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variation. Effectively, the free energies of complexation, $\Delta G_c$, are equal to $-6.24$, $-6.66$, $-7.15$, and $-6.51$ kcal mol$^{-1}$ in $|\text{Na}^+ \subset \text{A}|$, $|\text{Na}^+ \subset \text{B}|$, $|\text{K}^+ \subset \text{A}|$, and $|\text{K}^+ \subset \text{B}|$, respectively.

In conclusion, the optimum dimension of the intramolecular cavity of ligand $|221|$ is smaller than that of ligand $|222|$; the latter lies between 1.40 and 1.50 Å, that is, in between the radius of $\text{K}^+$ and $\text{Rb}^+$, whereas the former has a value near to 1.30 Å, which is nearer the radius of $\text{K}^+$ than that of $\text{Na}^+$. Selection being due to a cummulative effect of enthalpy and entropy of complexation the three-dimensional structures show that an enthalpic preselection is made by the ligand and an important entropic effect makes the final selection. Cavity size and ligand flexibility are major factors of preselection and can be designed a priori.

**Supplementary Material Available:** Listing of observed and calculated structural factors ($\times 10$) and positional atomic and anisotropic thermal parameters (18 pages). Ordering information is given on any current masthead page.

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# Manganese(II) Porphyrin Oxygen Carriers. Equilibrium Constants for the Reaction of Dioxygen with Para-Substituted *meso*-Tetraphenylporphinatomanganese(II) Complexes

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**Abstract:** The reaction of molecular oxygen at $-78$ °C in toluene with a series of para-substituted *meso*-tetraphenylporphinatomanganese(II) complexes, $\text{Mn}^{II}(\text{T}(p\text{-X})\text{PP})(\text{L})$, containing an axial ligand, L, is described. Spectrophotometric titrations of toluene solutions of these complexes at $-78$ °C with molecular oxygen confirm the stoichiometry of the porphyrinatomanganese dioxygen complexes as $\text{Mn}(\text{T}(p\text{-X})\text{PP})(\text{O}_2)$. Equilibrium constants for the reaction $\text{Mn}^{II}(\text{T}(p\text{-X})\text{PP})(\text{L}) + \text{O}_2 \rightleftharpoons \text{Mn}(\text{T}(p\text{-X})\text{PP})(\text{O}_2) + \text{L}$ were determined for the series where $X = \text{Cl, F, H, CH}_3$, and $\text{OCH}_3$ and $\text{L} = $ pyridine. Log $K$ ($-78$ °C, toluene) for the replacement of pyridine by $\text{O}_2$ ranged from $-5.75$ for $\text{Mn}^{II}(\text{T}(p\text{-OCH}_3)\text{PP})(\text{py})$ to $-6.53$ for $\text{Mn}^{II}(\text{T}(p\text{-Cl})\text{PP})(\text{py})$. (An error of $\pm 0.1$ is estimated for the log $K$ values; $K$ has units of mol/L·Torr.) Fitting the observed values for the equilibrium constants to the Hammett equation ($-\log K$ vs. $4\sigma$) gives a Hammett $\rho$ value of $-0.41 \pm 0.08$. The effect of substituting the phenyl groups of the tetraphenylporphinatomanganese complex on the binding of molecular oxygen is discussed. Equilibrium constants for the replacement of L by $\text{O}_2$ at $-78$ °C in toluene for $\text{Mn}^{II}(\text{TPP})(\text{L})$, where L is a nitrogen, phosphorus, or sulfur donor ligand, are reported. Equilibrium constants ($K_L$) for the reaction $\text{Mn}^{II}(\text{TPP}) + 4$-cyanopyridine $\rightleftharpoons \text{Mn}^{II}(\text{TPP})(4$-cyanopyridine) were determined in toluene at 40.0, 23.0, and 0.0 °C. At 23.0 °C, the equilibrium constants for 4-cyanopyridine addition was determined as log $K_L = 3.58$. A value for $\Delta H$ of $-10.7 \pm 0.$ kcal/mol for the reaction was calculated. Extrapolation of these data to $-78$ °C permits an estimate for the equilibrium constant at $-78$ °C for the oxygenation of four-coordinate $\text{Mn}^{II}(\text{TPP})$ as $K_{\text{O}_2} \sim 10^{2.1}$ Torr$^{-1}$.

## Introduction

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.[1]

Recently, *meso*-tetraphenylporphinatomanganese(II) complexes of the form $\text{Mn}^{II}(\text{TPP})(\text{L})$,[2] where L represents a coordinating ligand, have been shown to act as reversible oxygen carriers in toluene solution at $-78$ °C.[3]

On the basis of EPR and chemical evidence, the bonding of dioxygen in the *meso*-tetraphenylporphinatomanganese dioxygen complex has been shown to differ significantly from the bonding observed in the cobalt(II) and iron(II) oxygen carriers. These differences include the following. (1) The coordinated dioxygen in the cobalt- and iron-containing dioxygen complexes has been described as being "superoxide-like",[4] whereas EPR evidence indicates that in $Mn(TPP)(O_2)$ the metal–dioxygen bond can be formally described in terms of a manganese(IV) peroxide ground-state electronic configuration.[5] (2) Both the porphyrinatocobalt and -iron dioxygen complexes have a strong tendency to form six-coordinate complexes of the type $M(porphyrin)(L)(O_2)$, whereas in the presence of a coordinating ligand the porphyrinatomanganese dioxygen complexes, $Mn(porphyrin)(O_2)$, have a vacant axial position. (3) For the iron and cobalt dioxygen complexes, the dioxygen binds in an end-on (Pauling) configuration to the metal center, whereas by analogy with other metal-peroxo complexes, it has been suggested that in $Mn(TPP)(O_2)$ the dioxygen adopts a triangular (Griffith) conformation.[5] It is not obvious why these differences in bonding should occur. An examination of these differences is intrinsic to an understanding of the fundamental properties of the oxygen-carrying complexes.

The equilibrium constants for oxygen uptake by cobalt(II) complexes increase with increasing ease of oxidation ($Co^{II/III}$) of the cobalt centers. This was originally shown to be true for a series of cobalt(II) Schiff base complexes[6] and has recently been observed for a series of para-substituted *meso*-tetraphenylporphinatocobalt(II) complexes.[7] This is consistent with the accepted formalism that the cobalt(II) center undergoes oxidation upon complexation with $O_2$ to form a $Co^{III}-O_2^-$ species.[8] Since EPR evidence[5] indicates that the bonding of $O_2$ to $Mn^{II}(TPP)$ involves delocalization of electron density from the manganese center to the coordinated dioxygen, a correlation between the oxygen affinity of porphinatomanganese(II) complexes with ease of oxidation of the manganese(II) center is to be expected.

With the exception of the exhaustive analysis of the ground-state electronic configuration of $Mn(TPP)(O_2)$ from EPR and optical spectroscopy,[5] little is known about the oxygenation of manganous porphyrin complexes. In this paper we report on the solution behavior of para-substituted tetraphenylporphinatomanganese(II) complexes and determine the equilibrium constants at $-78\ ^\circ C$ in toluene for the reaction

$$Mn^{II}(T(p\text{-}X)PP)(L) + O_2 \overset{K}{\rightleftharpoons} Mn(T(p\text{-}X)PP)(O_2) + L$$

(1)
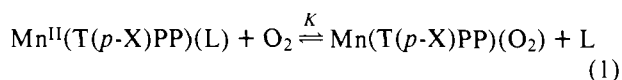
where L represents a basic donor ligand and X = Cl, F, H, $OCH_3$, and $CH_3$.

## Experimental Section

**Reagents.** Toluene was reagent grade and was distilled under $N_2$ from sodium benzophenone ketyl immediately prior to use. Pyridine was Aldrich Gold-Label grade and was distilled from BaO under $N_2$ immediately prior to use. The $N_2$ was Matheson prepurified grade and was passed through a Ridox column to remove residual $O_2$ 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 $-130\ ^\circ C$. The 4-cyanopyridine was recrystallized from benzene/heptane several times. Except where otherwise noted, all other reagents were reagent grade and were used without further purification.

**Analyses.** Elemental analyses of C, H, and N were performed by H. Beck of this department.

**Syntheses.** *meso*-Tetraphenylporphine ($TPPH_2$) was prepared by the method of Adler and co-workers.[9] The $TPPH_2$ was purified (to remove any *meso*-tetraphenylchlorin impurity) by refluxing[10] with 2,3-dichloro-5,6-dicyanobenzoquinone in $CH_2Cl_2$.

**Chloro-*meso*-tetraphenylporphinatomanganese(III) [Mn(TPP)(Cl)].** This procedure is based on the method published by Adler and co-workers.[11] The porphyrin $TPPH_2$ (5.0 g, chlorin-free) was dissolved in 500 mL of refluxing DMF. After we waited for several minutes to allow the porphyrin to dissolve, $Mn(C_2H_3O_2)_2\cdot4H_2O$ (4 g) was added to the solution. The solution was allowed to reflux for 30 min. At this point a visible spectrum in $CHCl_3$ of an aliquot taken from the reaction mixture revealed the absence of any remaining free-base porphyrin. Refluxing was stopped and the mixture allowed to cool to room temperature. (Had the visible spectrum revealed the presence of $TPPH_2$, an additional quantity of $Mn(C_2H_3O_2)_2\cdot4H_2O$ ($\sim0.1$ g) would have been added to the reaction mixture and reflux continued for another 10 min. The process of adding small amounts of $Mn(C_2H_3O_2)_2\cdot4H_2O$ to the solution would be continued until no free-base porphyrin was found in the visible spectrum.) The cooled reaction mixture was then poured into a flask containing 500 mL of an ice-cold NaCl solution (150 g of $NaCl/0.5$ L of $H_2O$). The resulting green precipitate was collected by filtration and washed with 2 L of $H_2O$. The solid was allowed to air dry for about 15 min; then it was dissolved in the minimum amount of $CH_3OH$ ($\sim1$ L) and the solution was filtered. The $CH_3OH$ solution was poured into an equal volume of 6 M aqueous HCl solution. The green precipitate which formed was collected on a filter and washed with $H_2O$ and air dried as done previously. The resulting solid was recrystallized from benzene/hexane to yield 5.02 g of [Mn(TPP)Cl] (88% based on $TPPH_2$). The optical spectrum of the complex in $CHCl_3$ is identical with the published spectrum.[12]

**Pyridine-*meso*-tetraphenylporphinatomanganese(II) [Mn$^{II}$(TPP)(py)].** These procedures for the reduction of $Mn^{III}(TPP)(Cl)$ to give $Mn^{II}(TPP)(py)$ are modifications of the method given by Kobayashi and Yanegawa.[13] The reductions were carried out in a nitrogen atmosphere using standard Schlenk-type glassware and techniques.[14]

**Method I.** The complex $Mn^{III}(TPP)(Cl)$ (1 g) was added to a 500-mL airless-type round-bottom flask containing a magnetic stir bar. To the flask were added MeOH (210 mL), $CHCl_3$ (60 mL), and pyridine (30 mL). The flask was then attached to a distillation apparatus, the solution was stirred, and both the solution and apparatus were thoroughly purged with $N_2$ for 1 h. At this point, $NaBH_4$ (0.6 g) was added to the solution. The addition of the $NaBH_4$ resulted in a vigorous evolution of gas which continued for several minutes. This was accompanied by a change in color of the solution from green to purple. The solution was allowed to stir for 5 min at which point heating was begun; the solvent was removed by distillation until the final volume of the solution was about 30 mL. After the solution had cooled to room temperature, the distillation apparatus was dismantled and a double-ended Schlenck filter attached to the 500-mL flask. The apparatus was then thoroughly flushed with $N_2$. With the porphyrin solution stirring vigorously, deoxygenated MeOH (30 mL) was added to precipitate the Mn(II) product. After stirring for about 5 min, the solid product was collected on a filter and washed twice with 10-mL portions of deoxygenated MeOH. The solid was dried in vacuo at room temperature overnight to give a blue powder, which was stored under $N_2$. Yields were always about 70% (based on $Mn^{III}(TPP)(Cl)$).

Anal. Calcd for [Mn($C_{44}H_{28}N_4$)($C_6H_5N$)]: C, 78.18; H, 5.22; N, 9.30. Found: C, 77.42; H, 4.54; N, 9.06.

**Method II.** The complex $Mn^{III}(TPP)(Cl)$ (1 g) was added to a 200-mL round-bottom Schlenk flask containing a magnetic stir bar. A mixture of pyridine (15 mL) and methanol (15 mL) was then added to the flask. A double-ended Schlenk fritted funnel was then attached to the flask and a second 200-mL round-bottom Schlenk flask connected to the open end of the fritted funnel. The apparatus was flushed with $N_2$ for 15 min, after which $NaBH_4$ (0.6 g) was added to the solution. This was accompanied by the vigorous evolution of $H_2$. The solution was then heated to a gentle reflux for 15 min, at which point the reflux was terminated and the solution allowed to cool to room temperature. Previously $N_2$ flushed MeOH (20 mL) was added to the reaction mixture. Stirring was stopped, and the solution allowed to stand for 15 min. The solid $Mn^{II}(TPP)(py)$ was collected on a filter and washed three times with 15-mL portions of deoxygenated methanol. The solid product was then dried in vacuo at room temperature for several hours. Yields were similar to those obtained by method I. The optical spectrum of the material in pyridine proved identical with the material obtained by method I.

**_meso_-Tetraphenylporphinatomanganese(II) [Mn$^{II}$(TPP)].**[15] Base-free $Mn^{II}(TPP)$ was prepared from the corresponding pyridine adducts 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 the pyridine.

Anal. Calcd 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.

$Mn^{II}(TPP)(L)$. 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. For L equals 1-MeIm, 4-CN-py, or *sec*-BuNH₂, the complexes were prepared by the reduction of $Mn^{III}(TPP)(Cl)$ with NaBH₄ in the presence of excess ligand, L, using a similar procedure with that given above 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 CH₃OH (for L equals 3,4-lutidine or $(n$-Bu$)_3$P), hexane (for L equals thioanisole), or isooctane (for L equals $(C_2H_5O)_3$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% 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.

**Syntheses of the Tetrasubstituted *meso*-Tetraphenylporphine Complexes.** The compounds $T(p$-X)PPH₂, $Mn^{III}(T(p$-X)PP)(Cl)$, $Mn^{II}(T(p$-X)PP)(py)$, and $Mn^{II}(T(p$-X)PP)$ were prepared using similar procedures with those described above. Satisfactory elemental analyses were obtained. Whenever possible, solution optical spectra were compared with literature spectra to confirm the identity of the complexes.

**Equilibrium Constant Determinations.** Equilibrium constants for the oxygenation reaction (eq 1) were measured by a spectrophotometric titration technique using a 4-cm path length low-temperature visible cell.[6] Solid $Mn^{II}(T(p$-X)PP)(L)$ (~0.3 mg) was added to the visible cell containing a magnetic stir bar and the cell was then carefully flushed with N₂. The cell was then cooled to ~−50 °C, toluene (~18 mL) was added, and the mixture was allowed to stir under N₂ until all of the metalloporphyrin had dissolved. The cell was then cooled to −78 °C. The purpose of the precooling procedure is to avoid irreversible oxidation of the manganous porphyrin on addition of the toluene by trace amounts of O₂. In the absence of this precaution, the presence of an oxidized product was usually observed in the initial spectrum at −78 °C. Precooling the solution to a temperature lower than −50 °C slowed the dissolution of the manganese porphyrin complex to an impractical extent. After cooling to −78 °C, the cell was attached to a vacuum line and degassed for 15 min. Aliquots of O₂ were then added from a gas manifold via a gas-tight valve to the system and the solution allowed to stir until equilibrium had been attained.

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 volmeter (Model 1450).

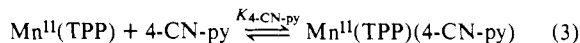Data from the spectrophotometric titration were fitted to the equation[16]

$$\log [y^2/(1 - y)] = n \log P_{O_2} + \log (K/[Mn(T(p\text{-}X)PP)(L)]_{total}) \quad (2)$$

where $[Mn(T(p$-X)PP)(L)]_{total}$ represents the initial concentration of the complex and $y$ is the fraction of manganese(II) sites binding dioxygen, i.e., $y = [Mn(T(p$-X)PP)(O_2)]/[Mn(T(p$-X)PP)(L)]_{total}$. For a plot of $\log [y^2/(1 - y)]$ 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 were fitted using a nonweighted linear least-squares method. Values for $K/[Mn(T(p$-X)PP)(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 (vide infra) the equilibrium constants, $K$, for the reaction of eq 1 were sufficiently 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, $A_\infty$, were determined by systematically varying $A_\infty$ to obtain a best straight-line fit to eq 2.

The concentrations of $Mn^{II}(T(p$-X)PP)(L)$ used in measuring $K$ 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 $Mn^{II}(T(p$-X)PP)$ was calculated to be present in insignificant amounts.

Equilibrium constants for the reaction

$$Mn^{II}(TPP) + 4\text{-CN-py} \underset{}{\overset{K_{4\text{-CN-py}}}{\rightleftharpoons}} Mn^{II}(TPP)(4\text{-CN-py}) \quad (3)$$

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 $40.0 \pm 0.1$ °C. In general the spectra were recorded in the 630–530-nm region during the titration.

The data were fitted to the Hill equation[17]

$$\log [y/(1 - y)] = n \log [4\text{-CN-py}] + \log K_{4\text{-CN-py}} \quad (4)$$

where $y$ equals the fraction of $Mn^{II}(TPP)$ binding 4-CN-py; i.e., $y = [Mn(TPP)(4$-CN-py$)]/[Mn(TPP)]_{total}$. Values for $\log K_{4\text{-CN-py}}$ 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.

## Results

The reduction of $Mn^{III}(T(p$-X)PP)(Cl)$ with NaBH₄ in CHCl₃/MeOH solution in the presence of a nitrogen-donor ligand, L, results in the formation of the solid, five-coordinate manganese(II) complexes $Mn^{II}(T(p$-X)PP)(L)$.[13] As solids, these complexes are moderately stable with respect to aerial oxidation and transfers of the solid materials can be performed in contact with the atmosphere without special precautions. Exposing a solution of the $Mn^{II}(T(p$-X)PP)(L)$ complexes to the atmosphere at room temperature in the absence of a large excess of a coordinating base results in a rapid, irreversible oxidation of the manganous porphyrin. The optical spectra of the resulting solutions are similar to those obtained from para-substituted tetraphenylporphinatomanganese(III) complexes.[18] When dissolved in strongly coordinating solvents, e.g., pyridine or 1-methylimidazole, at room temperature and in contact with the atmosphere, the $Mn^{II}(T(p$-X)PP)$ complexes are stable for periods of at least several hours.

Heating solid $Mn^{II}(T(p$-X)PP)(py)$ in vacuo at 250 °C for several hours results in the formation of the corresponding four-coordinate, base-free $Mn^{II}(T(p$-X)PP)$ complexes.[19] The identity of these complexes 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). The visible electronic absorption spectra obtained at room temperature (under N₂) for these complexes are typical of tetraphenylporphinatomanganese(II) complexes.[20] Absorption maxima and extinction coefficients for several $Mn^{II}(T(p$-X)PP)$ complexes are given in Table I. We note that the effect of adding an axial ligand to the four-coordinate $Mn^{II}(T(p$-X)PP)$ complexes is to red shift the optical spectrum.

Spectrophotometric titrations of toluene solutions of $Mn^{II}(TPP)$ with toluene solutions containing 4-CN-py were performed. 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 $1.0 \pm 0.2$. Adequate isosbestic points were maintained throughout the titration. Values for the slopes and equilibrium constants for the addition of 4-CN-py to $Mn^{II}(TPP)$ are given in Table II.

Dissolving $Mn^{II}(T(p$-X)PP)(L)$ in toluene under N₂ results in the formation of an equilibrium mixture of the four-coordinate, $Mn^{II}(T(p$-X)PP)$, and five-coordinate, $Mn^{II}(T(p$-X)PP)(L)$, species in solution. (At 10 °C, a solution nominally $10^{-4}$ M in $Mn^{II}(TPP)(py)$ was found to have ~40% of the manganous porphyrin as the base-free, $Mn^{II}(TPP)$ complex.) At −78 °C, however, the equilibrium constants for the association of the ligand, L, with the base-free species are suffi-

**Table I.** Visible Absorption Spectral Data for $Mn^{II}T(p\text{-}X)PP$ at Room Temperature[a]

| porphyrin | solvent | $\alpha$ | $\beta$ | $\beta'$ | Soret |
|---|---|---|---|---|---|
| $Mn^{II}T(p\text{-}OMe)$-PP | toluene | 605 | 567 | 524 | 437 |
| $-1.072^b$ | log $\epsilon$ | 4.04 | 4.10 | 3.62 | |
| | pyridine | 617 | 577 | 534 | 444 |
| $Mn^{II}T(p\text{-}Me)PP$ | toluene | 603 | 565 | 524 | 435 |
| $-0.68^b$ | log $\epsilon$ | 3.99 | 4.14 | 3.60 | |
| | pyridine | 616 | 577 | 534 | 443 |
| $Mn^{II}TPP$ | toluene | 601 | 564 | 522 | 435 |
| $0.00^b$ | log $\epsilon$ | 3.91 | 4.13 | 3.68 | |
| | pyridine | 613 | 575 | 530 | 442 |
| | log $\epsilon$ | 4.09 | 4.08 | 3.79 | |
| | 4-CN-py[c] | 610 | 573 | 530 | 439 |
| | log $\epsilon$ | 4.07 | 4.09 | 3.73 | |
| | THF | 606 | 568 | 527 | 433 |
| $Mn^{II}T(p\text{-}F)PP$ | toluene | 601 | 564 | 523 | 444 |
| $+0.248^b$ | | | | | |
| | pyridine | 614 | 573 | 531 | 454 |
| $Mn^{II}T(p\text{-}Cl)PP$ | toluene | 602 | 563 | 523 | 442 |
| $+0.904^b$ | log $\epsilon$ | 3.87 | 3.98 | | |
| | pyridine | 613 | 574 | 537 | 442 |
| $Mn^{II}T(p\text{-}NO_2)$-PP[d] | toluene | | | | 443 |
| $+3.112^b$ | | | | | |
| | pyridine | 618 | 576 | 523 | 451 |

[a] Given in nm. The $\alpha$, $\beta$, and Soret designations are standard nomenclature, ref 18. The $\beta'$ band represents a peak occurring between 520 and 535 nm. [b] Represents $4\sigma$ values taken from K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1966, Table 3-25. [c] Measured in a $6.3 \times 10^{-2}$ M solution of 4-CN-py in toluene. [c] Complex was too insoluble to obtain any but the Soret band.

ciently large so that upon dissolution of solid $Mn(T(p\text{-}X)\text{-}PP)(L)$ in toluene at concentrations of $Mn^{II}(T(p\text{-}X)PP)$ greater than $\sim 10^{-5}$ M, the manganous porphyrin is present predominantly in the five-coordinate form.

Spectrophotometric titrations for the oxygenation of $Mn^{II}(T(p\text{-}X)PP)(L)$, eq 1, were performed in toluene at $-78$ °C. The results from a typical titration are shown in Figure 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 (Figure 2) with slopes of $1.00 \pm 0.10$, with the exception that for the oxygenation of $Mn^{II}(TPP)(1\text{-}MeIm)$ slopes of 1.14 and 1.18 were observed. Values for the slopes and the calculated equilibrium constants are given in Table III. Equilibrium constants were checked at a second wavelength and proved independent of the wavelength chosen.

## Discussion

Four-coordinate para-substituted tetraphenylporphinato-manganese(II) complexes have visible absorption and ESR spectra typical of high-spin manganese(II) porphyrin complexes.[21] In the presence of excess coordinating ligand, L, where L represents an oxygen, nitrogen, phosphorus, or sulfur donor, toluene solutions of $Mn^{II}(T(p\text{-}X)PP)$ form the five-coordinate adducts, $Mn^{II}(T(p\text{-}X)PP)(L)$. This is consistent with the results of our spectrophotometric titrations of four-coordinate $Mn^{II}(TPP)$ and is in agreement with previous studies of the solution properties of $Mn^{II}(TPP)^3$ as well as with single-crystal x-ray studies on complexes of the form $Mn^{II}(TPP)(L)$.[22] That formation of the five-coordinate complexes, $Mn^{II}(T(p\text{-}X)PP)(L)$, is characteristic of the series of para-substituted manganese(II) porphyrins was confirmed by the stepwise addition of toluene solutions of strongly coordinating N-donor ligands to toluene solutions of the four-coordinate complexes at room temperature. In all cases adequate isosbestic points were obtained. No evidence was found
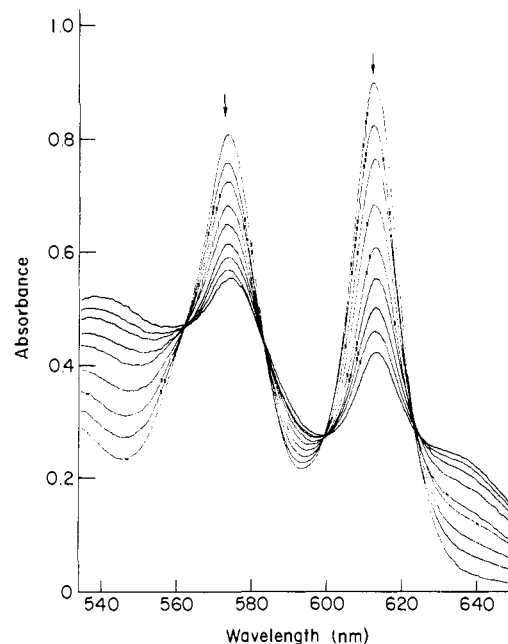


**Figure 1.** Optical spectral changes on the addition of molecular oxygen to a $1.1 \times 10^{-4}$ M toluene solution of $Mn^{II}(TPP)(sec\text{-}BuNH_2)$ at $-78$ °C. The final spectrum was run at a pressure of $O_2$ of 1004 Torr. At this pressure the manganous porphyrin is 79% oxygenated.

**Table II.** Equilibrium Constants for the Addition of 4-Cyanopyridine to $Mn^{II}(TPP)$ in Toluene

$$Mn^{II}(TPP) + 4\text{-}CN\text{-}py \underset{}{\overset{K_{4\text{-}CN\text{-}py}}{\rightleftharpoons}} Mn^{II}(TPP)(4\text{-}CN\text{-}py)$$
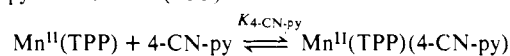
| ligand | temp, °C[a] | slope $(n)^b$ | log $K_{4\text{-}CN\text{-}py}^c$ |
|---|---|---|---|
| 4-cyanopyridine | 40.0 | 0.94 | 3.16 |
| | 40.0 | 1.05 | 3.04 |
| | 23.0 | 1.14 | 3.60 |
| | 23.0 | 1.17 | 3.59 |
| | 23.0 | 1.08 | 3.55 |
| | 0.0 | 1.12 | 4.19 |
| | 0.0 | 1.20 | 4.21 |
| | $-78$ (extrapolated) | | 7.63 |

[a] $\pm 0.1$ °C. [b] Slope from fitting the data to the Hill equation (eq 4). [c] Errors estimated at $\pm 0.1$. 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.

during the course of this investigation to suggest the formation of the six-coordinate complexes, $Mn^{II}(T(p\text{-}X)PP)(L)_2$.

In the presence of molecular oxygen at low temperatures in toluene solution, an equilibrium between the five-coordinate monoligated species, $Mn(T(p\text{-}X)PP)(L)$, and the dioxygen complex, $Mn(T(p\text{-}X)PP)(O_2)$, is established (eq 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 porphyrins with molecular oxygen confirm that the manganous porphyrins add only 1 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 porphyrin complexes, $Mn^{II}(T(p\text{-}X)PP)(L)$, 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.[17] The resulting plots of log $[y/(1 - y)]$ vs. log $P_{O_2}$ (where $y$ equals the fraction of manganese sites oxygenated)
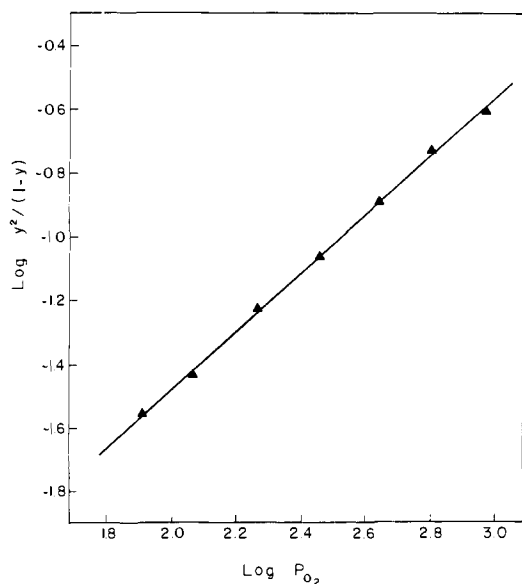
**Figure 2.** Plot of log $[y^2/(1 - y)]$ vs. log $P_{O_2}$ for the oxygenation of $Mn^{II}(TPP)((n\text{-}Bu)_3P)$ in toluene solution at $-78$ °C. The slope is 0.91 and log $K = -8.44$. An $R$ factor of 0.9998 was calculated.
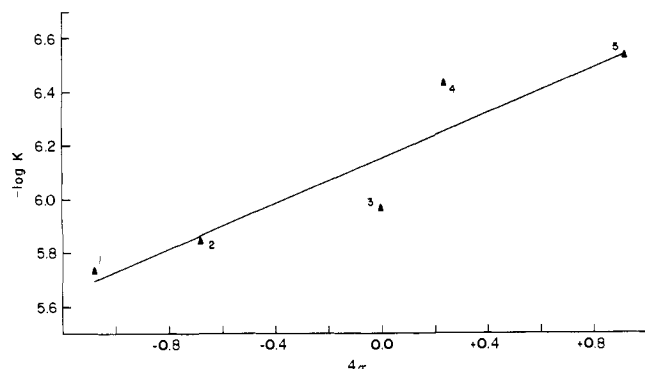


**Figure 3.** A Hammett plot $(-\log K$ vs. $4\sigma)$ for the reaction $Mn^{II}(T(p\text{-}X)PP)(py) + O_2 \rightleftharpoons Mn(T(p\text{-}X)PP)(O_2) + py$. The numbers refer to the $p$-X substituents: $1 = p\text{-}OMe$; $2 = p\text{-}Me$; $3 = p\text{-}H$; $4 = p\text{-}F$; $5 = p\text{-}Cl$. The values for $-\log K$ are the average values. Values for $\sigma$ are given in Table I.

**Table III.** Equilibrium Constants $(K)$ for the Reaction $Mn^{II}(T(p\text{-}X)PP)(L) + O_2 \rightleftharpoons Mn^{II}(T(p\text{-}X)PP)(O_2) + L$ at $-78$ °C Toluene

| porphyrin | L | $n^a$ | $-\log K^b$ |
|---|---|---|---|
| $Mn^{II}(TPP)$ | 4-CN-py$^c$ | 1.08 | 5.57 |
| | $pK_a = 1.86^d$ | 0.93 | 5.58 |
| | py | 1.09 | 5.91 |
| | $pK_a = 5.27^e$ | 1.06 | 5.95 |
| | | 1.06 | 5.97 |
| | | 1.01 | 6.02 |
| | 3,4-lut | 1.04 | 7.09 |
| | $pK_a = 6.46^e$ | 1.10 | 7.19 |
| | 1-MeIm | 1.14 | 7.94 |
| | $pK_a = 7.25^e$ | 1.18 | 8.00 |
| | sec-$BuNH_2^e$ | 0.93 | 7.33 |
| | $pK_a = 8.43$ | 1.00 | 7.39 |
| | $(n\text{-}Bu)_3P^f$ | 1.00 | 8.52 |
| | $pK_a = 8.43$ | 0.91 | 8.44 |
| | $(C_2H_5O)_3P$ | 0.91 | 5.43 |
| | $pK_a = 3.50^g$ | 0.91 | 5.59 |
| | thioanisole | 1.03 | 7.43 |
| | | 0.99 | 7.46 |
| $Mn^{II}(T(p\text{-}Cl)PP)$ | py | 1.02 | 6.48 |
| | | 1.01 | 6.57 |
| $Mn^{II}(T(p\text{-}F)PP)$ | py | 1.09 | 6.43 |
| | | 1.04 | 6.43 |
| | | 1.07 | 6.34 |
| $Mn^{II}(T(p\text{-}Me)PP)$ | py | 1.03 | 5.92 |
| | | 0.99 | 5.82 |
| $Mn^{II}(T(p\text{-}OMe)PP)$ | py | 1.08 | 5.77 |
| | | 1.09 | 5.73 |

$^a$ Calculated from a least-squares analysis of log $[y^2/(1 - y)]$ vs. log $P_{O_2}$. See text for details. $^b$ $K$ has units of mol/L·Torr. From a least-squares analysis of the data all values for log $K$ fell within $\pm 0.1$ (see text for details). $^c$ For abbreviations see ref 2. $^d$ K. Schofield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, N.Y., 1967, p 146. $^e$ A. Albert, *Phys. Methods Heterocycl. Chem.*, 1 (1963). $^f$ C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960). $^g$ Estimated value; see ref 35.

showed both deviations from straight-line behavior and slopes significantly different from $n = 1.00$. (For example, the results of the titration of $Mn(TPP)((n\text{-}Bu)_3P)$ with $O_2$, shown in Figure 2 when analyzed according to the Hill equation, see eq 4, gave a slope of 0.52.) (2) The values obtained for the logarithm of the equilibrium constants for the oxygenation of $Mn(TPP)(py)$ were found to be directly proportional to the logarithm of the concentration of manganese porphyrin used when the data were analyzed by the Hill method. Such results are inconsistent with the oxygenation of the manganous porphyrins being a straightforward addition reaction but are consistent with the replacement by oxygen of the axial ligand.

The effect of substitution on the phenyl rings of tetraphenylporphinatometal complexes on the electronic properties and reactivities of the metal center have been shown to be adequately described by the Hammett relationship:[7,23,24]

$$\log (K^X/K^H) = \sigma\rho \qquad (5)$$

where $K^X$ represents the equilibrium constant observed for the substituted porphyrin and $K^H$ is the value observed for the unsubstituted TPP complex. The Hammett $\sigma$ constant is characteristic of the substituent and reflects the relative

electron donating/withdrawing properties of the substituent X. (The $\sigma$ value for H is defined as 0.00.) The value of the Hammett $\rho$ parameter indicates the sensitivity of the metal center to the changes in electron density arising from the substitution of the phenyl ring. In dealing with the para-substituted tetraphenylporphinatomanganese(II) complexes, the proper form of the Hammett equation is

$$\log (K_X/K_H) = 4\sigma\rho \qquad (6)$$

The equilibrium constants measured for the replacement of pyridine by dioxygen for the series $Mn^{II}(T(p\text{-}X)PP)(py)$, eq 1, agree reasonably well with expected Hammett behavior. A plot of $-\log K$ vs. $4\sigma$ is shown in Figure 3. The calculated $\rho$ value of $-0.41 \pm 0.08$ indicates that donation of electron density to the porphyrin ring by the para substituents enhances the ability of the five-coordinate manganous porphyrin complexes to undergo replacement by dioxygen. A similar linear correlation between log $K$ and the ease of oxidation $(Mn^{II/III})$ has been observed.[25]
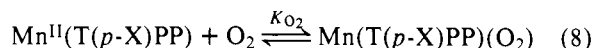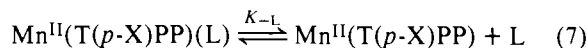
Although the relationship discussed above between log $K$ and the Hammett $\sigma$ values is consistent with the well-documented phenomenon that an increase in electron density at the metal center increases the affinity of the complex for binding molecular oxygen,[6,7] it must be noted that the equilibrium constants reported here are not simply for dioxygen uptake. In order to determine the magnitude of the effect of para substitution on the affinity of the manganous center for dioxygen, we must assess the effect of para substitution of the phenyl groups on the dissociation of the axial pyridine ligand from the five-coordinate species to give the base-free four-

**Table IV.** Equilibrium Data for the Monoligation of Four-Coordinate Para-Substituted *meso*-Tetraphenylporphinato Metal Complexes

$$M(T(p\text{-}X)PP) + L \underset{}{\overset{K_L}{\rightleftharpoons}} M(T(p\text{-}X)PP)(L)$$

| porphyrin | L | conditions | log $K_L{}^a$ | $\rho$ | ref |
|---|---|---|---|---|---|
| Zn(T(p-X)-PP) | pyridine | 25 °C, benzene | 3.72 | 0.188 | 23 |
| Co(T(p-X)-PP) | pyridine | 25 °C, toluene | 2.88 | 0.168 | 7 |
| | piperidine | 25 °C, toluene | 3.62 | 0.145 | 7 |
| VO(T(p-X)-PP | piperidine | 25 °C, toluene | −0.40 | 0.113 | 24 |
| Ni(T(p-X)PP | piperidine | 25 °C, toluene | −0.37$^b$ | 0.166$^c$ | 24 |

$^a$ For the TPP complex. $^b$ Ni$^{II}$(T(p-X)PP) adds 2 mol of a nitrogenous base to yield the bis adducts, Ni$^{II}$(T(p-X)PP)(L)$_2$. $^c$ Estimated for the addition of a single piperidine to the Ni(II) complexes. See ref 7.

coordinated manganese(II) complexes. The oxygen uptake (eq 1) can be rewritten in terms of the two equilibria

$$Mn^{II}(T(p\text{-}X)PP)(L) \overset{K_{-L}}{\rightleftharpoons} Mn^{II}(T(p\text{-}X)PP) + L \quad (7)$$

$$Mn^{II}(T(p\text{-}X)PP) + O_2 \overset{K_{O_2}}{\rightleftharpoons} Mn(T(p\text{-}X)PP)(O_2) \quad (8)$$

The Hammett $\rho$ value observed for eq 1 represents, therefore, the sum of the $\rho$ values for reactions 7 and 8 by the equation

$$\log (K^X/K^H) = \log \left( \frac{K_{-L}{}^X K_{O_2}{}^X}{K_{-L}{}^H K_{O_2}{}^H} \right) = 4\sigma(\rho_{-L} + \rho_{O_2}) \quad (9)$$

where $\rho_{-L}$ and $\rho_{O_2}$ are the Hammett $\rho$ values associated with reactions 7 and 8, respectively.

The determination of the effects of para substitution on the binding strength of dioxygen to manganous porphyrins can in theory be obtained by measuring the equilibrium constants for the oxygenation reaction (eq 8) directly. Unfortunately, we have so far not been able to determine these values. Upon cooling a toluene solution of the base-free manganous porphyrins to −78 °C, both the $\alpha$ and $\beta$ bands in the visible spectrum were observed to change both in intensity and position. (For Mn(TPP) the $\alpha$ band was observed to shift from 601 to 605 nm, with the $\beta$ band shifting from 564 to 568 nm.) The resulting spectrum is similar to, but not identical with, the spectrum we observe for Mn(TPP) in the presence of excess MeOH. Although we do not know the nature of the impurity, the spectral results are consistent with the interpretation that upon cooling the toluene solution to −78 °C we are observing the formation of Mn(TPP)(H$_2$O) arising from residual water in the toluene solution.[26] For the same reasons, it was not possible to determine $K_L$ directly in toluene solution at −78 °C.[27]

Fortunately Hammett $\rho$ values for the reaction

$$M(T(p\text{-}X)PP) + L \rightleftharpoons M(T(p\text{-}X)PP)(L) \quad (10)$$
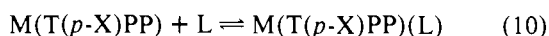
have been reported at room temperature for several para-substituted tetraphenylporphinato metal systems (Table IV). Despite wide variations in the electronic configuration of the metal center (as evidenced by the large variations in the equilibrium constants for the M(TPP) complexes) the $\rho$ values for monoligation all fall within a narrow range.[28] The magnitude of the Hammett $\rho$ value at room temperature for the dissociation of a pyridine from Mn$^{II}$(T(p-X)PP)(py), eq 7, is therefore expected to be similar to the values listed in Table V. (The sign of $\rho_L$ for reaction 7 will be negative as it represents the dissociation of a base from the metalloporphyrin complex.)

**Table V.** Equilibrium Constants for the Oxygenation of Metalloporphyrin Complexes at −78 °C$^a$

| complex | conditions | log $K_{O_2}$ | $E_{1/2}$ (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 Me$_2$SO. Values reported in volts vs. SCE. $^c$ For Co(TPP) and Co$^{II}$(T(p-OMe)PP); ref 7. $^d$ F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1154 (1973). $^e$ TpivPP represents the dianion of the "picket-fence" porphyrin. J. P. Collman, J. I. Braumau, and K. S. Suslick, *J. Am. Chem. Soc.*, **97**, 7185 (1975). $^f$ K. M. Kadish, M. M. Morrison, L. A. Constant, L. Dickens, and D. G. Davis, *J. Am. Chem. Soc.*, **98**, 8387 (1976). $^g$ This work. $^h$ Reference 25. $^i$ The dioxygen adduct forms irreversibly. S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).

The dependence of the Hammett $\rho$ value on temperature has been shown to take the functional form[29]

$$\rho = \alpha + \beta T^{-1} \quad (11)$$

with the sign of $\beta$ in general being positive. An estimate of the effect of a change in temperature on the Hammett $\rho$ value for the monoligation reaction of para-substituted tetraphenylporphinato metal complexes can be made using the equilibrium data published by Walker and co-workers[30] for the addition of piperidine to Ni$^{II}$(T(p-X)PP) complexes. From this analysis, the temperature dependence of $\rho_L$ (the Hammett constant for eq 7 for L = py) has been estimated as $\rho_L(-78$ °C$) - \rho_L(25$ °C$) \approx -0.18$. Using a reasonable estimate for $\rho_L(25$ °C$)$ as −0.15 (Table IV) (and recalling that the Hammett $\rho$ value for the replacement of pyridine by O$_2$ at −78 °C in toluene has been measured as −0.41), we observe that the affinity of dioxygen for the four-coordinate Mn$^{II}$(T(p-X)PP) complexes is relatively insensitive ($\rho_{O_2} \sim -0.08$) to para substitution of the tetraphenylporphinato phenyl rings. A relatively small effect of para substitution of the TPP ring on dioxygen bonding has also been observed[7] for the addition of O$_2$ to Co$^{II}$(T(p-X)PP)(py) in toluene solution at low temperature to form the six-coordinate complexes Co(T(p-X)PP)(py)(O$_2$). The Hammett $\rho$ value for O$_2$ addition in these cobalt(II) complexes was observed to be −0.105 at −72 °C, which compares with our rough estimate of −0.08 for O$_2$ addition to Mn$^{II}$(T(p-X)PP).

The bonding of an axial ligand, L, to tetraphenylporphinatomanganese(II) was investigated at −78 °C in toluene by determining the equilibrium constant for oxygenation of Mn$^{II}$(TPP)(L), eq 1, for a variety of ligands (Table III).[31] A plot of −log $K$ vs. the $\sigma$-donor strength of the ligand L (represented as p$K_a$ for LH$^+$) is shown in Figure 4. Deviations of the values for −log $K$ from a straight-line plot indicate that the equilibrium constants for the addition of a ligand to a manganous porphyrin cannot be interpreted solely in terms of the relative $\sigma$-donor strength of the ligand L.

We have recently reported[32] that for the binding of a sixth ligand to Cr$^{III}$(TPP)(Cl) in toluene a good correlation exists between the affinity of the ligand for the Cr(III) center and the $\sigma$-donor ability of the ligand, when L is a substituted pyridine or primary amine. The only deviation from straight-line behavior was observed for the addition of 1-methylimidazole, which showed an anomalously strong affinity for the Cr(III)
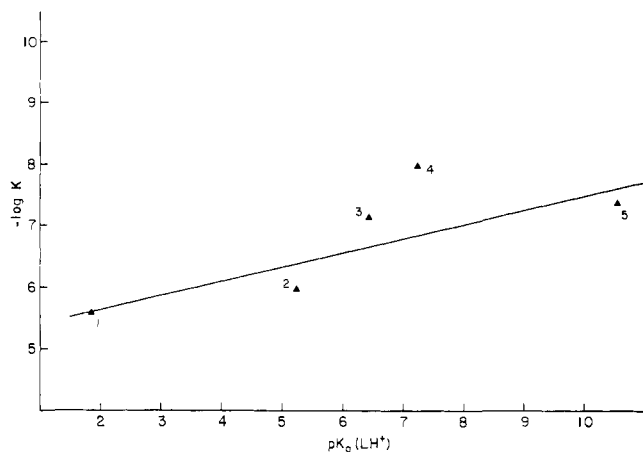
**Figure 4.** Correlation between $pK_a$ for the conjugate acids (LH$^+$) and $-\log K$ for the reaction Mn$^{II}$(TPP)(L) + O$_2 \rightleftharpoons$ Mn(TPP)(O$_2$) + L in toluene at $-78$ °C. Ligands are 1 = 4-CN-py; 2 = py; 3 = 3,4-lut; 4 = 1-MeIm; 5 = *sec*-BuNH$_2$.[2] The straight line represents a least-squares regression line for points 1, 2, 3, and 5.

center. This behavior of imidazole toward other metal centers was interpreted as being due to the $\pi$ electron donation property of imidazole.[33]

Construction of a least-squares line for the values of $-\log K$ for the oxygenation of Mn$^{II}$(TPP)(L) vs. the $pK_a$ values for the substituted pyridine bases and *sec*-butylamine, Figure 4, shows that, although there appears to be a general correlation between the parameters, the 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 $-\log K$ observed for Mn$^{II}$(TPP)(1-MeIm) is similar to that observed previously for the ligation of Cr(III) porphyrins.[32]

An examination of the data for the bonding of the phosphorus-donor ligands, (C$_2$H$_5$O)$_3$P and (*n*-Bu)$_3$P, 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 III) obtained for the substituted pyridine ligands and *sec*-butylamine, (C$_2$H$_5$O)$_3$P and (*n*-Bu)$_3$P show affinities for the manganous porphyrin that are respectively weaker and stronger than would be predicted on the bases 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 $\pi$ bonding plays a relatively constant role in the bonding of the ligand to the metal center or that there exists an intimate balance between $\sigma$- and $\pi$-bonding effects. Both $\sigma$ and $\pi$ bonding have been implicated in the bonding of both pyridine and P-donor ligands to metal centers.[34] The variation in bonding of the neutral ligand to the manganese(II) porphyrin observed for the N- and P-donor series may therefore reflect differences in $\pi$ bonding between the manganese(II) center and the nitrogen- and phosphorus-donor ligands. This effect is similar to that previously reported[35] for the binding of an axial ligand to the four-coordinate diethyl ester of mesoporphyrincobalt(II) where it was observed that the influence of $\sigma$-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.

From the equilibrium constants for the binding of 4-CN-py to Mn$^{II}$(TPP) (Table II) and the value for the equilibrium constant for oxygenation of Mn$^{II}$(TPP)(4-CN-py) at $-78$ °C (Table III), we can estimate a value for the oxygenation of

four-coordinate Mn$^{II}$(TPP) at $-78$ °C. From the data in Table II we obtain a value for log $K_{4\text{-CN-py}}$, 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 $K = -5.57$, we calculated the value for the equilibrium constant for the oxygenation of Mn$^{II}$(TPP) at $-78$ °C as $K_{O_2} \sim 10^{2.1}$ Torr$^{-1}$.

A comparison of the equilibrium constants for oxygenation for a series of porphyrinato metal(II) complexes at $-78$ °C with the M$^{III/II}$ half-wave reduction potentials (Table V) shows that, with the exception of Mn$^{II}$(TPP), there is a direct relationship between the affinity of the complex for dioxygen and ease of oxidation of the metal(II) center. Thus, the $K_{O_2}$ observed for Mn$^{II}$(TPP) at $-78$ °C 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 porphyrinato 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. The geometry of the manganese–dioxygen bond in Mn(TPP)(O$_2$) has not yet been unambiguously determined (vide infra). The bonding in the metalloporphyrin–dioxygen complexes containing Fe, Co, and Cr has been shown to bind dioxygen in an end-on (Pauling) conformation. Since we expect the relationship between $K_{O_2}$ and $E_{1/2}$ 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. There is, however, another interpretation for the anomalous value for $K_{O_2}$. Basolo and co-workers[6] 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 $K_{O_2}$ = $-2.0$ at 0 °C for L equals 1-MeIm), only a small amount of the four-coordinate Co$^{II}$(benacen) complex is oxygenated under 1 atm 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 $K_{O_2}$ is consistent with the absence of a sixth axial ligand.

Finally it is interesting to compare the chemical properties observed for the dioxygen adducts of tetraphenylporphinatomanganese(II) complexes with some of the ground-state electronic configurations that have been suggested for these dioxygen complexes.[5,36] The EPR spectra of frozen toluene solutions containing Mn(TPP)(O$_2$) have been interpreted[5] in terms of a formal Mn$^{IV}$–O$_2^{2-}$ ground state. A recent study[32] on the chemical and spectroscopic properties of Cr$^{III}$(TPP)-(Cl), which contains a d$^3$ metal center, has shown that five-coordinate Cr$^{III}$(TPP)(Cl) has an exceptionally large affinity toward binding a sixth N-donor ligand. In contrast with this behavior, we have observed no tendency for the presumed d$^3$ Mn(IV) in Mn(TPP)((O$_2$) to bind a sixth ligand at $-78$ °C.[37]

The large difference in the affinities of the five-coordinate d$^3$ metalloporphyrin complexes Cr$^{III}$(TPP)(Cl) and Mn(TPP)(O$_2$) for an axial ligand can be interpreted as arising from either of two factors: (1) repulsive steric interactions between the coordinated dioxygen and the porphyrinato ring for Mn(TPP)(O$_2$), that result in the manganese center lying out of the plane of the porphyrin toward the coordinated dioxygen; or (2) differences in the ground-state electronic configurations of the chromium and manganese centers that favor the Mn(TPP)(O$_2$) structure.

Two geometric conformations (I and II) have been suggested for the bonding of dioxygen to the manganous porphyrins. On the basis of the formal Mn$^{IV}$–O$_2^{2-}$ ground-state configuration, it has been suggested[5] that geometry II is to be

I     II
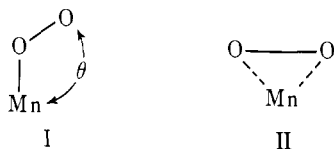
preferred in agreement with the geometries found for other metal–peroxo systems. This structural assignment is also consistent with the observation that the porphyrinatomanganese–dioxygen complexes do not bind an axial ligand.[5] For structure II, the manganese center would be drawn into the plane of the porphyrin by the bonding of an axial ligand. This would be expected to result in severe interactions between the coordinated dioxygen ligand and the porphyrinato ring. For geometry I, such severe repulsive interactions would not occur, and the manganese–dioxygen complex would be expected to bond an axial ligand readily.

The difference in affinities of $Cr^{III}(TPP)(Cl)$ and $Mn(TPP)(O_2)$ toward binding a second axial ligand can also be interpreted as arising from differences in the electronic ground state configuration of the manganese(IV) and chromium(III) centers. For the porphyrinatochromium(III) complexes the electrons adopt the expected $(d_{xy})^1(d_{xz})^1(d_{yz})^1$ configuration.[32,38] For the porphyrinatomanganese dioxygen complexes, however, the ground state electronic configuration has not yet been unambiguously determined.

We note that the presence of an electron in a $d_{z^2}$ orbital in Co(II) and Mn(III) metalloporphyrin complexes leads to these complexes being generally five coordinate, with the second axial ligand, if present, being bound only weakly.[39,40] Hence, if the electronic ground state configuration of the manganese center in $Mn(TPP)(O_2)$ has an unpaired electron in the $d_{z^2}$ orbital,[36] we would expect the complexes to be five coordinate, regardless of the geometry of the $MnO_2$ bond. However, recent EPR studies[41] on frozen toluene solutions of porphyrinatomanganese dioxygen complexes are consistent with the previous interpretation[5] that the ground-state electronic configurations of these manganese dioxygen complexes do not include an unpaired electron in the $d_{z^2}$ orbital.

## References and Notes

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(2) Abbreviations: TPP, the dianion of *meso*-tetraphenylporphine; T(*p*-X)PP, the dianion of the tetra-para-substituted *meso*-tetraphenylporphine; py, pyridine; DMF, *N,N*-dimethylformamide; 1-MeIm, *N*-methylimidazole; *sec*-BuNH₂, *sec*-butylamine; 3,4-lut, 3,4-lutidine (3,4-dimethylpyridine); 4-CN-py, 4-cyanopyridine; (*n*-Bu)₃P, tri-*n*-butylphosphine; Co(benacen), *N,N'*-ethylenebis(benzoylacetiminato)cobalt(II).

(3) (a) C. J. Weschler, B. M. Hoffman, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 5278 (1975). (b) That THF–toluene solutions of Mn(TPP) are capable of reversibly binding O₂ at −90 °C has been noted by B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner, and W. R. Scheidt, *ibid.*, **97**, 3247 (1975).

(4) On the basis on the O–O stretching frequency both the iron– and cobalt–dioxygen complexes can be classified as "superoxide-like". We do not intend to imply, however, that the ground-state electronic configuration of the metal–dioxygen moiety is necessarily $M^{III}(O_2^-)$. Whereas for the cobalt–dioxygen adducts, the conventional oxidation states are unambiguously Co(III) and (O₂⁻), there is still controversy as to whether the iron–dioxygen bond is best represented as either $Fe^{II}(O_2)$ or $Fe^{III}(O_2^-)$. See L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976), and references cited therein.

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(15) The bistoluene solvate of this molecule has been previously reported. The authors (ref 3b) note that the complex was prepared by the reduction of Mn^III^(TPP)(Cl) with Cr^II^(acac)₂ in toluene. The complete crystal and molecular structure of the toluene solvate has recently been reported: J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **99**, 1093 (1977).

(16) This equation can be derived in a straightforward manner from eq 1.

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(19) As solids these complexes are more susceptible to aerial oxidation than the corresponding five-coordinate adducts, Mn^II^(T(*p*-X)PP)(L). Although rapid transfers in contact with the atmosphere can be made, it is suggested that whenever possible the solid be handled exclusively in an inert atmosphere.

(20) The absorption maxima obtained by us for Mn^II^(TPP) in toluene at room temperature (601, 564, and 522 nm) differ slightly from those reported in ref 3b (605, 569, and 525 nm). These shifts are consistent with the presence of a small amount of a weakly coordinating ligand being present in the toluene solutions used by the previous workers.

(21) The 77 K EPR spectra of frozen toluene solutions of the Mn^II^(T(*p*-X)PP) complexes were typical of porphyrinatomanganese(II) complexes (ref 5). They all showed a six-line low-field resonance at $g \sim 6$ and a resonance at $g \sim 2$.

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(26) Efforts to ensure dry toluene included refluxing toluene over sodium benzophenone ketyl for a minimum of several days before use, direct transfer of the toluene from the still after distillation using a carefully dried gas-tight syringe, and drying the cold-temperature optical cell in an oven at 130 °C immediately prior to use. No "fogging" of the solution due to the formation of fine ice particles at −78 °C was observed for any of the reported runs.

(27) In addition to the presence of a coordinating ligand in the solution, determination of $K_L$ at −78 °C is precluded by the magnitudes of $K_L$ at this temperature. In theory values for $K_L$ could be obtained at higher temperatures where the complexes are exclusively four coordinate and the results extrapolated to −78 °C. The extreme air sensitivity of dilute solutions of the four-coordinate Mn^II^(T(*p*-X)PP) complexes led to comparatively large errors in room temperature determinations of $K_L$. Errors involved in determining extrapolated values for $K_L$ at −78 °C precluded our attempts to determine these values in this manner.

(28) The relatively small range observed for the Hammett $\rho$ values for the monoligation of the four-coordinate Zn(II), Co(II), and VO porphyrin complexes (Table V) suggests that the stoichiometry of the addition reaction has a dominant effect on the $\rho$ value. The $\rho$ value for the monoligation of Ni^II^(T(*p*-X)PP), $\rho = 0.166$, has been previously estimated as being one-half the $\rho$ value observed for the addition of two molecules of piperidine to the Ni(II) metalloporphyrin complexes (ref 7).

(29) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, New York. N.Y., 1972, Chapter 1, and references cited therein.

(30) Hammett $\rho$ values for the reaction Ni^II^(T(*p*-X)PP) + 2 piperidine $\rightleftharpoons$ Ni(T(*p*-X)PP)(piperidine)₂ were calculated from the equilibrium constants reported by Walker and co-workers for the addition of piperidine to Ni^II^(TPP) and Ni^II^(T(*p*-CN)PP) at four temperatures (ref 24). Following Walker and co-workers (ref 7) we take the Hammett $\rho$ values for monoligation of two piperidine molecules. The calculated $\rho$ values were then fit to eq 5 to obtain a value of $\beta = 104.3$.

(31) As the product of the reaction is always Mn(TPP)(O₂), a comparison of −log $K$ as a function of the ligand reflects the affinity of the ligand for Mn^II^(TPP).

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(37) If we assume that the maximum amount of a six-coordinate Mn(TPP)(O₂)(py) complex that could go undetected in our titrations is 20% of the total porphyrinatomanganese dioxygen complex present, we can place an upper limit on the equilibrium constant for the binding of a pyridine to Mn(TPP)(O₂) at −78 °C of ~2 × 10⁴. From the equilibrium constant ($K^+$) at 23 °C in toluene determined for the replacement reaction Crᴵᴵᴵ(TPP)(Cl)(acetone) + py ⇌ Crᴵᴵᴵ(TPP)(Cl)(py) + acetone, ref 32, and using a reasonable value for the change in enthalpy of the reaction of $\Delta H = -10$ kcal/mol (similar

to those observed for the bonding of N-donor ligands to metalloporphyrin complexes, Table II), we estimate a value for the log $K'$ of the replacement reaction at −78 °C of ~8.1. We note that for the addition of a pyridine to the five-coordinate Crᴵᴵᴵ(TPP)(Cl), the equilibrium constant would be larger than this value.

(38) The axes chosen have the *xy* plane in the plane of the porphyrin with the core nitrogen atoms lying on the *x* and *y* axes.

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# Electrochemical Oxidations of Complexes of Rhenium(II) Containing Metal–Metal Triple Bonds. Synthesis and Characterization of Paramagnetic Cations of the Type [Re₂X₄(PR₃)₄]⁺, Where X = Cl or Br, Possessing Metal–Metal Bonds of Order 3.5

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**Abstract:** The electrochemical oxidation of the rhenium(II) dimers Re₂X₄(PR₃)₄, where X = Cl, Br, or I and R = Et, *n*-Pr, or *n*-Bu, has been investigated using cyclic voltammetry and coulometry techniques. These studies, coupled with related ones on complexes of the types Re₂X₅(PR₃)₃ and Re₂X₆(PR₃)₂, show that the oxidation of Re₂X₄(PR₃)₄ to [Re₂X₄(PR₃)₄]ⁿ⁺, where $n = 1$ or 2, is followed by the conversion of these cations to Re₂X₅(PR₃)₃ and then Re₂X₆(PR₃)₂. The oxidation of Re₂X₄(PR₃)₄ to Re₂X₆(PR₃)₂ proceeds by both EECC and ECEC coupled electrochemical (E)–chemical (C) reaction series. The difference between these two pathways is the selection of the potential used for the oxidation of Re₂X₄(PR₃)₄. The occurrence of both pathways within the same system is unprecedented, and points to the existence of coupled reactions in the electrochemistry of other metal complexes containing triple and quadruple metal–metal bonds. The mechanism of the chemical reaction which follows the electrochemical oxidation of Re₂X₄(PR₃)₄ has been explored. It is believed that halide ion, generated by the complete disruption of a small proportion of the dimers, reacts with the electrochemically generated cations [Re₂X₄(PR₃)₄]⁺ and [Re₂X₄(PR₃)₄]²⁺ to produce Re₂X₅(PR₃)₃ and [Re₂X₅(PR₃)₃]⁺, respectively. [Re₂X₅(PR₃)₃]⁺ then reacts further with X⁻ to form the final product, Re₂X₆(PR₃)₂. The chemical oxidation of Re₂X₄(PEt₃)₄, where X = Cl or Br, has been achieved using NO⁺PF₆⁻ to afford the salts [Re₂X₄(PEt₃)₄]PF₆. These paramagnetic species possess a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ ground-state electronic configuration and have ESR and electronic absorption spectra which are in accord with a structure in which the cations retain the eclipsed configuration of the parent Re₂X₄(PEt₃)₄ complexes and therefore possess a metal–metal bond order of 3.5. The properties of these new complexes are discussed in detail.

## Introduction

There are three main groups of transition metal dimers which are currently recognized as possessing metal–metal triple bonds.[1,2] Those of molybdenum(III) and tungsten(III) which are of the type M₂L₆, where L = CH₂SiMe₃, NMe₂, NEt₂, OCH₂CMe₃, or OSiMe₃,[3-8] or derivatives thereof, have a $(\sigma)^2(\pi)^4$ ground-state electronic configuration and have been the subject of detailed crystallographic and spectral characterizations.[2] The second group comprises the tertiary phosphine derivatives of rhenium(II), Re₂X₄(PR₃)₄, where X = Cl, Br, or I, which may be prepared[9,10] by the phosphine-induced reductions of the octahalodirhenate(III) anions. These complexes have a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ electronic configuration[11] and possess a molecular structure[12] which is similar to that of Re₂X₅(PR₃)₃ and Re₂X₆(PR₃)₂, which contain metal–metal bonds of order 3.5 and 4, respectively.[9,13] In addition, there are the carbonyl derivatives (η⁵-C₅X₅)₂M₂(CO)₄, where X = H or Me and M = Cr, Mo, or W,[14-17] for which an 18-electron configuration would require the presence of a metal–metal triple bond, an assumption which is supported by crystallographic studies.[15,17]

Of these three groups, it is the derivatives of rhenium(II)

which exhibit the most interesting and extensive redox chemistry, arising as a consequence of changes within the δ and δ* sets of metal-based orbitals. Re₂Cl₄(PR₃)₄ can be oxidized to Re₂Cl₅(PR₃)₃, Re₂Cl₆(PR₃)₂, and (R₃PCl)₂Re₂Cl₈ by O₂, CH₃OH–HCl, and CCl₄, respectively,[9,18] while their preparation via the phosphine reductions of (Bu₄N)₂Re₂Cl₈ and (Bu₄N)Re₂Cl₉ show[9,19] that the Re₂ⁿ⁺ core may survive at least a four-electron oxidation or reduction without being disrupted. In order to explore the possibility that the Re₂X₄(PR₃)₄ dimers may be reduced still further and to gain further insight into the consequences of oxidizing dimers which possess the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ electronic configuration and therefore a metal–metal triple bond, we have carried out a detailed investigation of their electrochemistry. The present study has led to the discovery of a novel series of coupled electrochemical–chemical reactions, the isolation and characterization of paramagnetic cations of the type [Re₂X₄(PR₃)₄]⁺, and an understanding of the mechanism of the oxidation sequence Re₂X₄(PR₃)₄ → Re₂X₅(PR₃)₃ → Re₂X₆(PR₃)₂. We previously reported,[20] in preliminary form, the existence of these coupled electrochemical–chemical reactions and we now describe in full the results of our detailed studies on the electrochemistry of Re₂Cl₄(PR₃)₄.