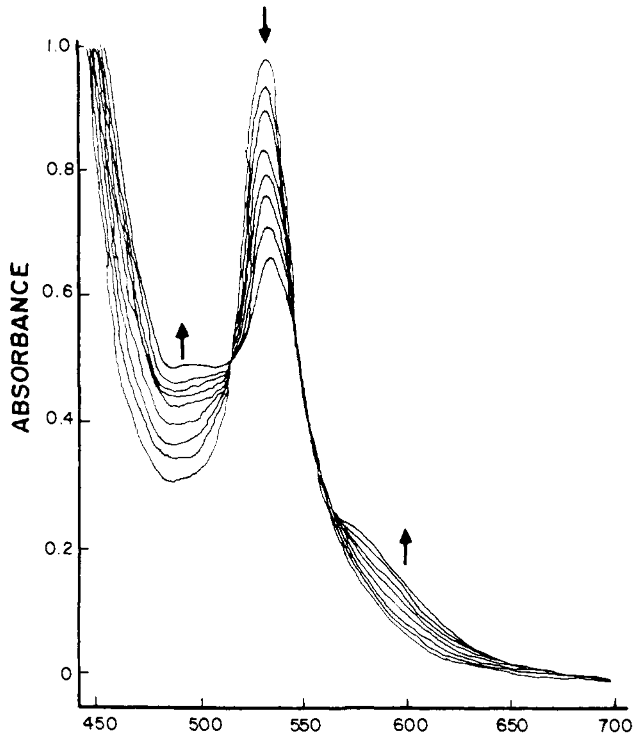

**Figure 2.** Spectral changes for the reaction of Co(T($p$-$CH_3O$)PP) with piperidine in methylene chloride at 25 °C.

constant of 6.3 at 25 °C; a 50–50 mixture had a dielectric constant of 11.5 at 25 °C.

**Thermodynamic Calculations.** Thermodynamic quantities were determined by using a nonweighted linear least-squares program.

The equilibrium constants were obtained by using the Hill relation

$$\log Y/(1 - Y) = n \log [B] + \log K \qquad (5)$$

where

$$Y = \frac{A_{obsd} - A_0}{A_\infty - A_0}$$

and $A_{obsd}$ = absorbance at a specific [B], $A_0$ = initial absorbance where [B] = 0, and $A_\infty$ = final absorbance for the "five-coordinate" complexes. Values for log $K$ were obtained from the $y$ intercept of the regression line from a plot of log $[Y/1 - Y]$ vs. log [B].

The temperature dependence of log $K$ was used to determine $\Delta H$ and $\Delta S$ for the reaction. The enthalpy change was determined from the slope, and $\Delta S$ from the $y$ intercept of plots of log $K$ vs. $1/T$.

## Results

The molar extinction coefficient of the 532-nm band of Co(T($p$-$CH_3O$)PP) was used to gauge both the purity of the complex and the solvent. The molar extinction coefficient of the absorbance for all the solvents was (1.55 ± 0.05) × $10^4$ with one exception. The extinction coefficient of the 532-nm band for the complex in dimethylformamide was 1.27 × $10^4$ which was obtained in that solvent by using the molecular sieve drying technique. Lower extinction coefficients were obtained when the solvent was dried over $CaH_2$. In fact, no discernible absorption change was observed upon addition of a base such as piperidine to the solution of the cobalt complex in dimethylformamide dried over $CaH_2$.[13]

Solutions of Co(T($p$-$CH_3O$)PP) were stable in air and in the presence of weakly coordinating amines. The presence of piperidine or $N$-methylimidazole in the solution resulted in a slow color change corresponding to oxygenation of the compound. Consequently, all manipulations (with the exception of the pyridine titrations in toluene and $o$-nitrotoluene/toluene mixtures) in this study were done under a dry nitrogen atmosphere.

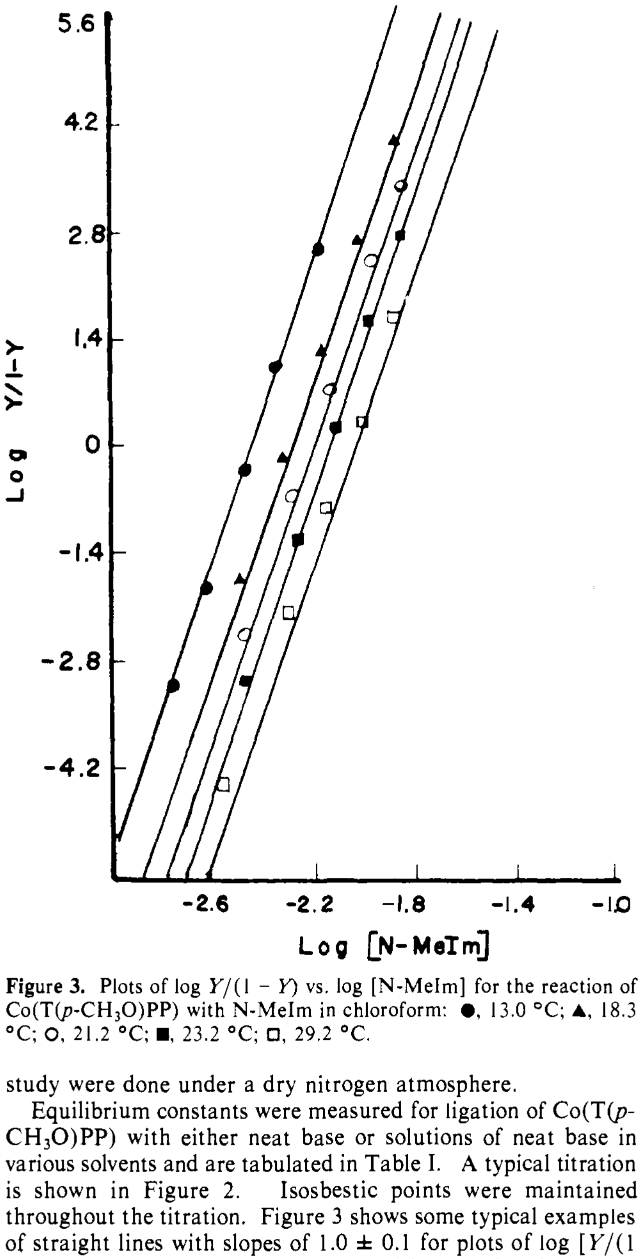

**Figure 3.** Plots of log $Y/(1 - Y)$ vs. log [N-MeIm] for the reaction of Co(T($p$-$CH_3O$)PP) with N-MeIm in chloroform: ●, 13.0 °C; ▲, 18.3 °C; ○, 21.2 °C; ■, 23.2 °C; □, 29.2 °C.

Equilibrium constants were measured for ligation of Co(T($p$-$CH_3O$)PP) with either neat base or solutions of neat base in various solvents and are tabulated in Table I. A typical titration is shown in Figure 2. Isosbestic points were maintained throughout the titration. Figure 3 shows some typical examples of straight lines with slopes of 1.0 ± 0.1 for plots of log $[Y/(1 - Y)]$ vs. log [B], where $Y$ represents [Co(T($p$-$CH_3O$)PP)B]/[Co(T($p$-$CH_3O$)PP]$_{total}$.

Table II gives enthalpy and entropy parameters derived from van't Hoff plots of log $K$. vs. $1/T$. Plots of this type are illustrated in Figure 4 and were constructed of no fewer than four points. The errors listed were obtained from the errors of the slope and intercept from the linear regression analysis. Great care was taken to obtain errors of less than 1 kcal/mol for $\Delta H$ and to assure that the data were internally consistent. In spite of continual efforts, it was not always possible to attain these self-imposed standards.

## Discussion

**Formation Constants.** Values of formation constants for the reaction of amines with Co(T($p$-$CH_3O$)PP) were nearly invariant to either the choice of amine or the solvent employed and were consistent with the values of formation constants previously obtained in toluene.[2] Plots of $\Delta H$ vs. $\Delta S$ are linear, and the slope gives the temperature at which reactions have the same free energy (log $K$).[14] This temperature is 320 ± 24 K. All points as shown in Figure 5 appear to lie along the same line. Calculations for each individual amine reaction result in isoequilibrium temperature

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(13) The recent controversy regarding thermodynamic constants of DMF adducts of of Co(PP(IX)DME) are probably due to amine impurities present in the solution from the decomposition of the solvent that results from refluxing over $CaH_2$.

(14) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 324–326. Cole, S. J.; Curthoys, G. C.; Magnusson, E. A. *J. Am. Chem. Soc.* **1970**, *92*, 2991–2996.

Table I. Equilibrium Constants For the Reaction of Co(T($p$-$CH_3O$)PP) with Bases in Various Nonaqueous Solvents

| | pyridine | | piperidine | | $N$-methylimidazole | |
|---|---|---|---|---|---|---|
| solvent | $T$,$^a$ °C | log $K^b$ | $T$,$^a$ °C | log $K^b$ | $T$,$^a$ °C | log $K^b$ |
| 1,2-dichloroethane | 29.8 | 2.54 | 29.0 | 3.29 | 29.5 | 2.79 |
| | 28.8 | 2.57 | 28.4 | 3.27 | 26.6 | 2.89 |
| | 24.2 | 2.70 | 26.0 | 3.36 | 23.2 | 2.90 |
| | 20.8 | 2.80 | 25.4 | 3.42 | 21.8 | 3.03 |
| | 19.3 | 2.89 | 24.7 | 3.44 | 18.5 | 3.05 |
| | 14.3 | 2.96 | 22.2 | 3.52 | 16.0 | 3.15 |
| | | | 19.0 | 3.57 | 12.8 | 3.26 |
| | | | 17.2 | 3.68 | | |
| | | | 16.2 | 3.65 | | |
| | | | 14.8 | 3.64 | | |
| methylene chloride | 34.9 | 2.58 | 28.8 | 3.22 | 30.0 | 2.87 |
| | 29.6 | 2.73 | 25.6 | 3.30 | 27.0 | 2.92 |
| | 24.4 | 2.83 | 23.2 | 3.40 | 24.2 | 3.05 |
| | 15.0 | 3.02 | 20.8 | 3.50 | 20.8 | 3.11 |
| | | | 19.2 | 3.52 | 18.3 | 3.15 |
| | | | 16.2 | 3.61 | 16.0 | 3.25 |
| | | | 13.6 | 3.64 | 12.8 | 3.29 |
| chlorobenzene | 42.0 | 2.38 | 40.0 | 2.94 | 38.8 | 2.79 |
| | 34.2 | 2.50 | 35.6 | 3.04 | 35.0 | 2.90 |
| | 24.3 | 2.71 | 31.6 | 3.18 | 31.6 | 3.03 |
| | 15.8 | 2.89 | 29.7 | 3.15 | 27.6 | 3.19 |
| | | | 29.5 | 3.16 | 23.6 | 3.22 |
| | | | 27.8 | 3.23 | 20.2 | 3.28 |
| | | | 26.4 | 3.20 | 15.8 | 3.34 |
| | | | 26.0 | 3.25 | | |
| | | | 24.2 | 3.36 | | |
| | | | 24.2 | 3.32 | | |
| | | | 23.8 | 3.43 | | |
| | | | 21.4 | 3.37 | | |
| | | | 21.0 | 3.40 | | |
| | | | 19.4 | 3.39 | | |
| | | | 15.8 | 3.53 | | |
| chloroform | 29.5 | 2.37 | 29.7 | 2.78 | 29.2 | 2.08 |
| | 24.3 | 2.43 | 25.8 | 2.83 | 26.2 | 2.09 |
| | 20.2 | 2.52 | 24.2 | 2.84 | 23.2 | 2.16 |
| | 13.0 | 2.64 | 21.2 | 2.88 | 21.2 | 2.22 |
| | | | 20.0 | 2.93 | 18.3 | 2.31 |
| | | | 19.0 | 2.93 | 15.6 | 2.32 |
| | | | 16.0 | 3.08 | 13.0 | 2.40 |
| | | | 12.8 | 3.21 | | |
| toluene | 42.2 | 2.58 | 38.2 | 3.08 | 34.3 | 2.99 |
| | 35.1 | 2.64 | 33.6 | 3.22 | 29.8 | 3.04 |
| | 25.0 | 2.83 | 30.4 | 3.27 | 26.2 | 3.14 |
| | 15.2 | 2.94 | 27.4 | 3.35 | 22.8 | 3.26 |
| | | | 23.6 | 3.41 | 20.6 | 3.29 |
| | | | 21.2 | 3.44 | 19.0 | 3.24 |
| | | | 18.3 | 3.54 | 11.4 | 3.40 |
| | | | 16.2 | 3.57 | | |
| | | | 12.2 | 3.65 | | |
| dimethylformamide | 43.5 | 1.98 | 44.0 | 2.48 | 44.0 | 2.23 |
| | 39.7 | 2.01 | 40.3 | 2.52 | 39.9 | 2.25 |
| | 34.7 | 2.19 | 39.9 | 2.56 | 35.7 | 2.37 |
| | 29.6 | 2.20 | 34.3 | 2.68 | 33.6 | 2.40 |
| | 25.5 | 2.30 | 29.7 | 2.69 | 26.4 | 2.52 |
| | 20.9 | 2.32 | 24.8 | 2.80 | 22.3 | 2.56 |
| | 16.8 | 2.42 | 21.4 | 2.90 | 21.6 | 2.61 |
| | | | 16.4 | 2.95 | 15.3 | 2.73 |
| 25% ONTOL$^c$ | 41.4 | 2.46 | | | | |
| | 33.6 | 2.55 | | | | |
| | 25.0 | 2.74 | | | | |
| | 15.4 | 2.87 | | | | |
| 50% ONTOL$^c$ | 41.4 | 2.41 | | | | |
| | 33.6 | 2.50 | | | | |
| | 25.0 | 2.68 | | | | |
| | 15.4 | 2.80 | | | | |
| 100% ONTOL$^c$ | 41.8 | 2.26 | | | | |
| | 33.8 | 2.40 | | | | |
| | 25.0 | 2.55 | | | | |
| | 15.0 | 2.68 | | | | |

$^a$ ±0.1 °C. $^b$ ±0.09. $^c$ ONTOL = $o$-nitrotoluene.

of 328 ± 40, 309 ± 30, and 283 ± 71 K for piperidine, pyridine, and $N$-methylimidazole, respectively. The isoequilibrium temperatures are obviously too close to room temperature for comparison of log $K$ values studied here. This reasoning also accounts for the similarity of log $K$ values observed for the reaction of Co(T($p$-$CH_3O$)PP) with pyridine in toluene and butyronitrile rather than the suggested[2c] possibility of similar solvent interactions.

**Table II.** Thermodynamic Parameters for the Reaction of Co(T($p$-CH$_3$O)PP) with Several Amines in Various Solvents

| amine | solvent | log $K^a$ | $\Delta H$, kcal/mol | $\Delta H$(solv),$^b$ kcal/mol | $\Delta S$, eu | $\Delta S$(solv),$^c$ eu |
|---|---|---|---|---|---|---|
| piperidine | 1,2-dichloroethane (10.36)$^d$ | 3.41 | −11.5 ± 1.0 | −3.5 | −23 ± 4 | −10 |
| | methylene chloride (9.08)$^d$ | 3.34 | −11.1 ± 1.0 | −3.1 | −22 ± 3 | −9 |
| | chlorobenzene (5.67)$^d$ | 2.90 | −9.3 ± 0.6 | −1.3 | −18 ± 2 | −5 |
| | chloroform (4.81)$^d$ | 2.90 | −9.6 ± 1.3 | −1.6 | −19 ± 5 | −6 |
| | toluene (2.38)$^d$ | 3.48 | −8.6 ± 0.2 | −0.6 | −13 ± 1 | ~0 |
| | dimethylformamide (36.71)$^d$ | 2.81 | −7.1 ± 0.4 | | −11 ± 1 | |
| pyridine | methylene chloride | 2.89 | −9.0 ± 2.0 | −3.5 | −17 ± 8 | −10 |
| | chlorobenzene | 2.82 | −8.3 ± 1.0 | −2.8 | −15 ± 3 | −8 |
| | chloroform | 2.52 | −6.7 ± 0.7 | −1.2 | −11 ± 2 | −4 |
| | 25% ONTOL (6.3)$^e$ | 2.74 | −7.0 ± 0.3 | −1.5 | −10 ± 1 | −3 |
| | 50% ONTOL (11.5)$^e$ | 2.68 | −6.4 ± 0.5 | | −10 ± 2 | |
| | 100% ONTOL (27.5)$^d$ | 2.55 | −6.4 ± 0.4 | | −10 ± 1 | |
| | toluene | 2.83 | −6.2 ± 0.9 | −0.1 | 8 ± 3 | −1 |
| | dimethylformamide | 2.81 | −6.0 ± 0.7 | | −12 ± 2 | |
| *N*-methylimidazole | 1,2-dichloroethane | 2.90 | −10.5 ± 0.7 | −3.0 | −22 ± 2 | −10 |
| | methylene chloride | 2.90 | −9.9 ± 0.8 | −2.4 | −20 ± 3 | −8 |
| | chlorobenzene | 3.26 | −9.8 ± 1.2 | −2.3 | −18 ± 4 | −6 |
| | chloroform | 2.08 | −8.5 ± 0.7 | −1.0 | −19 ± 2 | −7 |
| | toluene | 3.18 | −7.6 ± 0.6 | −0.1 | −11 ± 2 | ~0 |
| | dimethylformamide | 2.54 | −7.2 ± 0.3 | | −12 ± 1 | |

[a] Calculated at 25 °C from $\Delta H$ and $\Delta S$ values. [b] $\Delta H(\text{solv}) = \Delta H - \Delta H(\text{g})$. [c] $\Delta S(\text{solv}) = \Delta S - \Delta S(\text{g})$. [d] Dielectric constants from ref 12. [e] Dielectric constants from this study.

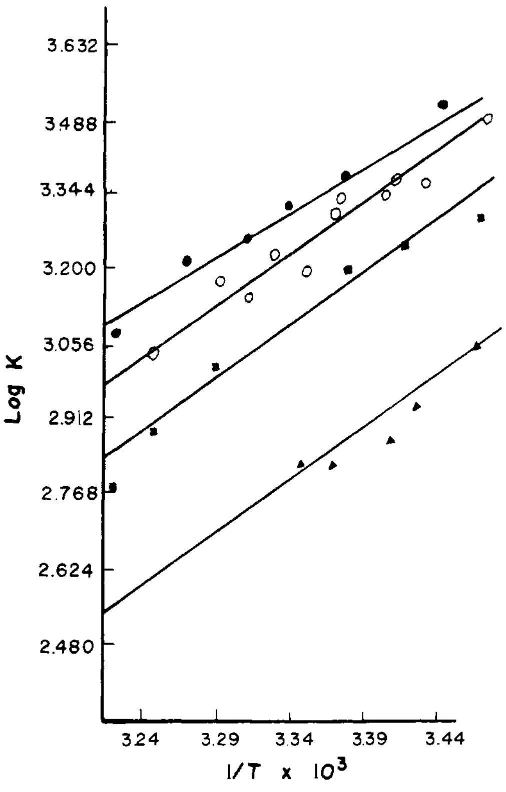

**Figure 4.** Plots of log $K$ vs. $1/T$ for the enthalpy and entropy change determinations for the formation of the five-coordinate species: ●, toluene/py; ○, chlorobenzene/pip; ■, chlorobenzene/N-MeIm; ▲, chloroform/pip.

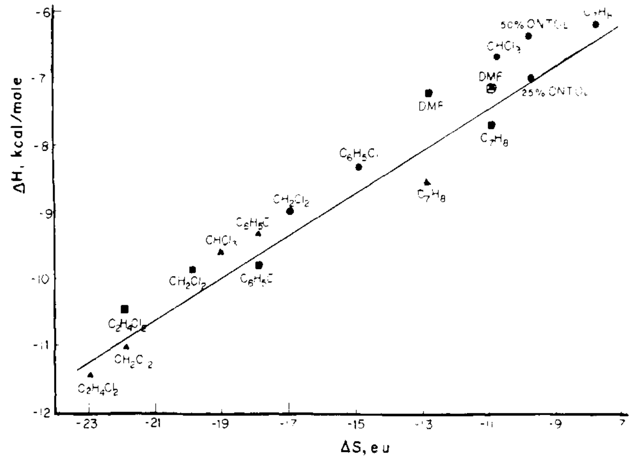

**Figure 5.** Plot of $\Delta H$ vs. $\Delta S$ for the determination of the isoequilbrium temperature: ▲, Co(T($p$-OCH$_3$)PP)/pip reactions; ■, Co(T($p$-OCH$_3$)PP)/N-MeIm reactions; ●, Co(T($p$-OCH$_3$)PP)/py reactions.

**Solvent Effects.** Plots of $\Delta H$ vs. $\Delta S$ clearly point out that the solvent does play a role in the equilibrium reaction. This role can be examined from plots of $\Delta H$ vs. $\epsilon$ ($\epsilon$ = dielectric constant), as illustrated in Figure 6. If $\epsilon$ is taken to be one for a vacuum, then gas-phase enthalpies can be obtained from Figure 6 by extrapolation. Values of $\Delta H$(g) and $\Delta S$(g) (determined from $\Delta S$ vs. $\epsilon$ plots) thus obtained for the piperidine, pyridine, and *N*-methylimidazole reactions follow respectively −8.0 ± 0.3 kcal/mol and −13 ± 1 eu, −5.5 ± 0.8 kcal/mol and −7 ± 2 eu, and −7.5 ± 0.6 kcal/mol and −12 ± 2 e.u.[15] It should be possible to correlate the "gas-phase" enthalpies with the $E$ and $C$ equation[16] given in the introduction, where the $E$ parameter can be interpreted as the susceptibility of the compound to undergo electrostatic interaction and the $C$ parameter can be interpreted as the susceptibility of the reagent to undergo covalent interaction. Both ZnTPP[17] (TPP = tetraphenylporphyrin) and CoPP(IX)DME[4] have been fitted to the equation as acids. For ZnTPP the $E_A$ and $C_A$ parameters were 5.15 and 0.624, respectively. Those of CoPP(IX)DME were 4.44 and 0.58, respectively. It is possible to calculate tentative values of $E_A$ and $C_A$ for Co(T($p$-CH$_3$O)PP) for reactions with piperidine and *N*-methylimidazole.[18] The values are 5.3 and 0.28, respectively. These can only be regarded as tentative because the intersection of two lines (plots of $E_A$ vs. $C_A$) does not meet the mathematical criterion for quantitative $E_A$ and $C_A$ determinations.[19] Calculations of $\Delta H$ using eq 1 and the $E_B$ and $C_B$ values for the reaction of Co(T($p$-CH$_3$O)PP) with 4-picoline in toluene result in an enthalpy which is within the error limits of the experimental value (8.2 kcal/mol (calculated) compared to 7.3 ± 1 kcal/mol (experimental)).

The value of $\Delta H$(g) for pyridine is less negative than required for an $E_A$ and $C_A$ fit. The reason for this is not understood, but

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[15] Error limits were taken from the errors in intercepts from plots of $\Delta H$ vs. $\epsilon$ and $\Delta S$ vs. $\epsilon$. Correlation coefficients were 0.9 ± 0.1 for the plots.

[16] Drago, R. S.; Wayland, B. B. *J. Am. Chem. Soc.* **1965**, *87*, 3571–3577.

[17] Vogel, G. C.; Stahlbush, J. R. *Inorg. Chem.* **1977**, *16*, 950–953.

[18] Values of $E_B$ and $C_B$ were taken from ref 4.

[19] Drago, R. S. *Struct. Bonding (Berlin)* **1973**, *15*, 73–139.

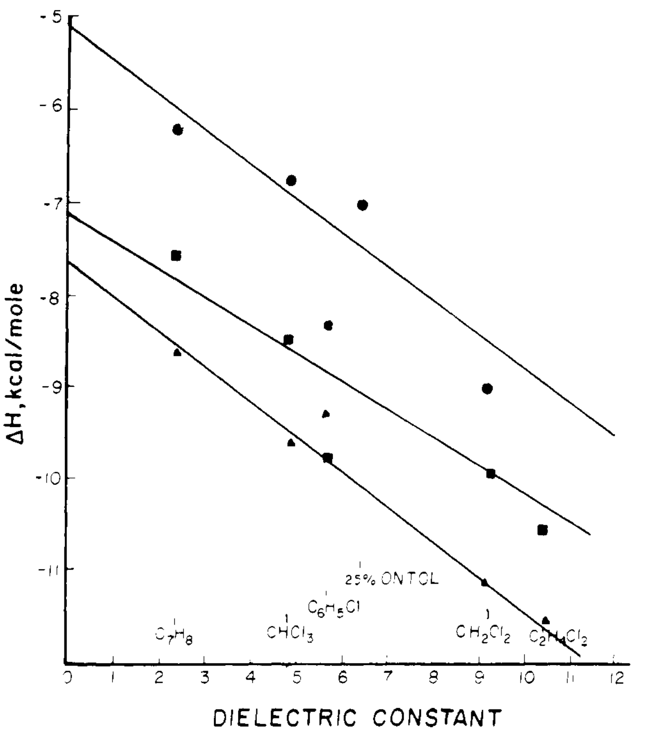

**Figure 6.** Plot of $\Delta H$ vs. $\epsilon$: ▲, Co(T($p$-$CH_3O$)PP)/pip reactions; ■, Co(T($p$-$CH_3O$)PP/N-MeIm reactions; ●, Co(T($p$-$CH_3O$)PP)/py reactions.

it may be due to the manner in which the data were collected for this series of reactions.[20]

The enthalpy changes involving the solution and gas-phase reaction are summarized in the following Born–Haber cycle.

$$\begin{tikzcd}
\text{Co(T(}p\text{-(CH}_3\text{O)PP)(g)} & + & \text{B(g)} \arrow[r, "\Delta H(\text{g})"] & \text{Co(T(}p\text{-(CH}_3\text{O)PP)B} \arrow[d, "\Delta H_3(\text{solv})"] \\
\text{Co(T(}p\text{-CH}_3\text{O)PP)(solv)} \arrow[u, "-\Delta H_1(\text{solv})"'] & + & \text{B(solv)} \arrow[u, "-\Delta H_2(\text{solv})"'] \arrow[r, "\Delta H"] & \text{Co(T(}p\text{-CH}_3\text{O)PP)B(solv)}
\end{tikzcd}$$

The solution enthalpy change can be obtained from

$$\Delta H = \Delta H(\text{g}) + \Delta H(\text{solv})$$

where

$$\Delta H(\text{solv}) = \Delta H_3(\text{solv}) - \Delta H_1(\text{solv}) - \Delta H_2(\text{solv})$$

Differences between the solution and gas-phase thermodynamic pairs lead to $\Delta H$(solv) and $\Delta S$(solv) factors listed in Table II. The values for $\Delta H$(solv) range from ~−1 to ~−4 kcal/mol and those of $\Delta S$(solv) from ~0 to ~−10 eu. The values are the most negative for solvents of high dielectric constant and more positive for solvents of low dielectric constant ($0 < \epsilon < 11$). For a given solvent, solvation factors are nearly constant regardless of the amine reaction under study. The mechanism for the solvation apparently involves greater dipole–dipole interactions between the cobalt porphyrin base complex, and the solvent than was present in the reactants. This increased dipolar character of the porphyrin adduct arises from displacement of the cobalt atom from the plane of the porphyrin ring upon coordination of an axial base. Ibers and co-workers found that the cobalt atom was pulled 0.16 Å out of the porphyrin plane toward imidazole in a crystal structure of Co(OEP)(N-MeIm) (OEP = octaethylporphyrin).[21] The net result is the formation of a molecule with stronger dipole characteristics giving rise to the observed correlation of $\Delta H$(solv) and $\Delta S$(solv) with the dielectric constant of the solvent.

For the aromatic *o*-nitrotoluene/toluene mixtures, thermodynamic parameters varied little with the dielectric constant of the medium. The mechanism of interaction with the cobalt porphyrin base complex is clearly of a different type. It has been proposed that $\pi$ "complexes" form between the $\pi$ cloud of the porphyrin ring and that of the solvent.[22] It is interesting to note that the enthalpy change predicted by the *E* and *C* equation for the 1:1 adduct formation of Co(T($p$-$CH_3O$)PP) with benzene[23] is ~−1 kcal/mol and this value is observed for solvation in toluene. It seems reasonable then that the solvation process in the case of higher concentrations of ONTOL results in the formation of $\pi$ complexes which interfere in the dipolar process causing near constant enthalpy and entropy changes.

Dimethylformamide (DMF) is the only solvent where solvent coordination is indicated prior to addition of the base. The extinction coefficient of the 532-nm band was less than found in other solvents but more than found for the five-coordinate Co($p$-$CH_3O$)PP)B complexes (Figure 2). Further proof for DMF coordination was observed by studying absorption changes of the 532-nm band of Co(T($p$-$CH_3O$)PP) in toluene upon addition of DMF. The absorbance decreased upon addition of DMF, but the absorbance change never reached the normal limiting value, even after adding DMF in great excess. It is important to note that the enthalpy changes for the reactions in DMF with the three amines are similar and are comparable to those of reactions in toluene and also that the enthalpy changes are less than expected from the correlation observed for solvents of low dielectric constants ($\epsilon < 11$). This change in behavior from a constant decrease in $\Delta H$ with $\epsilon$ to an increase in DMF is expected for reactions requiring the displacement of solvent from the coordination sphere of the complex[8] and is in agreement with reaction 4.

## Conclusion

The role of the solvent in affecting the position of equilibrium of a chemical reaction depends upon the particular reaction under study and the type of solvent employed. In low dielectric media reaction 3 was followed and the enthalpy and entropy changes were linearly related to the dielectric constant of the solvents which allow the determination of "gas-phase" enthalpy and entropy changes. This linear relationship of $\Delta H$ with $\epsilon$ was not expected on theoretical grounds which would predict a direct correlation with $1/\epsilon$.[24] Solvent studies in general have been frustrated by a lack of correlation with theory,[25] and the fact that there is a correlation of $\Delta H$ with $\epsilon$ in this study is an important observation.

The linear change of $\Delta S$ with $\epsilon$ in this study implies greater ordering of the solvent during the course of the reaction. This ordering can be explained by the greater dipole interaction of the solvent with the dipole of the five-coordinate complex. The only exceptions to the behavior were in the *o*-nitrobenzene/toluene mixtures where $\pi$ bonding between the solvent and solute appears to occur and in dimethylformamide where solvent coordination interferes. The latter reaction appears to be more readily understood on the basis of the donor number concept.

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**Registry No.** [Co(T($p$-$CH_3O$)PP)B] (B = piperidine), 41618-50-2; [Co(T($p$-$CH_3O$)PP)B] (B = pyridine), 41736-30-5; [Co(T($p$-$CH_3O$)PP)B] (B = *N*-methylimidazole), 41618-49-9; 1,2-dichloroethane, 107-06-2; methylene chloride, 75-09-2; chlorobenzene, 108-90-7; chloroform, 67-66-3; toluene, 108-88-3; dimethylformamide, 68-12-2; *o*-nitrotoluene, 88-72-2.

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(20) Titrations with pyridine were done in a closed container like that in Figure 1 but no effort was made to remove air. Side reactions with $O_2$ were not observed in the titration process. All other titrations were carried out as described in the experimental section.

(21) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4452–4463.

(22) Walker, F. A.; Avery, G. L. *Tetrahedron Lett.* **1971**, 4949–4952.

(23) $E_B$ and $C_B$ parameters were taken from ref 19.

(24) Yoder, C. H. *J. Chem. Educ.* **1977**, *54*, 402–408.

(25) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 45–46.