Equilibrium Constants for the Axial Coordination of *meso*-Tetraphenylporphinatomanganese(II) and -chromium(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The reaction of molecular oxygen at -78 °C in toluene with five-coordinate *meso*-tetraphenylporphinatomanganese(II) complexes, Mn(II)-(TPP)(L), where L represents a neutral N-, P-, or S-donor ligand, is described. Spectrophotometric titrations of toluene solutions of these complexes at -78 °C with molecular oxygen confirm the stoichiometry of the porphinatomanganese dioxygen complexes as Mn(TPP)(O$_2$). Equilibrium constants for the reaction are reported. Equilibrium constants for axial ligation reactions of Cr(III) and Mn(II) tetraphenylporphinato complexes are reported and the results discussed.

Variations in the biological role of the naturally occurring heme proteins are intimately associated with changes in the axial ligation of the heme moiety. Relevant to our understanding of the mechanism of the action of the heme proteins is an understanding of the manner in which axial ligation affects the electronic structure and reactivity of a metalloporphyrin system. Such studies are particularly important since the reactivities of the metal center in some metalloporphyrin complexes have been shown to differ significantly from the reactivities that would be predicted by comparison with Werner-type complexes containing the same metal center. For example, whereas classical Cr(III) and Co(III) Werner-type complexes are known to be substitution inert,[1] substitution of axial ligands has been shown to occur quite rapidly in Cr(III)[2] and Co(III)[3] metalloporphyrin complexes.

Recently we have been engaged [4,5] in studying the reactions of some metalloporphyrin systems with both neutral nitrogen-, phosphorus-, and sulfur-donor ligands. We have further been investigating the chemical and spectroscopic properties of the dioxygen carrying porphinato complexes of iron(II)[6] and manganese(II).[5] In this paper we report on the equilibrium constants for the bonding of dioxygen to *meso*-tetraphenylporphinatomanganese(II) complexes, as well as on the relative affinities of neutral donor ligands to *meso*-tetraphenylporphinatomanganese(II) and chromium(III) complexes.

NOMENCLATURE

The abbreviations used in this paper are: TPP, the *meso*-tetraphenylporphinato dianion; L represents a neutral ligand such as pyridine; py, pyridine; 1-MeIm, 1-methylimidazole; *sec*-BuNH$_2$, *sec*-butylamine; 3,4-lut, 3,4-lutidine(3,4-dimethylpyridine); 4-CN-py, 4-cyanopyridine; Co(benacen), *N,N′*-ethylenebis(benzoylacetiminato)cobalt(II); (n-Bu)$_3$P, tri-n-butylphosphine.

EXPERIMENTAL

Reagents. Toluene was reagent grade and was distilled under N$_2$ from sodium-benzophenone ketyl immediately prior to use. Acetone was Baker Spectrophotometric grade. Pyridine and 1-methylimidazole were dried over BaO and KOH respectively, and were distilled prior to use. The 4-cyanopyridine was recrystallized from benzene/heptane several times. The N$_2$ was Matheson pre-purified grade and was passed through a Ridox column to remove O$_2$ and water. Gaseous dioxygen

was Airco Ultra Pure (containing less than 2 ppm H_2O) and was further dried by passing the gas over molecular sieves at -130 °C. All other reagents were reagent grade and were used as received without further purification.

Syntheses. *meso*-Tetraphenylporphine (TPPH$_2$) was prepared by the method of Adler and co-workers[7] and was purified (to remove any *meso*-tetraphenylchlorin impurity) by refluxing[8] with 2,3-dichloro-5,6-dicyanobenzoquinone in CH_2Cl_2. Chloro-*meso*-tetraphenylporphinatochromium(III), Cr(III)(TPP)(Cl), was prepared and purified using literature methods.[4] Chloro-*meso*-tetraphenylporphinatomanganese(III), Mn(III)(TPP)(Cl), was synthesized and reduced to the porphinatomanganese-(II) complex pyridine-*meso*-tetraphenylporphinatomanganese(II), Mn(II)(TPP)(py), using published procedures.[5] All the above complexes were characterized by comparison with published spectra. Suitable analyses were obtained for Cr(III)(TPP)(Cl) and Mn(II)(TPP)(py). The base-free complex *meso*-tetraphenylporphinatomanganese(II), Mn(II)(TPP), was prepared from the corresponding monopyridine adduct, Mn(II)(TPP)(py), by heating the solid material in a vacuum line at 250 °C. The loss of pyridine from the solid was monitored with a thermocouple vacuum gauge. Heating was continued until the vacuum gauge indicated that no further pyridine was being evolved. In all instances, heating for 2 h resulted in complete removal of pyridine. *Anal.* Calc. for Mn($C_{44}H_{28}N_4$): C 79.15; H 4.23; N 8.39. Found: C 79.67; H 4.34; N 8.51.

The series of complexes Mn(II)(TPP)(L), where L represents a nitrogen, phosphorus, or sulfur-donor ligand, were prepared by two different methods, depending on the ligand, L. Where L equals 1-MeIm, 4-CN-py, or *sec*-BuNH$_2$, the complexes were prepared by the reduction of Mn(III)(TPP)(Cl) with NaBH$_4$ in the presence of excess ligand, L, using a similar procedure with that in Ref. 5 for the preparation of Mn(II)(TPP)(py). The complex Mn(II)(TPP)(L), where L is 3,4-lutidine, (n-Bu)$_3$P, thioanisole, and (C_2H_5O)$_3$P were prepared by dissolving the base-free complex Mn(II)(TPP) in a toluene solution containing the ligand, L, and precipitation of the solid Mn(II)(TPP)(L) by the addition of either CH_3OH (for L equal to 3,4-lutidine or (n-Bu)$_3$P), hexane (for L equal to thioanisole) or isooctane (for L equal to (C_2H_5O)$_3$P). The solids were washed several times with the solvent used for precipitation and were dried *in vacuo* overnight. In all cases, optical spectra of the complex Mn(II)(TPP)(L) dissolved in a toluene solution containing approximately 10 °/$_o$ v/v of the ligand, L, were identical with the spectra obtained from a toluene solution of the complex at -78 °C, when correction is made for solvent contraction. Cooling to -78 °C is necessary since dissolving

Mn(II) (TPP)(L) at room temperature under N$_2$ results in the formation of an equilibrium mixture of Mn(II) (TPP) and Mn(II)(TPP)(L) in solution.

Equilibrium constant determinations. Equilibrium constants for the dioxygen replacement reaction

$$Mn(II)(TPP)(L) + O_2 \overset{K^{Mn}}{\rightleftharpoons} Mn(TPP)(O_2) + L \qquad (1)$$
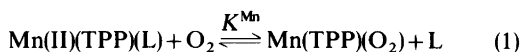
were measured in toluene at -78 °C by a spectrophotometric titration technique using a 4 cm path length low-temperature visible cell.[9] Aliquots of O$_2$ were added from a gas manifold to the system *via* a gas tight valve and the solution was stirred until equilibrium was obtained (~ 5 min). The pressure of dioxygen above the solution was determined with an MKS Baratron, Type 221 Series pressure gauge having a range of $0-1000$ Torr. Pressures were obtained in a digital format from a Data Precision digital voltmeter (Model No. 1450). Values for K^{Mn} were then determined by monitoring the optical spectra of the solution at different pressures of O$_2$.

Data from the spectrophotometric titration were fitted to eqn. (2), where

$$\log \frac{y^2}{1-y} = n \log P_{O_2} + \log K^{Mn}([Mn(TPP)(L)]_{total}) \qquad (2)$$

$[Mn(TPP)(L)]_{total}$ represents the initial concentration of the manganous prophyrin complex. In this expression y is the fraction of manganese(II) sites binding dioxygen, *i.e.*, $y = [Mn(TPP)(O_2)]/[Mn(TPP)(L)]_{total}$ which can be related to the experimentally observed absorbances by the relation

$$y = \frac{A_{deoxy} - A_{obs}}{A_{deoxy} - A_{oxy}} \qquad (3)$$

where

A_{obs} = absorbance differences at two different wavelengths at a specific oxygen pressure, P_{O_2};

A_{deoxy} = absorbance difference at two wavelengths of the parent complex, Mn(II)(TPP)(L); and

A_{oxy} = absorbance difference at two wavelengths of the totally oxygenated complex, Mn(TPP)O$_2$.

To eliminate any problems arising from baseline drift in obtaining the optical spectra, the absorbances at two different wavelengths were monitored to determine the percentage of oxy and deoxy species present. Data were collected at the maximum of either the α or β band of the deoxy species, Mn(II)(TPP)(L), (570 to 620 nm) with the second wavelength being chosen in a region where

the manganese porphyrin complexes do not absorb strongly, ~ 650 nm.

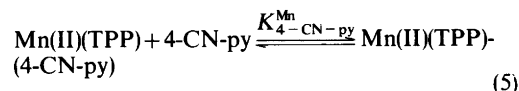Eqn. (2) is readily derived from the equilibrium expression

$$K^{Mn} = \frac{[Mn(TPP)(O_2)_n][py]}{[Mn(TPP)(py)]P_{O_2}^n} \qquad (4)$$

where n represents the number of dioxygen molecules being bound to the manganese center. For a plot of $y^2/(1-y)$ *vs.* log P_{O_2} the parameter n represents the slope of the straight line. For a simple replacement reaction $n=1.00$. The data obtained from the spectrophotometric titration were fitted to eqn. (2) using a non-weighted linear least-squares method. Values for $K^{Mn}[Mn(TPP)(L)]_{total}$ were obtained from the y-intercept of the regression line for a plot of log $y^2/(1-y)$ *vs.* log P_{O_2}.

In several cases the equilibrium constants, K^{Mn}, for the reaction of eqn. 1 were so low that oxygenation of the manganous porphyrin complex was not complete at a P_{O_2} of 1000 Torr. In these cases calculated values for the absorbances of the solutions at 100 % oxygenation were used to determine a value of y. The calculated values for the absorbance of the fully oxygenated solution, A_∞, were determined by systematically varying A_∞ to obtain a best straight-line fit to eqn. 2.

The concentrations of Mn(II)(TPP)(L) used in measuring K^{Mn} were in the range $1-4 \times 10^{-5}$ M. Data points were generally taken between 25 and 95 % oxygenation. Over this range the concentration of base-free Mn(II)(TPP) was calculated to be present in insignificant amounts.

Equilibrium constants for the reaction

$$Mn(II)(TPP)+4\text{-}CN\text{-}py \underset{}{\overset{K^{Mn}_{4-CN-py}}{\rightleftharpoons}} Mn(II)(TPP)\text{-} \\ (4\text{-}CN\text{-}py) \qquad (5)$$

in toluene were measured by a spectrophotometric titration method. Aliquots of a toluene solution containing 4-CN-py were added to a toluene solution of Mn(II)(TPP) in a 1 cm optical cell at 0.0, 23.0 and $40.0 \pm 0.1°$. In general the spectra were recorded in the 630 to 530 nm region during the titration.

The data were fitted to the Hill equation [10]

$$\log y/(1-y) = n \log [4\text{-}CN\text{-}py] + \log K^{Mn}_{4-CN-py} \qquad (6)$$

where in this case y equals the fraction of Mn(II)-(TPP) binding 4-CN-py; *i.e.*, $y=[Mn(TPP)(4\text{-}CN\text{-}py)]/[Mn(TPP)]_{total}$ and n represents the number of molecules of 4-CN-py binding to the manganese(II) center.

In this expression, y can be experimentally determined from the expression

$$y = \frac{A_{obs} - A_0}{A_\infty - A_0} \qquad (7)$$

where

A_{obs} = the observed absorbance at a specific concentration of 4-CN-py;
A_0 = initial absorbance of Mn(II)(TPP)
A_∞ = final absorbance, *i.e.* Mn(II)(TPP) present totally as Mn(II)(TPP)(4-CN-py).

Values for log $K^{Mn}_{4-CN-py}$ were determined from the y-intercept of the regression line for a plot of log $y/(1-y)$ *vs.* log[4-CN-py]. Values for the equilibrium constant were found to be independent of the wavelength used.

Equilibrium constants for the replacement reaction, eqn. 8, were measured in

$$Cr(III)(TPP)(Cl)(acetone) + L \overset{K^{Cr}}{\rightleftharpoons} Cr(III)(TPP)(Cl)\text{-} \\ (L) + acetone \qquad (8)$$
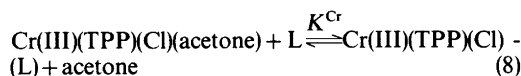
solutions of 60 % acetone in toluene (v/v) at 23.0 ± 0.1 °C, using a spectrophotometric titration method and analysis of data analogous with that used for determining $K^{Mn}_{4-CN-py}$. In all cases good isosbestic points were maintained throughout most of the titration. Deviations from isosbestic behavior during the latter stages of the titration could be quantitatively related to dilution effects. Since the equilibrium constants were measured in the presence of 60 % acetone, the equilibrium constants determined from experiment, K^{Cr}_{obs}, were corrected for acetone concentration by the expression $K^{Cr} = K^{Cr}_{obs}[acetone]$.

RESULTS

Spectrophotometric titrations for the oxygenation of Mn(II)(TPP)(L), eqn. (1), where L represents a neutral donor ligand, were performed in toluene at -78 °C. The results from a typical titration are shown in Fig. 1. Good isosbestic points were maintained throughout the titration. Plots of log $y^2/(1-y)$ *vs.* log P_{O_2} (see experimental section for details) gave straight lines (Fig. 2) with slopes of 1.00 ± 0.10, with the exception that for the oxygenation of Mn(II)(TPP)(1-MeIm) slopes of 1.14 and 1.18 were observed. Values for the slopes and the calculated equilibrium constants are given in Table 1. Equilibrium constants were checked at a second wavelength and proved independent of the wavelength chosen.
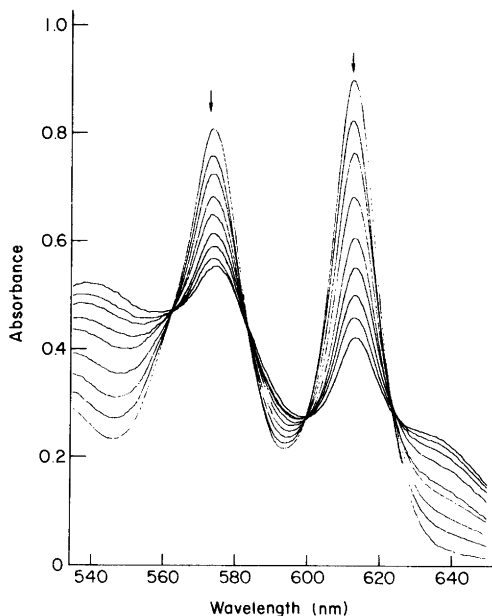
Fig. 1. Optical spectral changes on the addition of molecular oxygen to a 1.1×10^{-4} M toluene solution of Mn(II)(TPP)(sec-BuNH$_2$) at -78 °C. The final spectrum was run at a pressure of O$_2$ of 1004 torr. At this pressure the manganous porphin is 79 % oxygenated.
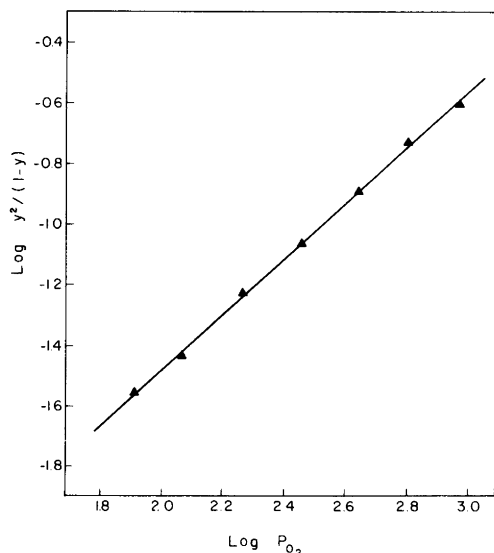

Fig. 2. Plot of log $y^2/(1-y)$ vs. log P_{O_2} for the oxygenation of Mn(II)(TPP)((n-Bu)$_3$P) in toluene solution at -78 °C. The slope is 0.91 and log $K = -8.44$. An R-factor of 0.9998 was calculated.

Table 1. Equilibrium constants for the reaction Mn(II)(TPP)(L)+O$_2$ $\overset{K^{Mn}}{\rightleftharpoons}$ Mn(II)(TPP)(O$_2$)+L at -78 °C in toluene.

L	n^a	$-\log K^{Mn}$
4-CN-py ^{a}	1.08	5.57
pK_a = 1.86 ^{b}	0.93	5.58
py	1.09	5.91
pK_a = 5.27 ^{c}	1.06	5.95
	1.06	5.97
	1.01	6.02
3,4-lut	1.04	7.09
pK_a = 6.46 ^{c}	1.10	7.19
1-MeIm	1.14	7.94
pK_a = 7.25 ^{c}	1.18	8.00
sec-BuNH$_2$ ^{c}	0.93	7.33
pK_a = 8.43	1.00	7.39
(n-Bu)$_3$P ^{d}	1.00	8.52
pK_a = 8.43	0.91	8.44
(C$_2$H$_5$O)$_3$P	0.91	5.43
pK_a = 3.50 ^{e}	0.91	5.59
Thioanisole	1.03	7.43
	0.99	7.46

^{a} Calculated from a least-squares analysis of log $y^2/(1-y)$ vs. log P_{O_2}. See text for details. K^{Mn} has units of mol/L Torr. From a least-squares analysis of the data all values for log K^{Mn} fell within ± 0.1. ^{b} Schofield, K. Hetero-Aromatic Nitrogen Compounds, Plenum, New York 1967, p. 146. ^{c} Albert, A. Phys. Methods Heterocyclic Chem. 1 (1963). ^{d} Streuli, C. A. Anal. Chem. 32 (1960) 985. ^{e} Estimated value, see Ref. 23.

Heating solid Mn(II)(TPP)(py) in vacuo at 250 °C for several hours results in the formation of the corresponding four-coordinate, base-free Mn(II)-(TPP) complex. The identity of this complex has been confirmed both by elemental analysis and by the spectrophotometric titration of these complexes with toluene solutions containing an N-donor ligand (vide infra).

Spectrophotometric titrations of toluene solutions of Mn(II)(TPP) with toluene solutions containing 4-CN-py were performed at several temperatures. Plots of log $y/(1-y)$, where y equals [Mn(II)(TPP)-(4-CN-py)]/(Mn(II)(TPP)]$_{total}$, vs. log[4-CN-py] gave straight lines with slopes of 1.0 ± 0.2. Good

Table 2. Equilibrium constants for the addition of 4-cyanopyridine to Mn(II)(TPP) in toluene

$$Mn(II)(TPP) + 4\text{-CN-py} \underset{\rightleftharpoons}{\overset{K^{Mn}_{4-CN-py}}{}} Mn(II)(TPP)\text{-}(4\text{-CN-py})$$

Ligand	$t\,(°C)^a$	Slope$(n)^b$	$\log K^c_{4-CN-py}$
4-Cyanopyridine	40.0	0.94	3.16
	40.0	1.05	3.04
	23.0	1.14	3.60
	23.0	1.17	3.59
	23.0	1.08	3.55
	0.0	1.12	4.19
	0.0	1.20	4.21
	−78		7.63
	(extrapolated)		

^{a} ±0.1°. ^{b} Slope from fitting the data to the Hill equation (eqn. 6). ^{c} Errors estimated at ±0.1. Thermodynamic constants for the addition of 4-CN-py are $\Delta H = -10.7 \pm 0.4$ kcal/mol, and $\Delta S = -19.8 \pm 1.5$ eu.

isosbestic points were maintained throughout the titration. Values for the slopes and equilibrium constants for the addition of 4-CN-py to Mn(II)-

Table 3. Equilibrium constants ^{a} for the reaction

$$Cr(III)(TPP)(Cl)(acetone) + L \overset{K^{Cr}}{\rightleftharpoons} Cr(III)(TPP)(Cl)\text{-}(L) + acetone.$$

L ^{b}	Slope ^{c}	$\log K^{Cr}$
4-CN-py	1.03	3.20 ± 0.03
	1.00	3.12 ± 0.07
py	1.03	4.28 ± .06
	1.01	4.28 ± .04
3,4-Lut	1.02	5.01 ± 0.12
	0.97	5.01 ± 0.13
sec-BuNH$_2$	1.03	5.47 ± 0.08
	0.99	5.43 ± 0.17
1-MeIm	1.00	6.71 ± 0.13
	0.94	6.44 ± 0.16

^{a} Measured in 60 % acetone/toluene (v/v) at 23.0 ± 0.1 °C. Log K^{Cr} represents the equilibrium constant corrected for acetone concentration. Errors reported represent deviations of data from a least-squares analysis. ^{b} Ligands were in toluene solution: 4-CN-py, ~0.6 M; py, 0.1 to 0.6 M; 3,4-Lut, 0.27 M; *sec*-BuNH$_2$, ~2 × 10^{-2} M; 1-MeIm, ~2 × 10^{-2} M. ^{c} Calculated from a least-squares analysis of log $y/(1-y)$ *vs.* log (L); see text for details.

(TPP) are given in Table 2. Values for the equilibrium constant were found to be independent of the wavelength used.

Spectrophotometric titrations at 23 °C of 60 % acetone/toluene (v/v) of Cr(III)(TPP)(Cl) with toluene solutions of a nitrogenous ligand, L, were performed. The results from a typical titration are shown in Fig. 3. Plots of log $y/(1-y)$ where $y = [Cr(III)(TPP)(Cl)(L)]/[Cr(III)(TPP)(Cl)]_{total}$ *vs.* log [L] gave straight lines with slopes of 1.00 ± 0.1. Values for the slopes obtained from the titrations as well as the observed equilibrium constants are given in Table 3.
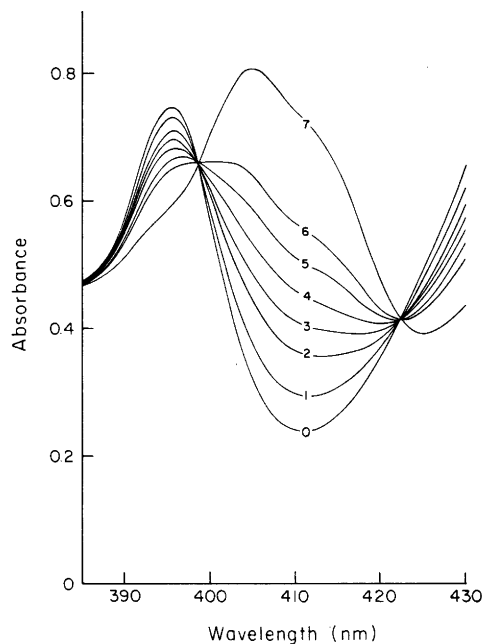

Fig. 3. Visible spectral changes on the addition of pyridine (in 60 % acetone/toluene, v/v) to a 1.50×10^{-5} M solution of Cr(TPP)(Cl) in 60 % acetone/toluene. The addition was performed using a two syringe technique. The spectrum labelled 0 is the spectrum of the initial acetone adduct. Spectra labelled 1 to 6 were obtained from solutions having pyridine concentrations ($\times 10^4$) of 0.56, 1.42, 2.27, 3.42, 5.14 and 8.00, respectively. Spectrum 7 was obtained at a final pyridine concentration of 5.84×10^{-2} M and corresponds to the spectrum of Cr(TPP)(Cl)(py).

DISCUSSION

Until recently, the only synthetic metal complexes of biological interest that had been observed to reversibly bind molecular oxygen were those containing Fe(II) or Co(II) centers.[11] Recently, *meso*-tetraphenylporphinatomanganese(II) complexes of the form Mn(II)(TPP)(L) have been shown to act as reversible oxygen carriers in toluene solution at -78 °C.[12,13] That the formation of tetraphenylporphinatomanganese-dioxygen complex involves the replacement of the coordinated neutral ligand, L, to form Mn(TPP)(O$_2$) has been inferred[12] both from EPR evidence and from the observation that the dioxygen complex is not observed in the presence of an excess of the ligand L.
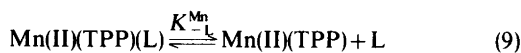
The study on the equilibrium reactions of Mn(II)-(TPP)(L) complexes with O$_2$ at -78 °C in toluene presented here confirms that the reaction of O$_2$ with the manganous porphyrins occurs *via* replacement of the axial ligand L, eqn. (1). The study also presents us with information as to the affinities of tetraphenylporphinatomanganese(II) complexes for dioxygen and neutral ligands.

Dissolving five-coordinate tetraphenylporphinatomanganese(II) complexes in toluene and cooling to -78 °C results in the manganous porphyrin being present predominantly as the five-coordinate, Mn(II)(TPP)(L), species with almost none of the base-free adduct being present. This result is consistent with an analysis of the cold temperature spectra of Mn(II)(TPP)(L), both in the absence and presence of extra ligand, L. Further, a calculation of the amount of base-free Mn(II)(TPP) present when a 10^{-5} M toluene solution of Mn(II)(TPP)(4-CN-py) is cooled to -78 °C, using the extrapolated value for $K^{Mn}_{4-CN-py}$ (Table 2), reveals that only about 0.2 % of the metalloporphin is present as the base-free complex.

In the presence of molecular oxygen at low temperature in toluene solution, an equilibrium between the five-coordinate mono-ligated species, Mn(II)(TPP)(L), and the dioxygen complex, Mn-(TPP)(O$_2$) is established, eqn. (1). The good isosbestic behavior and straight-line plots of log $(y^2/(1-y))$ *vs.* log P_{O_2} obtained from the spectrophotometric titrations of the five-coordinate manganous porphins with molecular oxygen confirm that the manganous porphyrins add only one mol of O$_2$ for every mol of metalloporphyrin, and that the dioxygen complexes have no ligand occupying the vacant axial position.

The possibility that the oxygenation of the ligated manganous porphin complexes, Mn(II)(TPP)(L), proceeds as the simple dioxygen addition reaction can be eliminated for two other reasons: (1) The data obtained from the titrations with molecular oxygen were analyzed using the Hill plot method. The resulting plots of log $y/(1-y)$ *vs.* log P_{O_2} (where y equals the fraction of maganese sites oxygenated) showed both deviations from straight-line behavior, and slopes significantly different from $n = 1.00$, (for example, the results of the titration of Mn(TPP)-((n-Bu)$_3$P) with O$_2$, shown in Fig. 2, when analyzed according to the Hill equation, eqn. (6), gave a slope of 0.52), and (2) the values obtained for the log of the equilibrium constants for the oxygenation of Mn(TPP)(py) were found to be directly proportional to the log of the concentration of manganese porphin used when the data were analyzed by the Hill method. Such results are inconsistent with the oxygenation of the manganous porphins being a straightforward addition reaction but are consistent with the replacement by oxygen of the axial ligand.

An examination of the dioxygen replacement reaction, eqn. (1), reveals that the equation can be rewritten in terms of the two equilibrium processes

$$Mn(II)(TPP)(L) \xrightleftharpoons{K^{Mn}_{-L}} Mn(II)(TPP) + L \tag{9}$$

$$Mn(II)(TPP) + O_2 \xrightleftharpoons{K^{Mn}_{O_2}} Mn(TPP)(O_2) \tag{10}$$

From the equilibrium constants for the binding of 4-CN-py to Mn(II)(TPP), Table 2, and the value for the equilibrium constant for oxygenation of Mn(II)(TPP)(4-CN-py) at -78 °C, Table 1, we can estimate a value for the oxygenation of four coordinate Mn(II)(TPP) at -78 °C. From the data in Table 2 we obtain a value for log $K^{Mn}_{4-CN-py}$, extrapolated to -78 °C, of 7.63. Using the value determined for this equilibrium constant for the oxygenation of Mn(TPP)(4-CN-py) at -78 °C, log $K^{Mn} = -5.57$, we calculate the value for the equilibrium constant for the oxygenation of Mn(II)-(TPP) at -78 °C as $K^{Mn}_{O_2} \sim 10^{2.1}$ Torr^{-1}.

A comparison of the equilibrium constants for oxygenation for a series of porphinato metal(II) complexes at -78 °C with the $M^{III/II}$ half-wave reduction potentials (Table 4) shows that, with the exception of Mn(II)(TPP), there is a direct relationship between the affinity of the complex for dioxygen and the ease of oxidation of the metal(II) center. Thus, the $K^{Mn}_{O_2}$ observed for Mn(II)(TPP) at -78 °C

Table 4. Equilibrium constants for the oxygenation of metalloporphyrin complexes at -78 °C.[a]

Complex	Conditions	$\log K_{O_2}$	$E_{\frac{1}{2}}(M^{III/II})$ [b]
Co(II)(TPP)(py)	toluene solution	-1.7 [c]	$+0.13$ [c]
Co(II)(T(*p*-OMe)PP)(1-MeIm)	toluene solution	-0.8 [d]	$+0.11$ [c]
Fe(II)(TpivPP)(1-MeIm)	solid	6.4 [e]	-0.11 [f]
Mn(II)(TPP)	toluene solution	~ 2.1 [g]	-0.27 [h]
Cr(II)(TPP)(py)	solid	large	-0.86 [i]

[a] The equilibrium constants reported in this table are for the addition of O_2 to a vacant axial coordination site on the metal(II) center. Values for $\log K_{O_2}$ at -78 °C are calculated from thermodynamic data given in the references cited. Units of K_{O_2} are Torr^{-1}. [b] In DMSO. Values reported in volt *vs.* SCE. [c] For Co(TPP) and Co(II)(T(*p*-OMe)PP); Walker, F. A., Beroiz, D. and Kadish, K. M. *J. Am. Chem. Soc.* 98 (1976) 3484. [d] Walker, F. A. *J. Am. Chem. Soc.* 95 (1973) 1154. [e] TpivPP represents the dianion of the "picket-fence" porphyrin. Collman, J. P., Braumau, J. I. and Suslick, K. S. *J. Am. Chem. Soc.* 97 (1975) 7185. [f] Kadish, K. M., Morrison, M. M., Constant, L. A., Dickens, L. and Davis, D. G. *J. Am. Chem. Soc.* 98 (1976) 8387. [g] This work. [h] Cape, T., Szymanski, T. and Basolo, F. *Unpublished results;* see also Kadish, K. M. and Morrison, M. M. *Bioelectrochem. Bioenergetics* 3 (1976) 480. [i] The dioxygen adduct forms irreversibly. Cheung, S. K., Grimes, C. J., Wong, J. and Reed, C. A. *J. Am. Chem. Soc.* 98 (1976) 5028.

is several orders of magnitude less than would be predicted on the basis of the half-wave reduction potential.

This apparent anomaly in the bonding of dioxygen to Mn(TPP) compared with the porphinato metal(II) complexes of cobalt, iron and chromium may indicate that the nature of the bond between manganese and dioxygen differs significantly from that observed with these other metals. Although the bonding in the metalloporphin-dioxygen complexes containing Fe, Co, and Cr have been shown to bind dioxygen in an end-on (Pauling) conformation, the geometry of the manganese-dioxygen bond in Mn(TPP)(O$_2$) has not yet been unambiguously determined. Since we expect the relationship between K_{O_2} and $E_{\frac{1}{2}}$ to be consistent for similarly bonded structures, the anomalous value observed for the oxygen affinity of Mn(II)(TPP) is consistent with a symmetrical, Griffith type conformation of the manganese-dioxygen bond as had been previously suggested on the basis of EPR results.[12] There is, however, another interpretation for the anomalous value for $K_{O_2}^{Mn}$. Basolo and co-workers[9] have reported that whereas five-coordinate complexes of the cobalt(II) Schiff base Co(II)(benacen)(L), where L represents an N-donor ligand, readily bind dioxygen in toluene solution at 0 °C (*e.g.* $\log K_{O_2}^{Co} = -2.0$ at 0 °C for L equal to 1-MeIm) only a small amount of the four-coordinate Co(II)(benacen) complex is oxygenated under one atmosphere of O_2 in toluene at -83 °C. Thus if the dioxygen moiety in Mn(TPP)(O$_2$) adopts the Pauling conformation, the seemingly low value for $\log K_{O_2}^{Mn}$ is

consistent with the absence of a sixth axial ligand.

Having determined that Mn(II)(TPP)(L) reacts reversibly with molecular oxygen to form Mn(TPP)-(O$_2$) it is interesting to compare the chemical properties observed for the tetraphenylporphinato-manganese dioxygen complex with those predicted on the basis of the ground-state electronic configuration as determined from EPR studies. Frozen solution EPR spectra of Mn(TPP)(O$_2$) have been interpreted[12] in terms of a d^3 electronic configuration about the manganese center. Such an electronic configuration has been interpreted[12] in terms of an Mn(IV)-O$_2^{2-}$ formalism for the metalloporphyrin complex. As such, the chemistry of the manganese dioxygen complex should be expected to be similar to that observed for tetraphenylporphinatochromium(III) complexes that contain a d^3 metal center.

Upon adding a toluene solution containing an N-donor ligand to a solution containing Cr(III)-(TPP)(Cl)(acetone), replacement of the acetone by the N-donor ligand, eqn. (8), is observed to occur.[4] The equilibrium constants for this replacement, K^{Cr}, at 23 °C are given in Table 3. Although we have been unable to obtain equilibrium constants for the addition of a neutral N-donor ligand to five-coordinate Cr(III)(TPP)(Cl) due to the insolubility of Cr(TPP)(Cl) in the absence of a coordinating ligand,[4] we can use the values of K^{Cr}, Table 3, as lower limits for the affinities of five-coordinate Cr(TPP)(Cl) for N-donor ligands. In contrast to the large affinity of five-coordinate Cr(TPP)(Cl) for a sixth N-donor ligand, we observed no tendency for Mn(TPP)(O$_2$) to bind a sixth ligand at -78 °C.[5]

Such a large difference in behavior for the two d^3-metalloporphin systems is consistent with the dioxygen bonding in a side-bonded Griffith conformation, with repulsive steric interactions between the coordinated oxygen atoms and N-atoms of the porphin ring accounting for the tendency of the d^3 manganese center not to bind a neutral axial ligand.

In addition to studying the equilibrium of manganese(II) tetraphenylporhin complexes with dioxygen, this study gives us information about the bonding of neutral ligands to Cr(III) and Mn(II) tetraphenylporphinato complexes. It is unfortunate that the insolubility of Cr(TPP)(Cl) in toluene has made it impossible for us to obtain any absolute values for the affinity of the five-coordinate Cr(TPP)-(Cl) for a sixth ligand. However, replacement of the acetone coordinated to the Cr(III) center in Cr-(TPP)(Cl)(acetone) by 1-methylimidazole occurs with an equilibrium constant of 4.0×10^6 (23 °C in 60 % v/v acetone − toluene). Using this value as a lower limit for the affinity of five-coordinate Cr(TPP)(Cl) for 1-MeIm we can contrast this value with the equilibrium constant obtained for the addition of a 1-MeIm to Fe(III)(TPP)(Cl) (in benzene at 25 °C)[14] where $K = 1.3 \pm$ 0.2, or of a pyridine to Mn(III)(TPP)(Cl) where $K = 2.5$.[15] Indeed, the binding of the sixth ligand by Cr(TPP)(Cl) compares favorably with the addition of the first imidazole to base-free Fe(II)(TPP) (in benzene at 25 °C)[16] where $K = 8.8 \times 10^3$ M^{-1}.

The imidazole ligand in its binding to metallo-porphin complexes has been shown to exhibit unusual behavior compared with other nonhindered nitrogenous bases. The lower lability of the coordinated dioxygen in Fe(TPP)(1-MeIm)(O$_2$) compared with that observed where pyridine or piperidine occupy the axial position has been attributed to the larger π-donor effect of the imidazole ligand relative to that of pyridine or piperidine.[6] Other anomalous effects of the imidazole ligand have been observed for O$_2$ and CO bonding to metalloporphyrin and metallophthalocyanin complexes.[9,17−19]

In this bis-imidazole complexes of some Fe(III) porphyrins (the bis-imidazole hemichromes), the imidazole ligand has been implicated as a π-donor from Mössbauer data[20] and as a π-acceptor from NMR studies compared with Hückel calculations.[21] It is therefore of interest to examine our equilibrium data for the binding of nitrogenous bases to Cr(TPP)(Cl).

A plot of log K^{Cr} values for the equilibrium reactions of Cr(TPP)Cl with L, eqn. (8), versus the basicity (pK_a for LH$^+$) of the N-donor ligand L is shown in Fig. 4. The linearity of the plot for the π-acceptor substituted pyridine ligands and the non π-bonding sec-butylamine suggests that metal-to-ligand π-bonding is relatively unimportant for these complexes. The anomalously strong binding of 1-MeIm is consistent with ligand-to-metal π-bonding from the imidazole to the chromium(III) being important in these complexes.
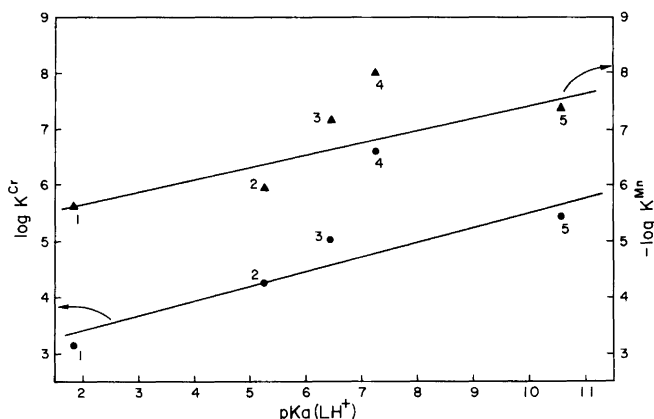
The relative affinities of base-free Mn(II)(TPP)

Fig. 4. Correlation between pK_a for the conjugate acids (LH$^+$) and the log of the equilibrium constants for reactions 1 and 8. The left hand ordinate and ● represent log K^{Cr} for the reaction Cr(III)(TPP)(Cl)(acetone) + L ⇌ Cr(III)(TPP)(Cl)(L) + acetone; the right hand ordinate and ▲ represent the − log K^{Mn} for the reaction Mn(II)(TPP)(L) + O$_2$ ⇌ Mn(TPP)(O$_2$) + L. Ligands (L) are 1 = 4-cyanopyridine; 2 = pyridine; 3 = 3,4-butadiene; 4 = 1-methylimidazole; 5 = sec-butylamine. The straight lines represent regression lines obtained for points 1, 2, 3 and 5.

for a neutral N-, P-, and S-donor ligand in toluene at -78 °C can be determined directly from the data in Table 1. A plot of $-\log K^{Mn}$ *vs.* the σ-donor strength of the N-donor ligands (represented as pK_a for LH^+) is shown in Fig. 4 along with the data for $\log K^{Cr}$ *vs.* L. Construction of a least-squares line for the values of $-\log K^{Mn}$ *vs.* pK_a for the substituted pyridine bases and *sec*-BuNH$_2$, Fig. 4, shows that although there appears to be a general correlation between the parameters, deviations from straight-line behavior are greater than those observed for the binding of these same ligands to Cr(III)(TPP)(Cl). The large deviation of the value of $-\log K^{Mn}$ observed for the 1-MeIm case is similar to that observed previously for the ligation of Cr(III) porphyrins.

An examination of the data for the bonding of the phosphorus-donor ligands, $(C_2H_5O)_3P$ and $(n\text{-}Bu)_3P$, to Mn(II)(TPP) shows an interesting correlation with the data obtained for the nitrogen-donor bases. In comparison with the equilibrium constant data (Table 3) obtained for the substituted pyridine ligands and *sec*-butylamine, $(C_2H_5O)_3P$ and $(n\text{-}Bu)_3P$ show affinities for the manganous porphin that are, respectively, weaker and stronger than would be predicted on the basis of the proton basicity of the P-donor ligands. The fact that a linear relationship is observed between the proton acidities of a series of ligands containing the same donor atom, *i.e.* N or P, and the equilibrium constants observed for the bonding to the manganese(II) center implies either that ligand-metal π-bonding plays a relatively constant role in the bonding of the ligand to the metal center or that there exists an intimate balance between σ- and π-bonding effects. Both σ- and π-bonding have been implicated in the bonding of both pyridine and P-donor ligands to metal centers.[22] The variation in bonding of the neutral ligand to the manganese(II) porphin observed for the N- and P-donor series may therefore reflect differences in π-bonding between the manganese(II) center and the nitrogen- and phosphorus-donor ligands. This effect is similar to that previously reported[23] for the binding of an axial ligand to the four-coordinate diethyl ester of mesoporphyrinatocobalt(II) where it was observed that the influence of σ-donor ability of the ligand (as measured by the pK_a) on the binding of P-donor ligands to the cobaltous porphyrin was much greater than the effect of pK_a obtained for a series of N-donor ligands.

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