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Axial Interaction of Vanadyl Tetraphenylporphyrin with Lewis Bases

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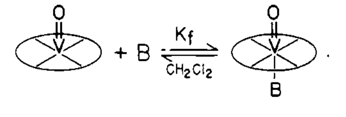
Metal contaminants in heavy oils, mainly vanadium,[1] raise serious problems in the processes involved in the refining of crude oil. Most of these metal contaminants are found to be coordinated to porphyrin macrocycles.[2] The conventional method used for oil demetalation consists of the deposition of the metals over catalytic surfaces in the presence of H_2(HDM).[3] The mechanism of the interaction between petroporphyrins and the catalytic surface is crucial toward effective demetalating activity. In order to evaluate the relevance of axial coordination of basic sites in the surface of HDM catalysts to vanadyl petroporphyrins, the interactions of different Lewis Bases (B) with the vanadyl *meso*-tetraphenylporphyrin (VO(TPP)) were studied. In this paper, the calculation of the formation constant (K_f) for the 1:1 adducts [VO(B)TPP] is presented (eq 1).[4]



(1)

Experimental Section

K_f values were calculated from spectrophotometric data by using Drago's method.[5,6] This method requires the solution of eq 2, which has

$$\frac{1}{K_f} = \frac{\Delta A}{\Delta\epsilon} - A_T - B_T + \frac{A_T B_T \Delta\epsilon}{\Delta A} \tag{2}$$

two unknowns where K_f = the formation constant of the adduct (unknown), $\Delta\epsilon$ = the extinction coefficient difference between VO(TPP) and the adduct (unknown), ΔA = the absorbance difference between VO(TPP) and the complex, A_T = the initial concentration of VO(TPP), and B_t = the initial concentration of base.

In the case of the complex being dealt with in this paper, experimental conditions are such that

$$\frac{\Delta A}{\Delta\epsilon} - A_T \ll \frac{A_T B_T \Delta\epsilon}{\Delta A} - B_T$$

Therefore, eq 2 can be approximated to Ketelaar's equation (3). A linear

$$\frac{A_T}{\Delta A} = \left[\frac{1}{k_f \Delta\epsilon}\,\frac{1}{B_T}\right] + \frac{1}{\Delta\epsilon} \tag{3}$$

least-squares fit to the experimental data for $A_T/\Delta A$ vs. $1/B_T$ was obtained for selected wavelengths (λ). $\Delta\epsilon$ and K_f were then calculated from the intercept and slope, respectively, of each straight line. The λ values in the spectra, at which K_f and $\Delta\epsilon$ were calculated, were those corresponding to maximum observed ΔA. The "best fit" values for K_f and $\Delta\epsilon$ for each chosen λ were obtained by means of the numerical method described by Drago et al.[6]

Spectrophotometric data were recorded on a Varian instrument, Model 2290, at 22 °C. All reagents and solvents were of analytical grade purchased commercially. Lewis bases (except imidazole) were twice distilled and dried over 4A molecular sieves.

Table I. Spectrophotometric Titration of VO(TPP) with Me_2SO in Dichloromethane at 22 °C ($A_T = 3 \times 10^{-5}$ M)

run no.	B_T/M	A_{423}	A_{436}	A_{547}	A_{562}	A_{602}
1	0.00	1.373	0.097	0.625	0.177	0.007
2	2.11	1.163	0.330	0.549	0.255	0.055
3	2.82	1.052	0.406	0.522	0.281	0.073
4	3.52	0.990	0.506	0.498	0.310	0.092
5	4.23	0.919	0.599	0.473	0.337	0.112
6	5.64	0.805	0.775	0.429	0.382	0.145
7	6.34	0.740	0.836	0.409	0.399	0.156
8	7.05	0.696	0.921	0.392	0.421	0.173
9	8.46	0.599	1.020	0.357	0.445	0.193
10	9.87	0.522	1.100	0.328	0.464	0.212
11	12.69	0.414	1.220	0.287	0.486	0.236
	K_f	0.057	0.045	0.045	0.061	0.045

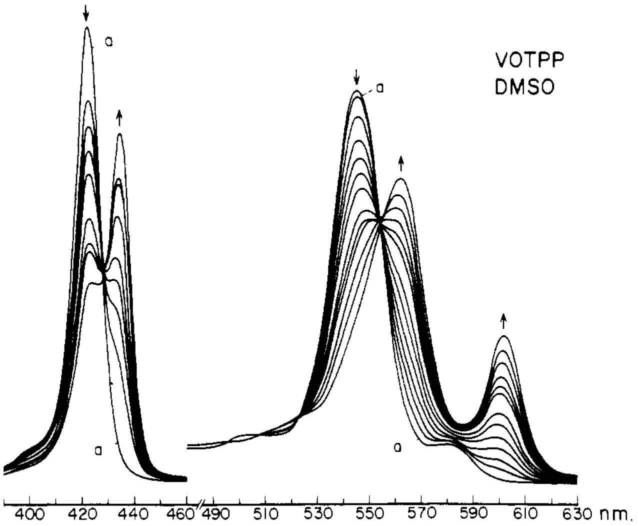


Figure 1. Visible spectra of VO(TPP) in the presence of increasing amounts of Me_2SO ($A_T = 3 \times 10^{-5}$ M; a = neat VO(TPP) in CH_2Cl_2).

meso-Tetraphenylporphyrin (TPP) was synthesized[8] and freed of chlorin[9] according to procedures already described. The vanadyl ion was inserted into TPP by Buchler's method,[10] using vanadyl bis(acetylacetonate) as metalating agent in refluxing quinoline[11] for 2 h. This process affords complete metalation. The average yield after isolation and recrystallization from CH_2Cl_2/CH_3OH was 90%. TPP and VO(TPP) gave satisfactory analytical characterization.

Results and Discussion

The visible spectrum of VO(TPP) in CH_2Cl_2 changes upon addition of increasing concentrations of coordinating Lewis bases. These spectral changes are associated with axial ligation of **B** to the vanadium in VO(TPP).[12] A typical experimental set is presented in Table I, for the coordination of dimethyl sulfoxide (Me_2SO) to VO(TPP). The corresponding spectrophotometric changes are shown in Figure 1. In general, the observed absorption pattern upon axial coordination is the same regardless the nature of the heteroatom in the base. VO(TPP)'s Soret band (423 nm) is red-shifted 10–15 nm. The peak at 547 nm also undergoes bathochromic shift to approximately 560 nm, and a new band appears around 605 nm. This effect was also observed by Walker et al.[12] for the coordination of piperidine to a series of para- and meta-substituted VO(TPP).

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(4) The oval represents the porphyrin macrocycle of TPP.

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(11) We were not able to fully metalate TPP in DMF or pyridine, even with a 10-fold excess of metalating agent and 48 h of reflux.

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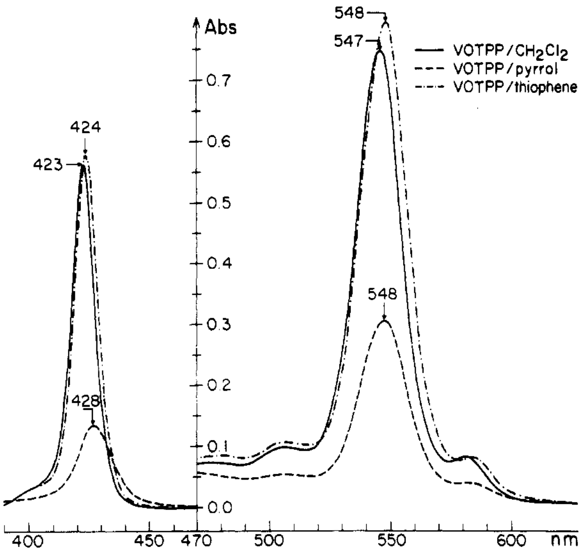

Figure 2. Comparative spectra of 1.5×10^{-5} M solutions of VO(TPP) in (a) dichloromethane, (b) pyrrole and (c) thiophene.

The calculated mean values (μ) and standard deviations (σ) for K_f were found to be the following:

	μ	σ
n-butylamine	1.24	0.060
tert-butylamine	0.07	0.017
aniline	0.186	0.005
piperidine[13]	0.75	0.050
pyridine[14]	0.148	0.015
imidazole	1.33	0.160
Me_2SO[16]	0.051	0.007

Diethylamine, pyrrole, *n*-butanol, and tetrahydrofuran weakly coordinated to VO(TPP). They bring small changes on the visible spectra but not enough to calculate K_f from spectrophotometric data. These K_f values must be smaller than those shown above. Triethylamine, acetonitrile, acetone, thiophene, and *n*-pentanethiol do not coordinate to VO(TPP).

The coordinating ability of the Lewis bases to VO(TPP) was found to follow the sequence in decreasing order nitrogenated > oxygenated ≳ sulfurated. It was also observed that axial ligation is sensitive to steric factors in the ligand, i.e. *n*-butylamine > *tert*-butylamine > diethylamine ≫ triethylamine. This effect can be understood from the results of X-ray structural studies of VO(TPP).[18] Vanadium is 0.53 Å above the plane formed by the nitrogen group of the porphyrin macrocycle. This means that the ligand has to enter a small cavity in order to effect coordination while hindered nucleophiles cannot reach the metal. Bonnett et al.[19] have qualitatively observed this effect in the interactions of several nitrogenated solvents with vanadyl octaethylporphyrin.

The presence of weakly coordinating aromatic solvents such as pyrrole causes the visible spectra of VO(TPP) to change in a different manner (Figure 2). The Soret band is widened and red-shifted 5 nm. The extintion coefficient of the peak's maxima diminishes considerably: $VO(TPP)/CH_2Cl_2$, $\lambda = 423$ ($\epsilon = 4.07 \times 10^5$) and 547 ($\epsilon = 2.01 \times 10^4$); VO(TPP)/pyrrole: $\lambda = 428$ ($\epsilon = 1.12 \times 10^5$) and 548 ($\epsilon = 7.63 \times 10^3$). Probably the VO(TPP)–base interaction is different from the one described above. The spectra changes could be the result of π–π interactions between the aromatic rings of the pyrrole and the porphyrin macrocycle (a tetrapyrrole), rather than an axial coordination of the nitrogen in the pyrrole to the vanadium. This effect was not observed in toluene nor in thiophene.

In general, it can be concluded that axial interactions of Lewis bases with vanadium are small ($K_f < 2$) and sterically affected.

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(13) Walker et al.[12] reported a K_f value of 0.28 for VO(TPP)–piperidine in toluene at 34.5 °C.

(14) Hambright et al.[15] reported a K_f value of 0.43 ± 15% for VO(TPP)–pyridine in chloroform at 25 °C.

(15) Hambright, P. *J. Chem. Soc. D* **1967**, 470.

(16) We observed Soret splitting of VO(TPP) with Me_2SO (Figure 1) and not just the presence of a shoulder as reported by Newton and Davis.[17]

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(19) Bonnett, R.; Brewer, P.; Noro, K.; Noro, T. *Tetrahedron* **1978**, *34*, 379.

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Boron Derivatives of 3-Methylpyrazole[1]

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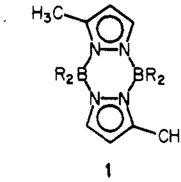
The knowledge of boron derivatives of 3-methylpyrazole, HpzMe, is extremely limited. This lack is likely due to the mobility of the N-bonded proton in 3-methylpyrazole, the replacement of which may yield isomeric products, i.e., derivatives of either 3- or 5-methylpyrazole. Indeed, when trimethylborane was reacted with 3-methylpyrazole, the resultant pyrazabole was found to be a mixture of **1** and **2** ($R = CH_3$) in approximately 4:3 molar ratio (based on ^1H NMR data) that could not be separated.[2] Stereochemically pure **1** with $R = C_2H_5$ was obtained from the interaction of (dimethylamino)diethylborane with 1,3-dimethyl-2-(methylpyrazol-1-yl)-1,3,2-diazaboracyclohexane.[3]



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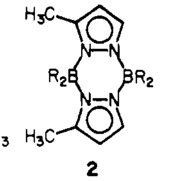
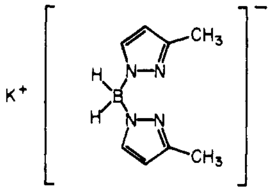


2

The only other known boron derivative of 3-methylpyrazole, i.e., the salt $K[H_2B(pzMe)_2]$, was obtained by condensation of KBH_4 with HpzMe. On the basis of high-resolution ^1H NMR data, the product of this latter reaction consisted of only one isomer, **3**, with the methyl group being exclusively in the 3-position of the pyrazole ring.[4]



3

We have now found that the salts $K[HB(pzMe)_3]$ and $K[B(pzMe)_4]$, which are also readily obtained from the interaction of KBH_4 with HpzMe, analogously exist in only one isomeric form corresponding to **3**.

As expected, reaction according to eq 1 yielded the two isomers **1** and **2** (R = H), which were obtained in approximately 3:2 molar ratio. It seems that base displacement is the first step of the reaction. For steric reasons, this should result in the formation

$$2HpzMe + 2(CH_3)_3N{\cdot}BH_3 \rightarrow 2(CH_3)_3N + 2H_2 + H_2B(\mu\text{-}pzMe)_2BH_2 \quad (1)$$

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