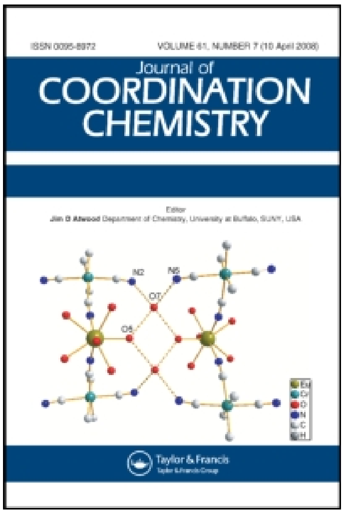


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

KINETICS OF THE SUBSTITUTION REACTIONS OF A Cr(III)-PORPHYRIN

Everly B. Fleischer[a]; M. Krishnamurthy[a]
[a] Chemistry Department, University of California, Irvine, California

To cite this Article Fleischer, Everly B. and Krishnamurthy, M.(1972) 'KINETICS OF THE SUBSTITUTION REACTIONS OF A Cr(III)-PORPHYRIN', Journal of Coordination Chemistry, 2: 2, 89 — 100
To link to this Article: DOI: 10.1080/00958977208072957
URL: http://dx.doi.org/10.1080/00958977208072957

J. Coord. Chem., 1972, Vol. 2, pp. 89–100

KINETICS OF THE SUBSTITUTION REACTIONS OF A Cr(III)-PORPHYRIN

EVERLY B. FLEISCHER and M. KRISHNAMURTHY

Chemistry Department, University of California, Irvine, California 92664

(*Received November* 29, 1971; *in final form March* 14, 1972)

INTRODUCTION

Substitution reactions of low-spin 'd^6' Co(III) cobalamins (derivatives of vitamin B12) are usually rapid.[1] The vitamin B12 model compounds[2] such as dimethylglyoximates of Co(III) are kinetically inert as are most other Co(III) complexes.[3, 4] In order to understand the cause for this, Fleischer *et al.*,[5] carried out some experiments on Co(III)-porphyrins. The substitution reactions of Co(III)-hematoporphyrins were found to be rapid although not as fast as similar reactions in the aquocobalamin system. In furtherance of that study, we have carried out some experiments on meso-tetra-(*p*-sulfonatophenyl)porphinato chromium(III).[6] The substitution reactions of this Cr(III)-porphyrin also were rapid unlike the normal inert Cr(III) complexes. The detailed results are presented in this paper with discussion concerning the basis for the porphyrin molecule labilizing the substitution reactions in the usually inert Co(III) and Cr(III) ions.

EXPERIMENTAL

All the chemicals employed were of reagent grade and used without further purification. A Beckman Century SS model *p*H meter was used for titrations and adjusting *p*H. A Cary model 14 Spectrophotometer was used to follow slow kinetics and for recording titrations. For fast reactions a Durram-Gibson stopped-flow spectrometer was used.

Synthesis of trisodium tetra-(*p*-sulfonatophenyl) porphinato chromium(III) (abbreviated as Cr(III)–TPPS) (Figure 1): Tetraphenylporphine (TPP) was synthesized by the method of Adler[7] and sulfonated and purified by the method of Fleischer.[8] The sodium salt of Cr(III)–TPPS was made by the method of Adler[9] with some modifications.

The sodium salt of TPPS (1.0 g) was taken in 100 ml of dimethylformamide in a 500 ml round-bottomed flask and heated to reflux. Anhydrous chromous chloride (0.2 g) was taken in a stoppered vial and dropped into the flask along with the vial, whose stopper was removed just before the addition. The reaction is fast and complete in a few minutes. The spectrum of a drop of the reaction flux was taken to make certain of the completion of the reaction. If it is incomplete, a further addition (0.2 g) of chromous chloride was made and the reaction mixture was then cooled in an ice-bath. When about 250 ml of acetone was added the sodium salt of Cr(III)–TPPS precipitates. It is filtered, dried and subjected to soxhlet extraction using methanol as the solvent. The final product was isolated from the methanol solution by the removal of solvent on a rotary-evaporator and

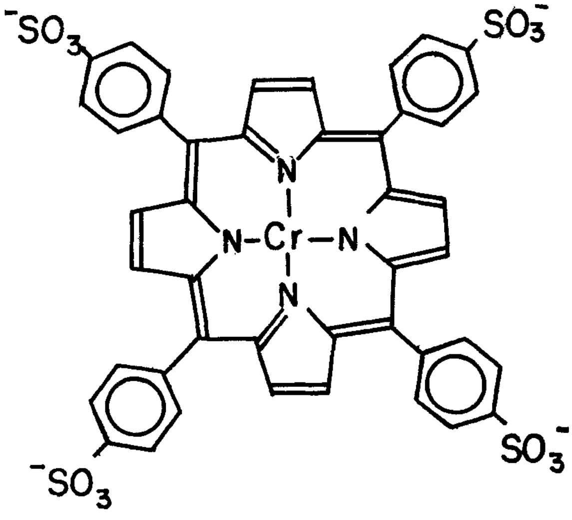


FIGURE 1 Chromium tetra-(*p*-sulfonatophenyl)porphine Cr(III)TPPS

dried in a drying-pistol under vacuum at 100° overnight.

Analysis for $Na_3CrTPPS$: C, H, N and S were analyzed by Chemalytics, Inc., Tempe, Arizona. Chromium was analyzed by activation analysis in this lab.

	C	H	N	S	Cr
Calc. for $Na_3CrC_{44}H_{48}N_4O_{24}S_4$:	41.74	3.79	4.43	10.12	4.11
Found:	41.64	2.99	4.64	10.17	4.76

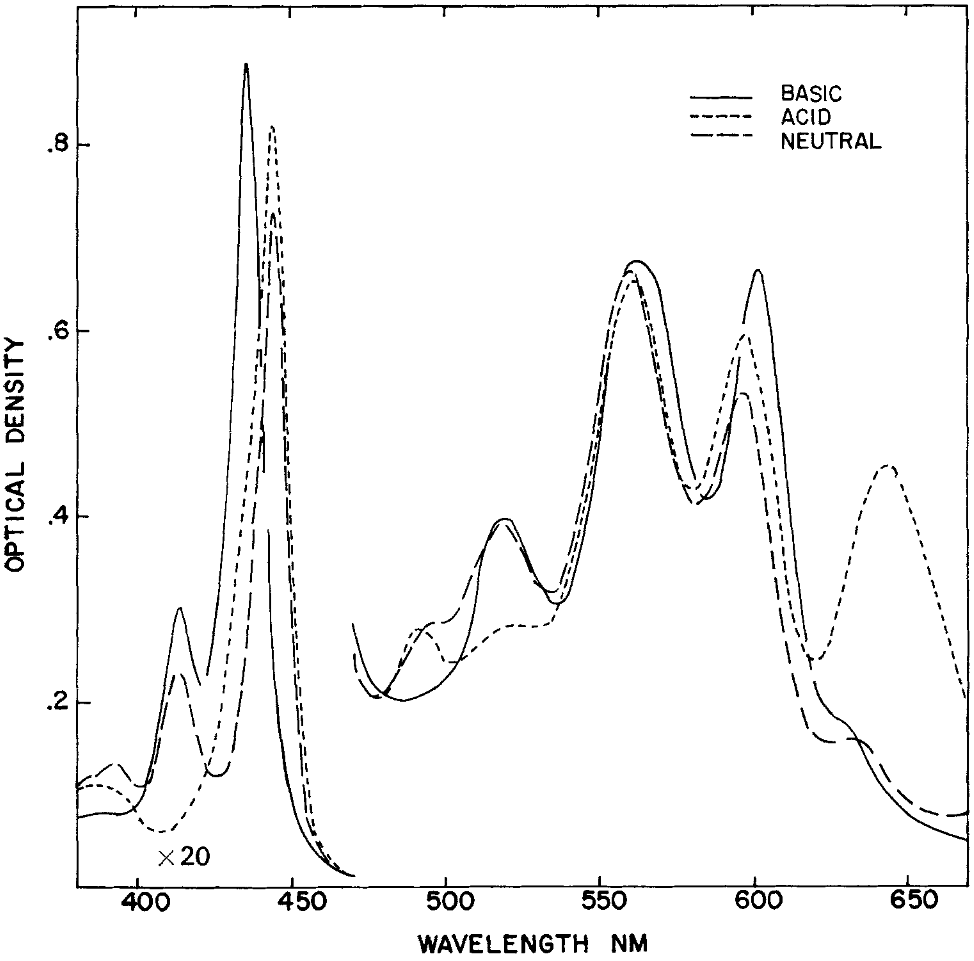


FIGURE 2 Visible absorption spectra of Cr(III)TPPS in neutral ($pH = 7.0$, $\mu = 0.1$ F $NaClO_4$) and basic ($[OH^-] = 0.1$ F) aqueous solutions.

Magnetic susceptibility at ($T = 305°C$): $\mu_{eff} = 3.87$ B.M. by Faraday balance. This demonstrates that the chromium in this compound is Cr(III)—d^3.

Equilibrium studies

Spectrophotometric titrations in the Soret region (380–450 nm) were carried out with various bases keeping metalloporphyrin concentration constant. The number of ligands coordinating with Cr(III)-TPPS is determined from an analysis of this data. The equilibrium constants were calculated either from the plots as discussed below or by using an iterative method program with a PDP-10 computer or by both. In cases where applicable the agreement between different methods is within 10%.

Let MP stand for metalloporphyrin, MPL_n for mixed complex and L for OH^-, CN^-, F^- and pyridine, then

$$\mathrm{MP} + \mathrm{nL} \rightleftharpoons \mathrm{MPL_n}$$

$$K_n = \frac{[\mathrm{MPL_n}]}{[\mathrm{MP}]\,[\mathrm{L}]^{\mathrm{n}}}$$

$$\log K_n = -\mathrm{n} \log [\mathrm{L}] - \log \left[\frac{\mathrm{MP}}{\mathrm{MPL_n}}\right]$$

since $\left(\frac{\mathrm{OD_O} - \mathrm{OD}}{\mathrm{OD} - \mathrm{OD_\infty}}\right) = \frac{(\mathrm{MP})}{(\mathrm{MPL_n})}$,

a plot[8] of log $\left(\frac{\mathrm{OD_O} - \mathrm{OD}}{\mathrm{OD} - \mathrm{OD_\infty}}\right)$

versus −log [L] should be a straight line with a slope of n and intercept of $p\mathrm{K_n}$.

Kinetic studies

All reactions were run under pseudo-first order conditions with excess ligand concentration at 25° ± 0.1° in thermostated cell compartments. The reactions with half-lives of more than a minute were followed in a Cary 14 spetrophotometer. The reactions with half-lives of a minute or less were followed in Durram–Gibson stopped-flow machine. All reactions were found to be first order in metalloporphyrin. The observed rate constant, k_{obs}, for all the kinetic runs was extracted from the plot of log ($\mathrm{OD_t} - \mathrm{OD_\infty}$) versus t. These plots are found to be straight lines over several half-lives and their slope is $k_{\mathrm{obs}}/2.303$. In stopped-flow runs several duplicate runs were made to assure reproducibility before the pictures were taken. In Cary 14 several duplicate runs were also made.

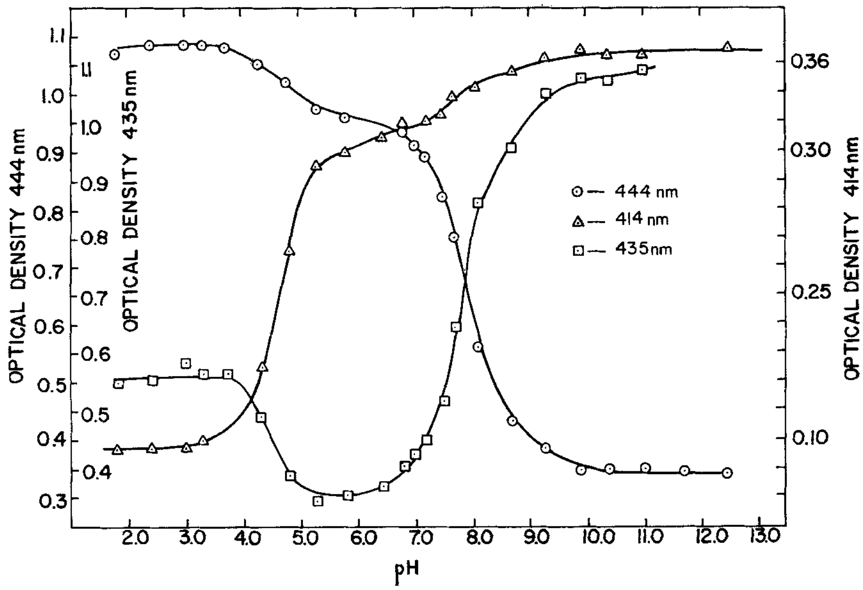
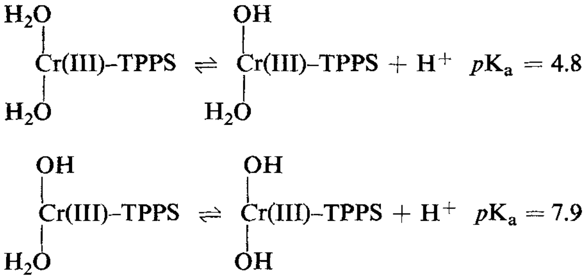


FIGURE 3 Spectrophotometric titration of Cr(III)TPPS with NaOH. Plot of OD at various λ's versus pH.

RESULTS

The spectra of Cr(III)–TPPS in neutral ($p\mathrm{H} = 7.0$, $\mu = 0.1$ F $\mathrm{NaClO_4}$) and in basic [$(\mathrm{OH})^- = 0.1$ F] solutions are shown in Figure 2. The spectrophotometric titration with base is followed in the wavelength region of 460–400 nm. As the titration progresses an isosbestic point is observed at 423nm, which later disappears as another isosbestic point at 440 nm appears. This would indicate that there are three different species possible in solution and that the species which is present in acidic solution transforms into another which further changes into a third as the hydrogen ion concentration of the solution decreases. In Figure 3 the optical density at 414, 435 and 444 nms of these solutions are plotted against their pH. Each of the curves shows two inflections; one in the pH range of 3.5 to 5.0 and another in the range of 7.0–9.0. This is consistent with the above conclusion about the possibility of three species in solution. A plot of log $\left(\frac{\mathrm{OD} - \mathrm{OD_\infty}}{\mathrm{OD_O} - \mathrm{OD}}\right)$ versus pH for each of the two inflections were found to be straight lines with a slope of about one. A potentiometric titration was carried out using $Na_3Cr(III)$–TPPS against standard base had two inflections with one equivalent of base each, in agreement with spectrophotometric titration. The following reactions[10] appear to be most probable and consistent with the data presented above.



$$\begin{array}{c}H_2O\\|\\Cr(III)\text{–}TPPS\\|\\H_2O\end{array} \rightleftharpoons \begin{array}{c}OH\\|\\Cr(III)\text{–}TPPS\\|\\H_2O\end{array} + H^+ \quad pK_a = 4.8$$

$$\begin{array}{c}OH\\|\\Cr(III)\text{–}TPPS\\|\\H_2O\end{array} \rightleftharpoons \begin{array}{c}OH\\|\\Cr(III)\text{–}TPPS\\|\\OH\end{array} + H^+ \quad pK_a = 7.9$$

Spectrophotometric titrations were carried out using a constant concentration of Cr(III)–TPPS and varying concentrations of pyridine and fluoride at pH = 7.0 (TRIZMA–0.05 M) and $\mu = 0.1$ F $NaClO_4$ and cyanide at pH — 11.5 ($\mu = 0.1$ F in NaOH). Figures 4 and 5 show the resulting spectra in the soret band region (390–450 nm).

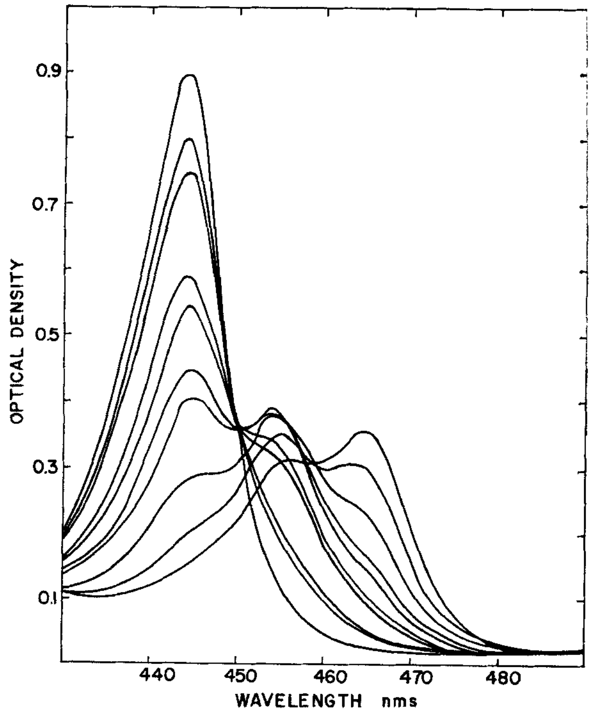


FIGURE 4 Spectrophotometric titrations of Cr(III)TPPS with pyridine. (pH = 7.0, $\mu = 0.1$ F $NaClO_4$)

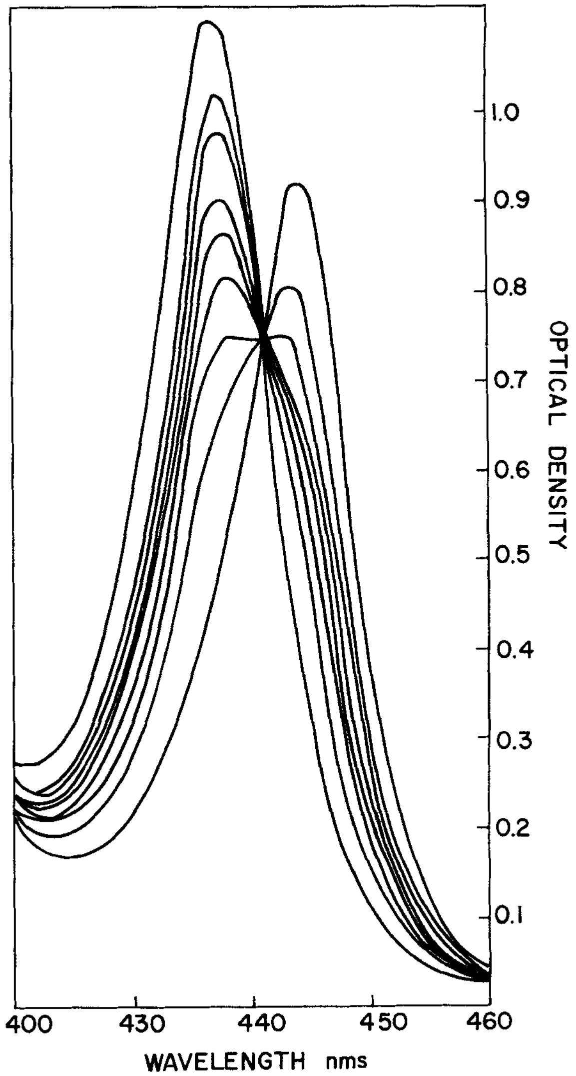


FIGURE 5 Spectrophotometric titration of Cr(III)TPPS with fluoride (pH = 7.0, $\mu = 0.1$ F $NaClO_4$).

In the case of pyridine an isosbestic point is observed at 451 nm, which later, as the titration progresses disappears with the appearance of another isosbestic point at 458 nm. Here again the change over of isosbestic points show the possibility of three species in solution in equilibrium with each other.

In Figure 6, the optical density of various solutions at 451 nm and 458 nm [the isosbestic points for 1:1 and 1:2 (metalloporphyrin: ligand) respectively] and also the λ_{max} of the three species were plotted against the concentration of pyridine. As

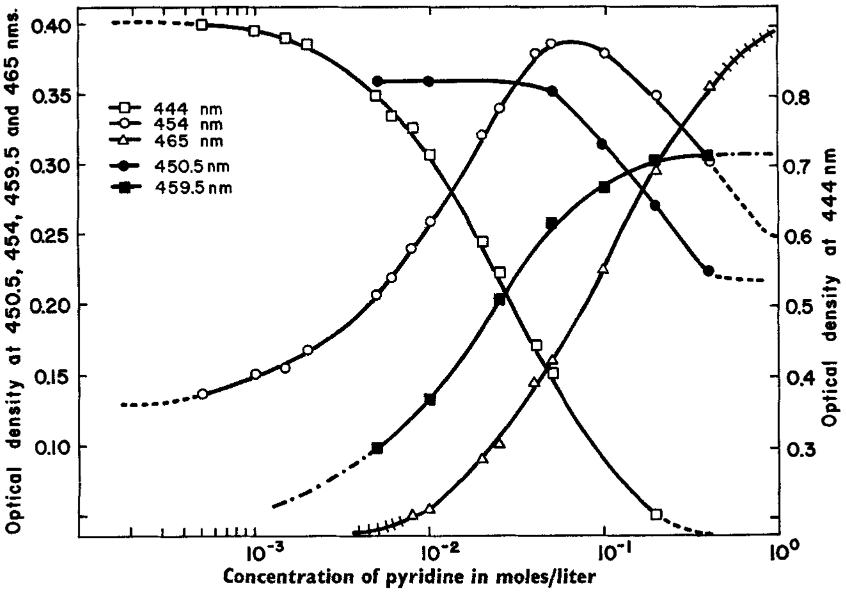


FIGURE 6 Optical density of Cr(III)TPPS at various wavelengths plotted against pyridine concentration.

one can see, as long as only the metalloporphyrin and the 1:1 pyridine complex are in equilibrium the optical density at 451 nm remains constant and it falls off as 1:2 pyridine complex began to form.

In the fluoride titrations an isosbestic point is observed at 441 nm. In the case of cyanide, as in the case of pyridine, an isosbestic point observed initially at 444 nm vanishes with the appearance of another at 463 nm. In Figures 7 and 8 the optical density of different solutions were plotted against the concentration of the ligands fluoride and cyanide respectively.

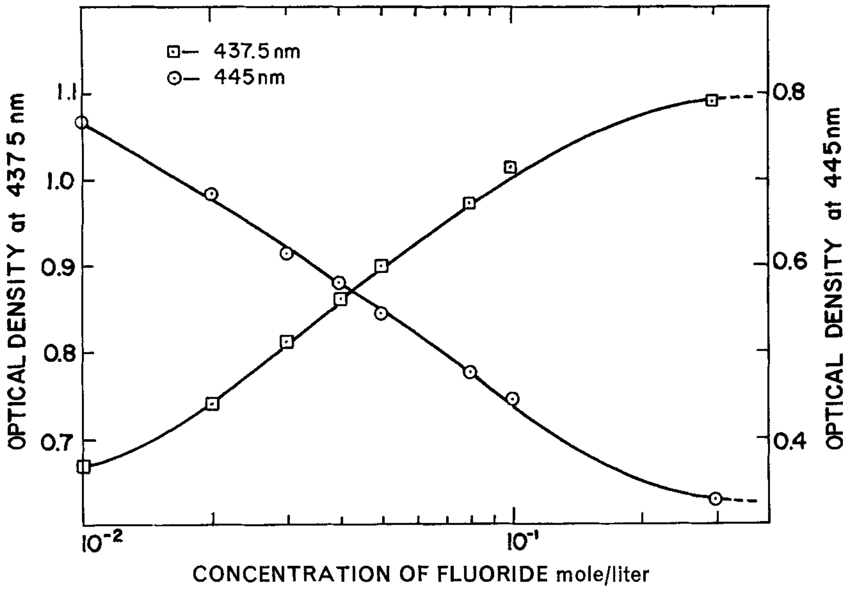


FIGURE 7 Optical density of Cr(III)TPPS at various wavelengths plotted against fluoride concentration.

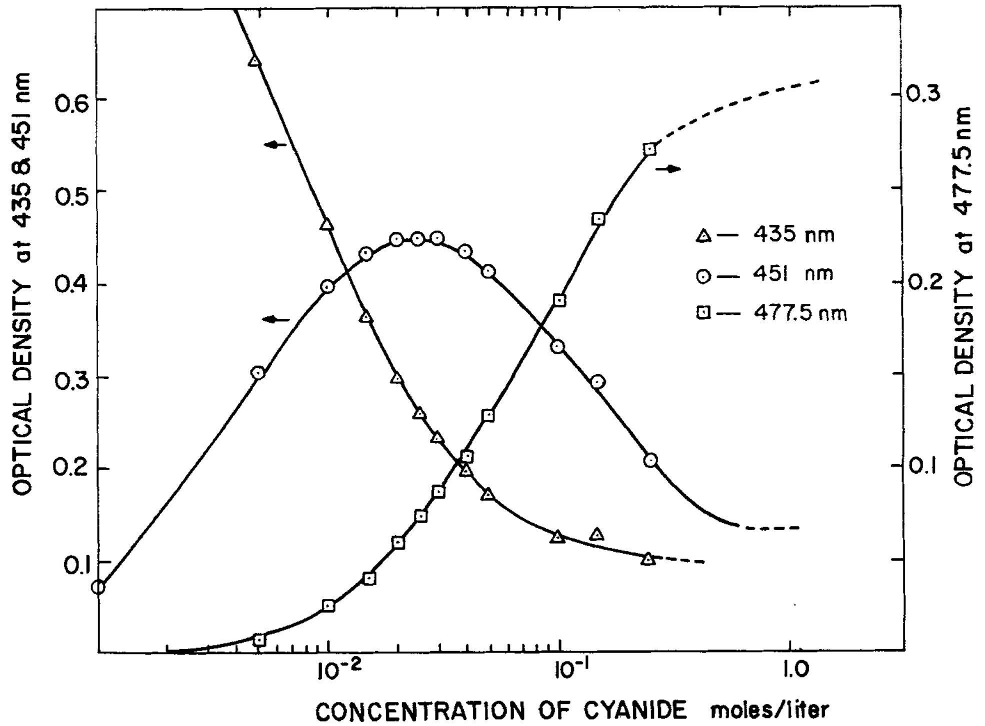
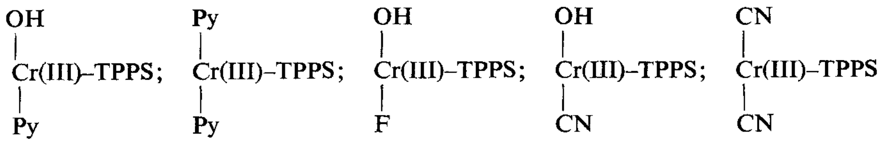


FIGURE 8 Optical density of Cr(III)TPPS at various wavelengths plotted against cyanide concentration.

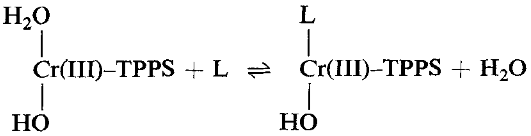
Besides the Cr(III)-TPPS and its conjugate bases, the other complex species may be formulated[11] as:



$$\underset{\text{Py}}{\overset{\text{OH}}{\text{Cr(III)–TPPS}}};\quad \underset{\text{Py}}{\overset{\text{Py}}{\text{Cr(III)–TPPS}}};\quad \underset{\text{F}}{\overset{\text{OH}}{\text{Cr(III)–TPPS}}};\quad \underset{\text{CN}}{\overset{\text{OH}}{\text{Cr(III)–TPPS}}};\quad \underset{\text{CN}}{\overset{\text{CN}}{\text{Cr(III)–TPPS}}}$$

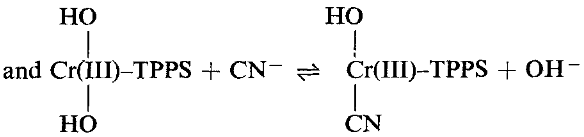
The plots of $\log\left(\frac{OD - OD_\infty}{OD_0 - OD}\right)$ against $\log [L]$ for pyridine, fluoride and cyanide all yield straight lines with slopes of 1.0. A typical plot for fluoride at 445 nm is shown in Figure 9. The formation constants for the species postulated calculated by the computer from the data of Figures 6, 7, and 8 and those obtained from the plots similar to Figure 9 agree very well and are presented in Table I.

Kinetic Studies: The following substitution reactions were studied.[12]



$$\underset{\text{HO}}{\overset{\text{H}_2\text{O}}{\text{Cr(III)–TPPS}}} + \text{L} \rightleftharpoons \underset{\text{HO}}{\overset{\text{L}}{\text{Cr(III)–TPPS}}} + \text{H}_2\text{O} \tag{1}$$

where L = pyridine and F^-



$$\text{and } \underset{\text{HO}}{\overset{\text{HO}}{\text{Cr(III)–TPPS}}} + \text{CN}^- \rightleftharpoons \underset{\text{CN}}{\overset{\text{HO}}{\text{Cr(III)–TPPS}}} + \text{OH}^- \tag{2}$$

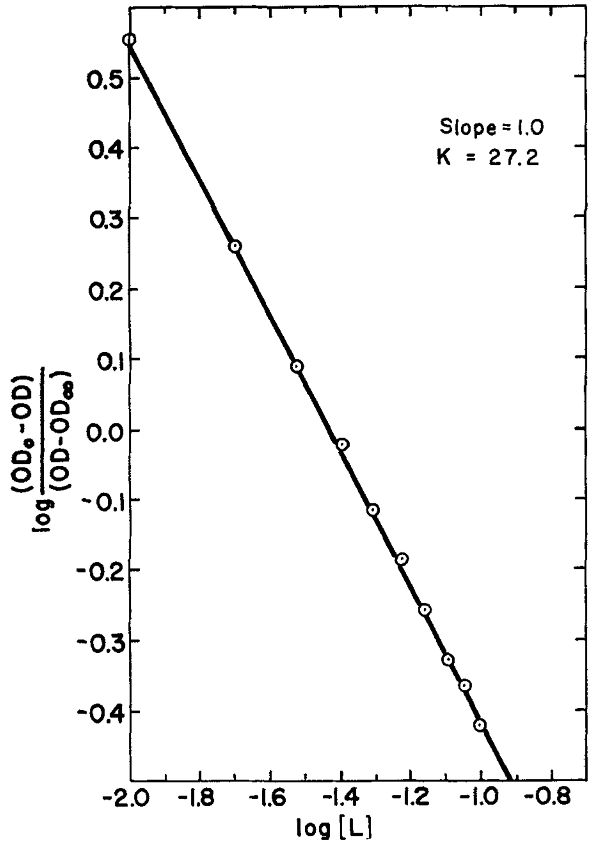


FIGURE 9 Plot of $\log\left(\frac{OD - OD_\infty}{OD_O - OD}\right)$ versus log [F−] for the Cr(III)TPPS-fluoride system at 445 nm.

Substitution reactions of pyridine and cyanide were studied in Durram–Gibson stopped-flow machine while that of fluoride was studied in a Cary 14.

Figure 10 shows a typical $\log(OD_t–OD_\infty)$ versus time plot, where OD_t and OD_∞ are optical density at time 't' and optical density after the reaction attained equilibrium. The observed rate constants are listed in Table II. A plot of k_{obs} versus [ligand] for the pyridine case is presented in Figure 11.

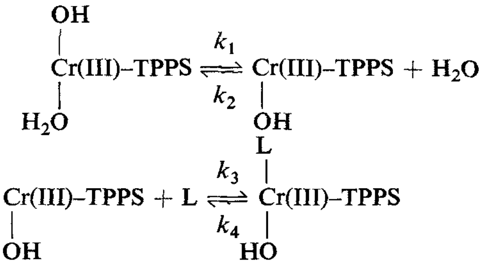
The pseudo first-order macroscopic rate constants. k_{obs}, all obeyed the law

$$\frac{d\ln(OD - OD_\infty)}{dt} = -k_{obs} = \frac{d\ln\left[\underset{OH}{\overset{OH_2}{(\mathrm{Cr(III)–TPPS})}} - \underset{OH}{\overset{OH_2}{(\mathrm{Cr(III)–TPPS})_\infty}}\right]}{dt}$$

$$k_{obs} = \alpha + \beta[L]$$

Assuming that the previously studied cobalt porphyrin systems[5] and the chromium porphyrin react similarily, the most likely mechanism is an SN_1 or D type mechanism.[13]

Mechanism.



$$\underset{H_2O}{\overset{OH}{\mathrm{Cr(III)–TPPS}}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{OH}{\mathrm{Cr(III)–TPPS}} + H_2O$$

$$\underset{OH}{\mathrm{Cr(III)–TPPS}} + L \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{HO}{\overset{L}{\mathrm{Cr(III)–TPPS}}}$$

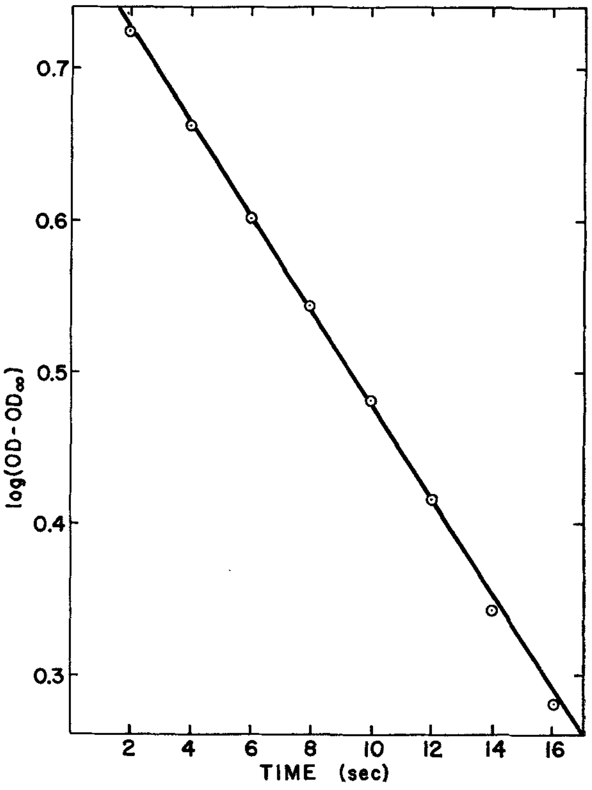


FIGURE 10 Kinetic run for reaction of Cr(III)TPPS with pyridine; plot of log $(OD_\epsilon - OD_\infty)$ versus time.

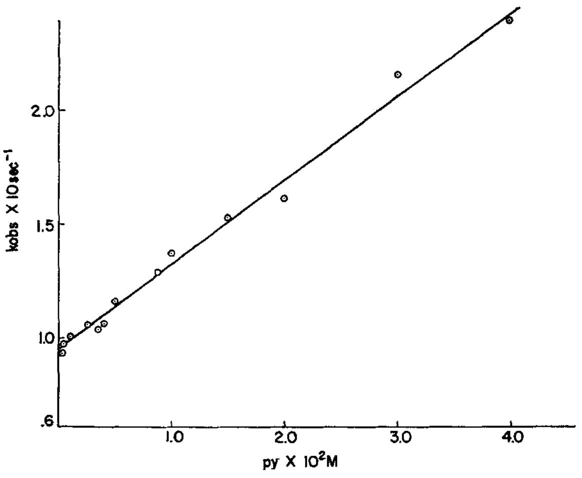


FIGURE 11 The k_{obs} plotted against the pyridine concentration for the reaction of Cr(III)TPPS with pyridine.

or this mechanism, $k_{obs} = \dfrac{k_1k_3[L] + k_2k_4}{k_2 + k_3[L]}$

But if the term $k_3[L] \ll k_2$, the equation reduces to $k_{obs} = \dfrac{k_1k_3}{k_2}[L] + k_4$;

where $\beta = \dfrac{k_1k_3}{k_2}$ and $\alpha = k_4$. Also $K_1 = \dfrac{k_1k_3}{k_2k_4} = \beta/\alpha$.

The case $k_3[L] \ll k_2$ could happen either due to [L] being small as in pyridine and cyanide reactions or k_3 being small as in fluoride reactions or both these circumstances holding. Raising the concentrations of pyridine or cyanide could lead to a situation, where $k_3[L] \approx k_2$, and thereby substantiate the proposed mechanism. But unfortunately raising the concentration would lead to a complicated kinetics as the metalloporphyrin : ligand (1:2) species would also form. The ruling out of a

TABLE I

Ligand [L]	*p*H	wavelength in nm	μ	composition Cr(III)-TPPS: [L]	K[a]
F^-	*p*H: 7.0 (tris)	437.5	0.1 F ($NaClO_4$ +KF)	1:1	26.7 ± 0.8
	*p*H: 7.0 (tris)	445	0.1 F ($NaClO_4$ + KF)	1:1	27.2 ± 0.8 27.2[b]
Pyridine	*p*H: 7.0 (tris)	444	0.1 F ($NaClO_4$)	1:1	49 ± 4
	*p*H: 7.0 (tris)	454	0.1 F ($NaClO_4$)	1-2	4.7 ± 0.66
	*p*H: 7.0 (tris)	464	0.1 F ($NaClO_4$)	1:2	6.1 ± 0.46
CN^-	$[OH^-] = 10^{-2} - 10^{-1}$ (*p*H = 11.5)	435	0.1 F [NaCN+ NaOH]	1:1	151 ± 5 155[b]
	$[OH^-] = 10^{-2} - 10^{-1}$ (*p*H = 11.5)	451	0.1 F [NaCN+ NaOH]	1:1	148 ± 9
	$[OH^-] = 10^{-2} - 10^{-1}$ (*p*H = 11.5)	451	0.1 F [NaCN+ NaOH]	1:2	14.5 ± 1.1
	$[OH^-] = 10^{-2} - 10^{-1}$ (*p*H = 11.5)	447.5	0.1 F [NaCN+ NaOH]	1:2	11.8 ± 0.9 14.3[b]

[a] Equilibrium constants evaluated by computer except where noted; all at temp. 25°C.
[b] Equilibrium constants evaluated graphically.

TABLE II

[a] Pseudo-first-order rate constants for the anation reactions

L	*p*H or $[OH^-]$	μ	concentration of L moles/liter	k_{obs} sec^{-1}
Pyridine	7.0 (tris)	0.1 F ($NaClO_4$)	2.5×10^{-4}	9.38×10^{-2}
			5.0×10^{-4}	9.77×10^{-2}
			1.0×10^{-3}	1.01×10^{-1}
			2.5×10^{-3}	1.06×10^{-1}
			3.5×10^{-3}	1.04×10^{-1}
			4.0×10^{-3}	1.06×10^{-1}
			5.0×10^{-3}	1.16×10^{-1}
			8.75×10^{-3}	1.29×10^{-1}
			1.0×10^{-2}	1.37×10^{-1}
			1.5×10^{-2}	1.53×10^{-1}
			2.0×10^{-2}	1.61×10^{-1}
			3.0×10^{-2}	2.16×10^{-1}
			4.0×10^{-2}	2.41×10^{-1}
F^-	7.0 (tris)	1.0 F (KNO_3 + KF)	1.0×10^{-2}	2.25×10^{-4}
			2.0×10^{-2}	2.90×10^{-4}
			3.0×10^{-2}	3.15×10^{-4}
			5.0×10^{-2}	3.90×10^{-4}
			7.0×10^{-2}	5.13×10^{-4}
			1.0×10^{-1}	7.10×10^{-4}
			2.0×10^{-1}	1.20×10^{-3}
			3.0×10^{-1}	1.58×10^{-3}
			4.0×10^{-1}	2.43×10^{-3}
			5.0×10^{-1}	3.13×10^{-3}
CN^-	$[OH^-] = 10^{-2}$ F	0.1 F [NaCN + $NaClO_4$ + NaOH]	2.0×10^{-4}	4.28×10^{-3}
			4.0×10^{-4}	4.62×10^{-3}
			5.0×10^{-4}	4.57×10^{-3}
			1.0×10^{-3}	5.98×10^{-3}
			2.0×10^{-3}	7.39×10^{-3}
			3.0×10^{-3}	8.33×10^{-3}
			4.0×10^{-3}	8.78×10^{-3}
			5.0×10^{-3}	1.07×10^{-2}
			6.0×10^{-3}	1.20×10^{-2}
			7.0×10^{-3}	1.37×10^{-2}
			1.0×10^{-2}	1.80×10^{-2}

[a] Porphyrin concentration for the kinetic studies: 1.95×10^{-6} F. All reactions were carried out at 25°; Py and F^- reactions followed at 444 nm; CN^- reactions followed at 451 nm. Runs were reproducible within 5%.

reversible SN_2 mechanism cannot be done with the data at hand but only by comparison with the Cobalt(III) porphyrin anation reactions. The "ion pair" or interchange mechanism is unlikely as the K ion-pair for the —3 charged Cr(III)–TPPS species and F^- should be very small indeed.

The rate constants for each of the reactions are given in Table III. The rate of decomposition of the product is also significant in agreement with equilibrium studies which indicated that the formation constants are not large.

The fluoride substitution reaction was also studied as a function of ionic strength. The pseudo first order rate constants at various ionic strengths are listed in Table IV. A plot of log (k_{obs}) versus ($\sqrt{\mu}$) gives a straight line of slope 0.33. Since the ionic strengths are too high to be used in any interpretation using the Delye–Huckel theory, no further comments will be made on this point.

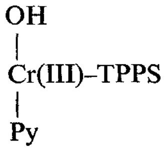
The acid-catalyzed dissociation of  $\overset{\displaystyle OH}{\underset{\displaystyle Py}{Cr(III)\text{–}TPPS}}$ was also studied.

TABLE III

Rate constants for substitution reactions of CrTPPS

Ligand	$\alpha_{sec}{}^{-1}$	$\beta_{sec}{}^{-1}M^{-1}$	K_1 kinetic	K_1 spectrophotometric
Pyridine	$9.52 \pm 0.18 \times 10^{-2}$	3.73 ± 0.11	39	49
F^-	$1.17 \pm 0.50 \times 10^{-4}$	$5.72 \pm 0.21 \times 10^{-4}$	49	27
CN^-	$4.13 \pm 0.18 \times 10^{-3}$	1.35 ± 0.04	327	150

[a] These constants are obtained by a least-square analysis of the data in Table II.

TABLE IV

Effect of changing ionic-strength on reaction rate

μ in F.KNO$_3$	k_{obs} sec^{-1}
0.1	1.20×10^{-4}
0.2	1.32×10^{-4}
0.3	1.48×10^{-4}
0.5	1.64×10^{-4}
0.6	1.75×10^{-4}
0.7	1.83×10^{-4}
0.8	1.87×10^{-4}
0.9	2.00×10^{-4}
1.0	2.24×10^{-4}

[a] Metalloporphyrin conc.: 1.45×10^{-6}F; $[F^-] = 1.0 \times 10^{-2}$F; temperature = 25°C; pH = 7.0 (TRIS)

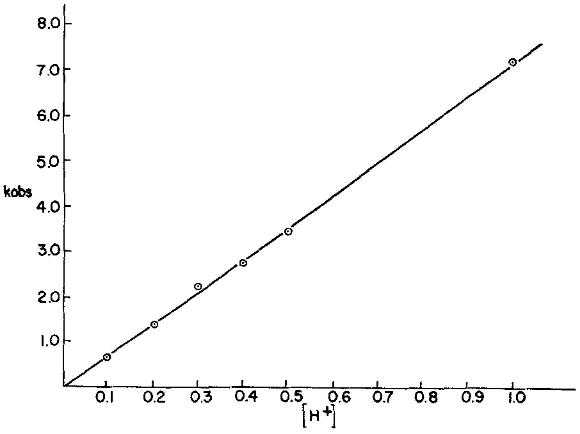
The observed pseudo-first order constants are listed in Table V and they are found to obey the rate law $k_{obs} = k_d\,[H^+]$. From a plot of k_{obs} versus $[H^+]$, Figure 12, k_d was found to be $7.26 \times 10^{-3}M^{-1}\,sec^{-1}$.

TABLE V

*Acid-hydrolysis of [Cr(TPPS)Py(H$_2$O)]

$[H^-]$ in M	k_{obs} sec^{-1}
0.1	6.60×10^{-4}
0.2	1.40×10^{-3}
0.3	2.27×10^{-3}
0.4	2.75×10^{-3}
0.5	3.47×10^{-3}
1.0	7.24×10^{-3}

*[Cr(TPPS)(H$_2$O)$_2$]; 1.45×10^{-6}F; [Py] = 2.5×10^{-2}M; μ = 1.0F(HClO$_4$ and NaClO$_4$) T = 25°



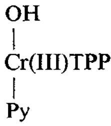


FIGURE 12 Reaction of $\overset{OH}{\underset{Py}{Cr(III)TPPS}}$ with acid; plot of k_{obs} versus acid concentration.

DISCUSSION

Since the earlier discovery of labile substitution reactions of Co(III)-porphyrins by Fleischer *et al.*,[5] several other instances of labile substitution reactions of Co(III) complexes have been reported. In comparison to the extensive investigations on the substitution reactions of Co(III), there are relatively fewer reports on the substitution reactions of Cr(III) complexes. It is interesting to compare the rates of these anation reactions of Cr(III)-TPPS with those of $Cr(H_2O)_6{}^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$ with thiocyanate ion. The k_1k_3/k_2 for an SN$_1$ mechanism for the reaction of $Cr(H_2O)_6{}^{3+}$ with thiocyanate is found to be about $1.9 \times 10^{-6}M^{-1}sec^{-1}$ (at a μ of approximately 0.3 F and 25°C).[14] Similarly for the reaction of $[Cr(NH_3)_5H_2O]^{3+}$ with CNS$^-$, the

k_1k_3/k_2 was found to be 5.0×10^{-5} M$^-$ sec^{-1} and $_4k$ was 3.3×10^{-7} sec^{-1} (at 29.9°C and μ of 0.1 F).[16] These indicate that the Cr(III)-porphyrin reactions are 10^3 to 10^4 times faster than any of these. Although the labilizing effect of the porphyrin ligand is not as great as in the case of Co(III), where the reactions are as much as 10^6 times faster than usual, there is a clear labilizing effect on chromium(III).

In purely qualitative terms there are three reasonable explanations that can be given as the cause of this observed lability of metalloporphyrins. (I). An internal redox of the type $M^{+++}P \rightleftharpoons M^{++}P^+$, observed by Wolberg and Manassen,[16] resulting in a lower oxidation state. This has been offered as a possible explanation earlier. Such a possibility can be ruled out in the case of the chromium(III) porphyrin as its reduction to Cr(II) is very difficult if not impossible to effect.[17] (II) The trivalent metallic ions, such as Cr(III), are out of the plane of the porphyrin as in Fe(III)TPPCl[18] Co(III)TPPCl,[18] and Mn(III)TPPCl.[19] The metal is then in a pentacoordinate geometry that closely resembles the pentacoordinate intermediate in SN_1 reactions, leading to faster substitution reactions than in a normal octahedral geometry. To put it in another way, the metal ion is in a geometry which already lies well along the reaction coordinate. While this explanation seems plausible, it relies on the assumption that the metal atom lies out of plane and that the system is five coordinate, a point which needs to be proved.

(III) Finally, the more reasonable of all the three seems to be that there is extensive π-bonding between metal d_{yz}, d_{xz} and porphyrin π^*-orbitals. Such a π-bonding between lowest unfilled antibonding ligand π orbital and metal "d" orbitals has been suggested in the case of Fe(III)TPPCl by nmr studies.[20, 21]

The effect of the strong interaction between the porphyrin orbitals and the metal ion orbitals leads to a loss of "d^6" and "d^3" metal ion character for the Co(III) and Cr(III) ions. This necessity to choose a strongly delocalized model of the electronic configuration of the complex as compared to the usual metal-ion centered description may be the key to the labilization effect of the porphyrin. Thus whenever a complex has a delocalized bonding description necessary to describe its electronic properties we may have a system that will labilize Co(III) and Cr(III) systems. Presumably this type of π interaction is the cause for the unusually rapid substitution reactions of aquocobalamin,[1, 25] iron-phthalocyanines,[22] ruthenium porphyrins[23] and cobalt(III) dithiolenes.[24]

It is clear that a vague explanation is available for the rationalization of the porphyrin labilization but that a detailed understanding of the problem is not yet available.

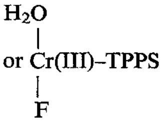
ACKNOWLEDGEMENT

One of the authors (M. K.) wishes to express his gratitude to Dr. Allen E. Gebala for many helpful discussions and encouragement throughout the period this work was carried out. This work was supported by grants from the NIH and NSF.

REFERENCES

1. W. C. Randall and R. A. Alberty, *Biochemistry* **5,** 3189 (1966); **6,** 1520 (1967).
2. G. N. Schrauzer, *Accounts Chem. Res.* **1,** 97 (1968).
3. D. N. Hague and J. Halpern, *Inorg. Chem.* **6,** 2059 (1967).
4. H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.* **7,** 2535 (1968).
5. E. B. Fleischer, S. Jacobs and L. Mestichelli, *J. Amer. Chem. Soc.* **90,** 2527 (1968).
6. E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.* **93,** 3784 (1971).
7. A. Adler, F. R. Lango, J. D. Finarelli, J. Goldmacher, J. Assour, J. Kovsakoff, *J. Org. Chem.* **32,** 476 (1967).
8. E. B. Fleischer, J. M. Palmer, T. S. Srivastava and A. B. Chatterjee, *J. Amer. Chem. Soc.* **93,** 3162 (1971).
9. A. D. Adler, F. Lango, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.* **32,** 2443 (1970).
10. Although all the available pieces of information suggest the species postulated, one cannot rule out the possibility of the Cr(III)-TPPS species existing as penta coordinate with only one water coordinating axially. This possibility is being further investigated by nmr techniques.
11. As equilibrium is attained in few minutes one might suggest these species being hydrogen bonded outer sphere complexes. In addition to the data presented, the following observations negate such a possibility.
    (a). The spectrum of Cr(III)–TPP Cl[9] in methanol is similar to that of Cr(III)–TPPS. Spectrophotometric titration of Cr(III)–TPP Cl in methanol against pyridine and thiocyanate were carried out. Thiocyanate, which forms only a very weak 1:1 complex in aqueous solutions, forms a 1:2 complex in methanol, presumably it could not compete with water. Pyridine, which forms a 1:2 complex in aqueous solutions, forms only a 1:1 complex, whose spectrum exactly resembles that in aqueous solution: Presumably, the dielectric constant of the medium prevents the formation of a polar species.
    (b). The spectra in the Soret band region of Cr(III)–TPP(Py) and Cr(III)–TPP(CN) (synthesized in this laboratory) agree with those observed in aqueous solution with the CrTPPS.
    In conjunction with acid dissociation constants of Cr(III)–TPPS and the *p*H at which the titrations were carried out, these species are formulated as water being substituted by the ligand initially. The greater affinity of

Cr(III) for hydroxide ion than for fluoride, etc., also supports this assumption. Although it just may be possible that hydroxide ion is substituted by the entering ligand. While in the case of pyridine and cyanide there can be no doubt about the final species being 1:2 (MP:L) an ambiguity exists about fluoride as to whether the final species is the one postulated above or Cr(III)–TPPS when two hydroxide ions coordinate the soret band is at 435 nm just as the final species in fluoride titration, which further suggests that the hydroxide and fluoride are coordinating rather than water and fluoride.



$$\underset{\displaystyle F}{\overset{\displaystyle H_2O}{\overset{|}{\underset{|}{\mathrm{Cr(III)–TPPS}}}}}$$

12. It is assumed that 1:2 (metalloporphyrin:ligand) species do not form in these kinetic runs as the highest concentration of the ligand used in kinetic runs is much less than that needed to form 1:2 species according to Figures 4 and 5.

13. F. Basolo and R. G. Pearson *Mechanism of Inorganic Reactions,* 2nd Ed., John Wiley and Sons, N.Y., 1967, p. 196.
    C. H. Langford and H. B. Gray, *Ligand Substitution Processes*, W. A. Benjamin, Inc., New York, N.Y., 1966, p. 15.
14. C. Postmus and E. L. King, *J. Phys. Chem.* **59,** 1216 (1955).
15. N. V. Duffy and J. E. Earley, *J. Amer. Chem. Soc.* **89,** 272 (1967).
16. A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.* **92,** 2982 (1970).
17. (a) L. Edwards, D. H. Dolphin, M. Gouterman and A. Adler, *J. Mol. Spectroscopy* **38,** 16 (1971); (b) Our experiments to reduce Cr(III)TPPS were not successful either.
18. E. B. Fleischer, *Account Chem. Research* **3,** 105 (1970).
19. Thesis, Betty Mei Horng Lee Chem, *Structure Determination of Manganese Tetraphenylporphyrin,* Michigan State, 1970.
20. D. R. Eaton and E. A. LaLancette, *J. Chem. Phys.* **41,** 3534 (1964).
21. A. P. Gurinovitch, A. N. Sevchenko and K. N. Solov'ev in *Spectroscopy of Chlorophyll and related compounds*, pp. 114–22) 1968. U.S. AEC Translation (1971), AEC-TR-719.
22. (a) J. G. Jones and M. V. Twigg, *Inorg. Chem.* **8,** 2120 (1969);
    (b) H. P. Bennetto, J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta.* **4,** 180 (1970).
23. M. Tsutsui, D. Ostfeld and L. Hoffman, *J. Amer. Chem. Soc.* **93,** 1821 (1971).
24. H. A. Tsiang and C. H. Langford, *Canadian J. Chem.* **48,** 2776 (1970).
25. D. G. Dewitt, M. J. Hynes, P. Sweigart, *Inorg. Chem.* **10,** 196 (1971). G. Costa, G. Mestroni, G. Tauzher, D. M. Goodall, M. Green and H. A. O. Hill, *Chem. Comm.* **34,** (1970).
    T. Sakurai, John P. Fox, and Lloyd L. Ingraham, *Inorg. Chem.* **10,** 1105 (1971).