Chromium(III) Porphyrins. Chemical and Spectroscopic Properties of Chloro-*meso*-tetraphenylporphinatochromium(III) in Nonaqueous Solutions

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Abstract: The spectroscopic and chemical behavior of the six-coordinate adducts formed by the association of chloro-*meso*-tetraphenylporphinatochromium(III), Cr(TPP)(Cl), and neutral oxygen, sulfur, and nitrogen donor ligands in nonaqueous solutions is described. In nonaqueous media, in the presence of a neutral ligand, Cr(TPP)(Cl) forms six-coordinate adducts of the type Cr(TPP)(Cl)(L) and Cr(TPP)(Cl)(B), where L and B denote neutral N-donor and O- or S-donor ligands, respectively. This behavior is confirmed by visible spectroscopy, spectrophotometric titrations, and conductivity data. Equilibrium constants for the substitution reaction Cr(TPP)(Cl)(B) + L $\rightleftharpoons$ Cr(TPP)(Cl)(L) + B are reported. The N-donor ligands are found to bind much more strongly to the Cr(III) center than the O- or S-donors. The replacement of acetone by 1-methylimidazole in the complex Cr(TPP)(Cl)(acetone) in 60% acetone/toluene (v/v) at 25 °C occurs with an equilibrium constant of 4.0×10^6. Fitting the EPR spectra of the six-coordinate adducts obtained from frozen solutions at 78 K to the spin Hamiltonian $H = \beta_e[g_xH_xS_x + g_yH_yS_y + g_zH_zS_z] + D[S_z^2 - 5/4] + E[S_x^2 - S_y^2]$, and using an assumed isotropic value for g of 1.995, results in values for $|D|$ in the range 0.156 ± 0.012 cm^{-1} for complexes of the type Cr(TPP)(Cl)(L) and values in the range 0.232 ± 0.004 cm^{-1} for the complexes of the type Cr(TPP)(Cl)(B). The only observed exception was the CH_3CN adduct for which a value of 0.208 cm^{-1} was obtained. In all cases $|E|$ was found to be small, having a maximum value of 0.013 cm^{-1} for the complex Cr(TPP)(Cl)(acetone). The Cr(octaethylporphyrin) complexes behave similarly.

Introduction

Variations in the biological role of the naturally occurring hemoproteins 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 hemoproteins is an understanding of the manner in which axial ligation affects the electronic structure and reactivity of a metalloporphyrin system.

We here discuss the properties of Cr(III) metalloporphyrins in nonaqueous solutions. Although a number of other workers have previously reported on the synthesis, spectroscopic properties, and reactivities of Cr(III) metalloporphyrin complexes,[1-6] no systematic investigation of these compounds has been reported. One feature of our investigations is the selective variations of the axial substituents on Cr(III) metalloporphyrins to obtain a variety of complexes of the type Cr(porphyrin)(X)(L), where X and L represent anionic and neutral ligands, respectively. In this initial report we discuss some aspects of the behavior of adducts of chloro-*meso*-tetraphenylporphinatochromium(III) in nonaqueous solutions.

Experimental Section

Reagents. Chromous chloride (98%, anhydrous) was obtained from Alfa Products. Octaethylporphyrin was obtained from Strem Chemicals, Inc. Toluene, tetrahydrofuran, dimethyl sulfoxide, pyridine, 1-methylimidazole, and acetonitrile were dried and purified by standard methods and distilled prior to use. 4-Cyanopyridine was recrystallized several times from benzene. Acetone was Baker spectrophotometric grade. All other reagents were reagent grade and were used without further purification, except where otherwise noted.

Syntheses. *meso*-Tetraphenylporphine ($TPPH_2$) was prepared by the method of Adler and co-workers.[7] The $TPPH_2$ was purified (to remove any *meso*-tetraphenylchlorin impurity) by refluxing with 2,3-dichloro-5,6-dicyanobenzoquinone in CH_2Cl_2 using the method of Barnett et al.[8]

Chloro-*meso*-tetraphenylporphinatochromium(III) [Cr(TPP)(Cl)]. This procedure is based on the method published by Adler and co-workers.[1] A typical synthesis is given below.

$TPPH_2$ (5.0 g, chlorin-free) was dissolved in 500 mL of refluxing DMF. After waiting for several minutes for the porphyrin to dissolve, $CrCl_2$ (1 g) was added to the refluxing solution. Reflux was continued for 10 min at which point a further addition of $CrCl_2$ (1 g) was made to the solution. After 10 min of further refluxing, an aliquot was taken from the reaction mixture and a visible spectrum taken ($CHCl_3$). The spectrum indicated that free-base porphyrin ($TPPH_2$) still remained in solution. A further addition of $CrCl_2$ (1 g) was then made to the solution, and reflux continued for 10 min more. At this point a visible spectrum of an aliquot taken from the reaction mixture revealed the absence of any remaining free-base porphyrin. Refluxing was stopped and the reaction mixture allowed to cool to room temperature. (Had the visible spectrum revealed the presence of $TPPH_2$, an additional quantity of $CrCl_2$ (1 g) would have been added and reflux continued. This process would have been repeated until no free-base porphyrin was found in the visible spectrum.) The cooled reaction mixture was poured into a flask containing 500 mL of ice-cold H_2O. The resulting precipitate was collected by filtration, washed with copious amounts of H_2O, and dried in a vacuum oven for 1 h at 100 °C, yield of crude Cr(TPP)(Cl) 6.0 g.

Purification of Cr(TPP)(Cl). Crude Cr(TPP)(Cl) (2.6 g) was dissolved in 150 mL of $CHCl_3$ and filtered. The filtrate was then applied to a dry alumina column (Alcoa F-20, 80–200 mesh) and eluted with $CHCl_3$. The remaining $TPPH_2$ was eluted as a reddish band with the solvent front. This was followed by a slow-moving green band. As the green band came off the column, it was monitored by visible spectroscopy. From the visible spectrum it appeared that a band was eluted from the column just prior to the Cr(TPP)(Cl) band. This band was discarded. After the Cr(TPP)(Cl) was eluted from the column, the volume of $CHCl_3$ was reduced to about 500 mL on a rotary evaporator. Aqueous HCl (12 M, 5 mL) was added to the $CHCl_3$ solution, and the flask was stoppered and left stirring with a magnetic stir bar overnight. The $CHCl_3$ was then removed on a rotary evaporator. The solid was recrystallized from $CHCl_3$/hexane and dried overnight in a vacuum oven at 115 °C, yield of purified Cr(TPP)(Cl) from chromatography 1.2 g. Anal.[9] Calcd for $C_{44}H_{28}N_4CrCl$: C, 75.48; H, 4.03; N, 8.00; Cr, 7.43; Cl, 5.06. Found: C, 74.86; H, 4.43; N, 7.98; Cr, 7.18; Cl, 4.92.

Preparation of Cr(TPP)(Br). Cr(TPP)(Br) was prepared from Cr(TPP)(Cl) by a metathesis reaction in $CHCl_3$ using $(n\text{-Bu})_4NBr$. A solution of (Cr(TPP)(Cl) dissolved in a chloroform solution containing at least a 50-fold excess of $(n\text{-Bu})_4NBr$ was allowed to stand at room temperature for several hours. At this point the $CHCl_3$ solution was extracted three times with an equal volume of water, and the $CHCl_3$ removed under reduced pressure. The solid was then washed thoroughly with water. The above procedure was repeated and the resulting solid dried overnight at 100 °C under vacuum. Anal. for Cl^- and Br^-. Calcd for Cr(TPP)(Br): Br, 10.73. Found: Br, 11.10; Cl, <0.1.

Chlorooctaethylporphinatochromium(III). [Cr(OEP)(Cl)] was prepared in the same manner as Cr(TPP)(Cl). The visible spectrum of the purified material agreed with that obtained by Gouterman et al.[2]

Instruments. Electron resonance spectra were taken on a Varian E4 spectrometer at 9 GHz. The field was calibrated with a strong pitch standard. The frequency was measured with a Sage Tunable Coherent Synchronizer Model 251 with a Transistor Specialties frequency counter.

Conductivities were measured with a YSI Model 3403 conductivity cell ($k = 1.00 \pm 1\%$). An audiogenerator was used to feed an operational amplifier both to create a constant current source and to drive a PAR phase lock detector that measured the voltage across the cell through an electrometer amplifier.

All electronic absorption spectra were measured on a Cary 14 spectrophotometer.

Ligand Substitution Measurements. Equilibrium constants were measured by a spectrophotometric titration method. Aliquots of a toluene solution containing either pyridine (0.1–0.6 M), *sec*-butylamine (~2×10^{-2} M), 4-cyanopyridine (~0.6 M), 3,4-lutidine (0.27 M), or 1-methylimidazole (~2×10^{-2} M) were added to a toluene solution of Cr(TPP)(Cl) which contained either acetone (20 or 60% v/v), tetrahydrothiophene (20% v/v), or dimethyl sulfoxide (~0.8 and 20% v/v). The temperature of the porphyrin solution was maintained at 23.0 ± 0.1 °C. In general, the spectra were recorded in the 430- to 380-nm region during the titration.

The data were fitted to the Hill equation

$$\log \frac{y}{1-y} = n \log (\mathrm{L}) + \log K \qquad (1)$$

using a nonweighted linear least-squares method, where y equals the fraction of Cr(TPP)(Cl) binding the nitrogeneous ligand, L; i.e., $y = [\mathrm{Cr(TPP)(Cl)(L)}]/[\mathrm{Cr(TPP)(Cl)}]_{\mathrm{total}}$. Values for log K were obtained from the y intercept of the regression line for a plot of log $y/(1-y)$ vs. log (L). Values for the equilibrium constant for substitution were found to be independent of the wavelength used. 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.

Analysis of EPR Spectra. The EPR spectra obtained from the freshly prepared and frozen solutions at 78 K between 0 and 7000 G were fitted to the spin Hamiltonian

$$H = \beta_e[g_xH_xS_x + g_yH_yS_y + g_zH_zS_z] + D[S_z{}^2 - 5/4] + E[S_x{}^2 - S_y{}^2] \qquad (2)$$

where g_i represent the principal axis components of the g tensor, the parameter D is nonzero for an ion in tetragonal symmetry, and a finite E implies that the ion experiences a rhombic distortion. The resonances were assigned and the approximate values of $|D|$ were determined for each spectrum from the general schemes presented by Hempel et al.[10] and Pedersen and Toftlund[11] and by using Gladney's program EPR for calculating absorption fields (Quantum Chemistry Program Exchange, No. 134). A further computer program was written to calculate the EPR parameters from the observed field positions for the transitions occurring with the field oriented along the x, y, and z axes, using the equations given by McGarvey.[12] These parameters are obtained by minimization of the function F:

$$F = \sum_i |h\nu_i - h\nu_{\mathrm{expt}}|^2$$

where $h\nu_i$ is the energy difference between the appropriate energy levels for the magnetic field located along the Cartesian axes.

To properly fit the five parameters $|D|$, $|E|$, g_x, g_y, and g_z, it would be necessary to have at least five accurately determined peak positions. The absence of a sufficient number of well-defined peak positions for a number of the spectra made it difficult, in general, for us to fit all five variables. Usually fits could be adequately made for $|D|$, $|E|$, and sometimes g_z. Therefore, for the purposes of this paper an isotropic value of 1.995 for the principal g values was assumed, but it should be pointed out that this value is generally consistent with our analysis of the spectra. It is difficult for us to assign an absolute value for the errors involved in the determination of $|D|$ and $|E|$. From an analysis of the probable errors involved in determining the field position of the resonances we feel that our values for $|D|$ and $|E|$ are accurate to within the 2% error estimated by Hempel and co-workers.[10] As to the precision of these values, we note that values for $|D|$ calculated from three different spectra from the THF adduct of Cr(TPP)(Cl) taken over a period of 1 year differed by less than 1%.

Results

The insertion of chromium into $TPPH_2$ by refluxing a DMF solution of the porphyrin with anhydrous $CrCl_2$ always resulted in the generation of a troublesome impurity. The presence of this unknown material was observed by the appearance of an extra band in the visible spectrum ($CHCl_3$) at ~630 nm. The intensity of this band varied from preparation to preparation. This band was found both in the visible spectrum of the crude reaction mixture and the product obtained after chromatography on alumina. Although no method was found to separate this impurity from the Cr(TPP)(Cl), stirring a $CHCl_3$ solution of the mixture in the presence of a few milliliters of 12 M HCl for several hours always resulted in the disappearance of the 630-nm band. An elemental analysis of the solid product obtained after reaction with HCl indicated only the presence of Cr(TPP)(Cl) and the visible spectrum in benzene agreed with the published spectrum.[1]

Solid Cr(TPP)(Cl) is insoluble in dry distilled toluene. Allowing a mixture of solid Cr(TPP)(Cl) and dry purified toluene to stand for several hours at room temperature under N_2 resulted in only a faint coloration of the toluene. The addition of even small amounts of a ligating base (e.g., pyridine, THF, or acetone) to the mixture, however, resulted in the rapid dissolution of the metalloporphyrin. We show below that the resulting solution species is Cr(TPP)(Cl)(L). Table I summarizes the data obtained from the absorption spectra of solutions of Cr(TPP)(Cl) in toluene containing 20% by volume of a coordinating ligand. We note that the dominant overall effect of replacing the weak-field ligands, such as THF, by a strong-field ligand, pyridine (vide infra) is to red-shift the spectrum.

The absorption spectra of the solutions of Cr(TPP)(Cl) listed in Table I were monitored with time. The spectra showed no changes over a period of at least 8 h. A typical spectrum is shown in Figure 1.

Addition of several drops of a neat nitrogenous ligand (i.e., 1-methylimidazole, pyridine, or *sec*-butylamine) to a cuvette containing a toluene solution of Cr(TPP)(Cl) containing either dimethyl sulfoxide, acetone, or tetrahydrothiophene results in an immediate change in the visible spectrum to one identical with the spectrum of the toluene solution of the chromium porphyrin containing only the nitrogenous base.

Spectrophotometric titrations at 23 °C of toluene solutions of Cr(TPP)(Cl) containing Me_2SO, acetone, or THTP with toluene solutions of a nitrogenous ligand, L, were performed. The results from a typical titration are shown in Figure 2. Plots of log $[\mathrm{Cr(TPP)(Cl)(L)}]/[\mathrm{Cr(TPP)(Cl)}]_{\mathrm{total}}$ 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 II.

Solution conductivity measurements were made on Me_2SO solutions of Cr(TPP)(Cl) at 25 °C. The results are presented in Table III. The data obtained for Cr(TPP)(Cl) dissolved in both neat Me_2SO and 20% pyridine/Me_2SO solution indicate that compared to the 1:1 electrolytes $(n\text{-Bu})_4N^+Cl^-$ and Fe^{III}(TPP)(Cl),[13] the complex initially formed when Cr(TPP)(Cl) is dissolved in the Me_2SO solutions is a nonelectrolyte. On standing at 25 °C the conductivities were observed to increase slowly. However, even after standing for 2 weeks the equivalent conductances calculated for the chro-

Table I. Absorption Spectra of Cr(TPP)(X)(L)[a] (X = Cl⁻, Br⁻)

Compd		Near IR bands			Visible bands				Soret bands				Near UV bands VI			
		I[b]	I′	II′	II	III	IV		V							
Cr(TPP)(Cl)(THF)[c]	λ[d]	808	758	690 (sh)	662	600	562	523	447		394		362	338	322	289
	ε	0.455	0.545	0.632	0.778	9.23	12.0	4.93	280		37.1		21.6	23.8	25.4	19.4
Cr(TPP)(Cl)(acetone)	λ		764	692	658	605	566	524	447		394		357	337		
	ε		0.508	0.599	0.810	11.7	12.5	5.22	299		41.4		22.1	25.7		
Cr(TPP)(Cl)(THTP)[e]	λ		760	690	668	605	567	527	447	408	394		362[f]	337[f]	320[f]	
	ε		0.121	0.255	0.939	10.5	10.7	4.93	227	16.4	30.8		20.3	23.7	22.8	
Cr(TPP)(Cl)(pyridine)	λ		777	700 (sh)	667	611	570	527	458	410 (sh) 404		372 (sh)	364	343	327	
	ε		0.458	0.551	0.752	12.3	10.6	5.45	182	37.0, 39.3		25.1	25.6	25.6	26.4	
Cr(TPP)(Br)(pyridine)[g]	λ		777		640 (sh)	608	573	528	461, 443	409		373			328	
	r[g]		0.097		0.648	1	0.949	0.576	9.69, 7.63	3.78		0.814			0.556	

[a] Measured in a 20% (v/v) solution of the ligand (L) in toluene. [b] Peaks are labeled after ref 2. [c] Abbreviations: THF, tetrahydrofuran; THTP, tetrahydrothiophene; sh indicates shoulder. [d] λ is wavelength (nm); ε is the molar extinction coefficient (M^{-1} cm^{-1}) × 10^{-3}. [e] The tetrahydrothiophene contained a small amount of an impurity (see text for details). [f] These bands were shoulders on a solvent peak. [g] r = ratio of absorbance at the wavelength indicated to the 608-nm band.

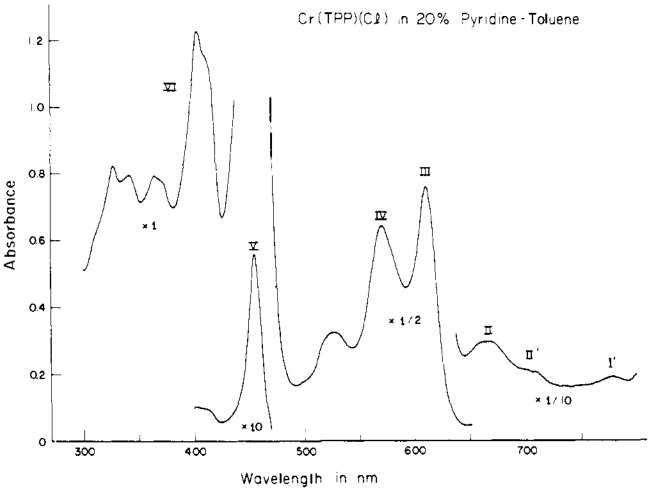


Figure 1. The electronic absorption spectrum at room temperature for Cr(TPP)(Cl) in 20% pyridine/toluene, run with a solvent reference. The bands are labeled after Gouterman, ref 2.

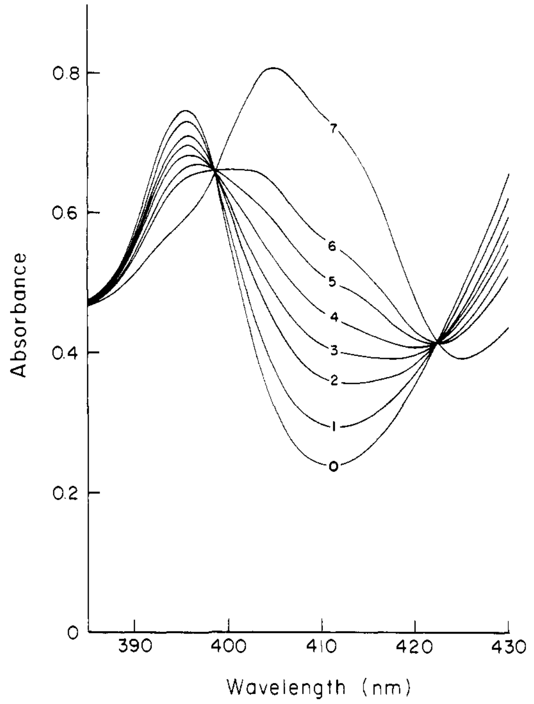


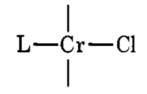
Figure 2. Visible spectral changes on the addition of pyridine (in 60% acetone/toluene, v/v) to a 1.59 × 10^{-5} M solution of Cr(TPP)(Cl) in 60% acetone/toluene. The addition was performed using a two-syringe technique. The spectrum labeled 0 is the spectrum of the initial acetone adduct. Spectra labeled 1-6 were obtained from solutions having pyridine concentrations (×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).

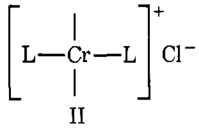
mium metalloporphyrin solutions were less than 75% of the value expected for a 1:1 electrolyte.

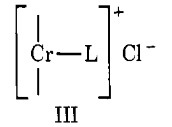
Finally, analysis of the EPR spectra obtained from the frozen solutions assuming an isotropic value for g of 1.995 resulted in the values for the electronic parameters |D| and |E| listed in Table IV. Typical EPR spectra are reproduced in Figures 3 and 4.

Discussion

Chlorotetraphenylporphinatochromium(III) dissolves in dry, purified toluene only in the presence of a coordinating base. Electronic absorption spectra of toluene solutions of Cr(TPP)(Cl) that contain added ligand are dependent upon the nature of that ligand. Three structures can be postulated for the chromium porphyrins in such solutions. Structures II and III can be eliminated for the following reasons: (1) A solution of Cr(TPP)(Br) in 20% pyridine/toluene solution gives a different electronic absorption spectrum than does a solution of Cr(TPP)(Cl) in the same solvent; and (2) the limited conductivities of fresh Me_2SO solutions of Cr(TPP)(Cl) (both in the presence and absence of added ligand, L) compared with those of the 1:1 electrolytes $(Et_4N)^+Cl^-$, $(Bu_4N)^+Cl^-$, and Fe^{III}(TPP)(Cl) indicates that in freshly prepared solutions of the chromium porphyrin in Me_2SO the chloride ion is largely or entirely associated. Although the conductivities were not measured in toluene solution, the lower dielectric strength of toluene (2.4) compared with that of Me_2SO (46.7)[14] indicates that Cr(TPP)(Cl) should also behave as a nonelectrolyte when dissolved in toluene. Thus, in the presence of a coordinating base, it appears that a toluene solution of Cr(TPP)(Cl) contains the six-coordinate species, Cr(TPP)(Cl)(L).


$$\text{L—Cr—Cl}$$
I


$$[\text{L—Cr—L}]^+\ \text{Cl}^-$$
II


$$[\text{Cr—L}]^+\ \text{Cl}^-$$
III

Substitution of the axial substituents of both Cr(III) and

Table II. Equilibrium Constants for the Reaction $Cr(TPP)(Cl)(B) + L \rightleftharpoons Cr(TPP)(Cl)(L)$

B[a]	L[b]	λ, nm	Slope[c]	Log K_{obsd}[c]	Log K[d]
Acetone (60%)	4-CN-py	410	1.03	2.29	3.20 ± 0.03
	pK_a = 1.86[e]	410	1.00	2.21	3.12 ± 0.07
	py	410	1.03	3.37	4.28 ± 0.06
	pK_a = 5.27[f]	410	1.01	3.36	4.28 ± 0.04
	3,4-Lut	410	1.02	4.10	5.01 ± 0.12
	pK_a = 6.46[f]	410	0.97	4.09	5.01 ± 0.13
	sec-BuNH$_2$	399	1.03	4.56	5.47 ± 0.08
	pK_a = 10.56[g]	398	0.99	4.52	5.43 ± 0.17
	1-MeIm[f]	402	1.00	5.80	6.71 ± 0.13
	pK_a = 7.25	402	0.94	5.53	6.44 ± 0.16
Acetone (20%)	4-CN-py	410	1.10	2.64	3.08 ± 0.11
		410	1.07	2.66	3.10 ± 0.10
	py	410	1.06	4.06	4.50 ± 0.11
		410	0.99	4.04	4.47 ± 0.03
	sec-BuNH$_2$	398	0.98	4.88	5.31 ± 0.13
		398	0.96	4.90	5.34 ± 0.47
THF (20%)	py	410	1.04	2.93	3.32 ± 0.06
		410	1.01	2.96	3.35 ± 0.04
THTP (20%)[h]	py	410	1.07	2.80	3.15 ± 0.04
		410	1.04	2.81	3.16 ± 0.03
Me$_2$SO (0.75%)	*sec*-BuNH$_2$	396	0.97	3.10	2.13 ± 0.10
		396	1.08	3.07	2.10 ± 0.05

[a] In toluene, numbers in parentheses indicate percent (v/v) of B in toluene. [b] For abbreviations see ref. 42. Ligands were in toluene solution: 4-CN-py, ~0.6 M; py, 0.1-0.6 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. [d] $K = K_{obsd}(B)$. Errors reported represent deviation of the data from a least-squares analysis. [e] K. Schofield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, N.Y., 1967, p 146. [f] A. Albert, *Phys. Methods Heterocycl. Chem.*, **1** (1963). [g] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds", Vol. 1, W. A. Benjamin, New York, N.Y., 1965, p 19. [h] A small amount of an N-donor impurity has been found in the (THTP). See text for details.

Table III. Observed Equivalent Conductances[a]

	[Cr(TPP)(Cl)] in Me$_2$SO	
Time, h	5.7 × 10^{-4} M	2.63 × 10^{-4} M
0.4	0.37	0.23
0.6	0.57	0.46
	[Cr(TPP)(Cl)] in 20% pyridine/Me$_2$SO	
Time, h	7.43 × 10^{-4} M	4.97 × 10^{-4} M
0.2	2.28	0.81
0.4	2.71	1.67
0.6	3.07	2.26
	Me$_2$SO	
$(n\text{-Bu})_4N^+Cl^-$ [b]	1.41 × 10^{-3} M	21.9
	0.35 × 10^{-3} M	21.5
Fe^{III}(TPP)(Cl)[c]	6.14 × 10^{-4} M	20.7

[a] At 25 °C, mho-cm/equiv. [b] $(n\text{-Bu})_4N^+Cl^-$: tetra-*n*-butylammonium chloride. [c] See ref 13.

Table IV

A. EPR Parameters for Cr(TPP)(Cl) and Cr(OEP)(Cl)

	Cr(TPP)(Cl)(L)		Cr(OEP)(Cl)(L)	
L[a]	$\lvert D\rvert$, cm^{-1} [b]	$\lvert E\rvert$, cm^{-1}	$\lvert D\rvert$, cm^{-1}	$\lvert E\rvert$, cm^{-1}
THF	0.235	<0.007		
Acetone	0.233	0.013	0.241	0.012
THTP	~0.233	~0[c]		
DMF	0.228	<0.001		
CH$_3$CN	0.207	0.001		
4-CN-py	0.167	0.002		
Pyridine	0.158	0.002	0.164	0.002
1-MeIm	0.151	0.010	0.157	0.009
n-Butyl isocyanide	0.146	0.001		
sec-BuNH$_2$	0.146	<0.001		
Piperidine	0.145	<0.001		

B. EPR Parameters for Some Cr(III) Complexes

Compd[d]	$\lvert D\rvert$, cm^{-1}	$\lvert E\rvert$, cm^{-1}	Ref
trans-$[Cr(py)_4Cl_2]^+$	0.164	<0.001	11
trans-$[Cr(py)_4Cl(H_2O)]^{2+}$	0.160	0.020	11
trans-$[Cr(NH_3)_4Cl_2]^+$	0.160	<0.002	11
trans-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ [e]	0.17	<0.005	11
trans-$[Cr(en)_2Cl_2]^+$ [f]	0.504	0.036	27

[a] In a frozen solution at 78 K; measured in 29% (v/v) L in toluene for the liquids and 1 M 4-CN-py in toluene; abbreviations appear in ref. 42. [b] An isotropic g value ($g_x = g_y = g_z$) of 1.995 was assumed to obtain these parameters. Absolute errors in D and E are assumed to be approximately 2% on the basis of errors in reading peak positions. See text for discussions of signs of D. [c] The value for $|D|$ is based on a value for E = 0. The value for $|E|$ appears to be <0.001. [d] Except as indicated, spectra were taken in a frozen solution of DMF-H$_2$O-MeOH (1:1:2 by volume) at −150 °C. [e] [H$^+$] = 0.5 M. [f] Single crystal.

Co(III) porphyrins has been observed to occur unusually rapidly for compounds of these classically inert metal ions.[4,5,15,16] Consistent with this apparent labilizing effect of the porphyrin moiety, we have observed that substitution of the neutral ligand of a six-coordinate complex of the form Cr(TPP)(Cl)(B) (where B is one of the O- or S-donors in Table II) by a second neutral N-donor ligand is complete within the time of mixing the nitrogenous base with the original solution.

Results of the spectrophotometric titrations show that upon titrating a solution of Cr(TPP)(Cl) in toluene in the presence of an added oxygen- or sulfur-containing ligand with a toluene solution containing a nitrogen donor ligand only one of the available axial positions is substituted. Consistent with spectrophotometric and conductometric results we can write the equilibrium as

$$Cr(TPP)(Cl)(B) + L \rightleftharpoons Cr(TPP)(Cl)(L) + B$$

$$B = \text{O- or S-donor},\ L = \text{N-donor}$$

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) in Cr(TPP)(Cl)(acetone) by 1-methylimidazole occurs with the remarkably large equilibrium constant of 4.0 × 10^6 (23 °C in 60% v/v acetone/toluene). This value can be used as a lower limit for the affinity of five-coordinate Cr(TPP)(Cl) for 1-MeIm and can be contrasted with the equilibrium constant obtained for the addition of a 1-MeIm to Fe^{III}(TPP)(Cl) (in benzene at 25 °C)[13] where K = 1.3 ± 0.2, or of a pyridine to Mn^{III}(TPP)(Cl) where K = 2.5.[17] Indeed, the binding of the *sixth* ligand by Cr(TPP)(Cl) is even far stronger than that of the *first* imidazole to base-free Fe^{II}(TPP) (in benzene at 25 °C)[18] where K = 8.8 × 10^3 M^{-1}.

The imidazole ligand in its binding to metalloporphyrin 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 pyri-

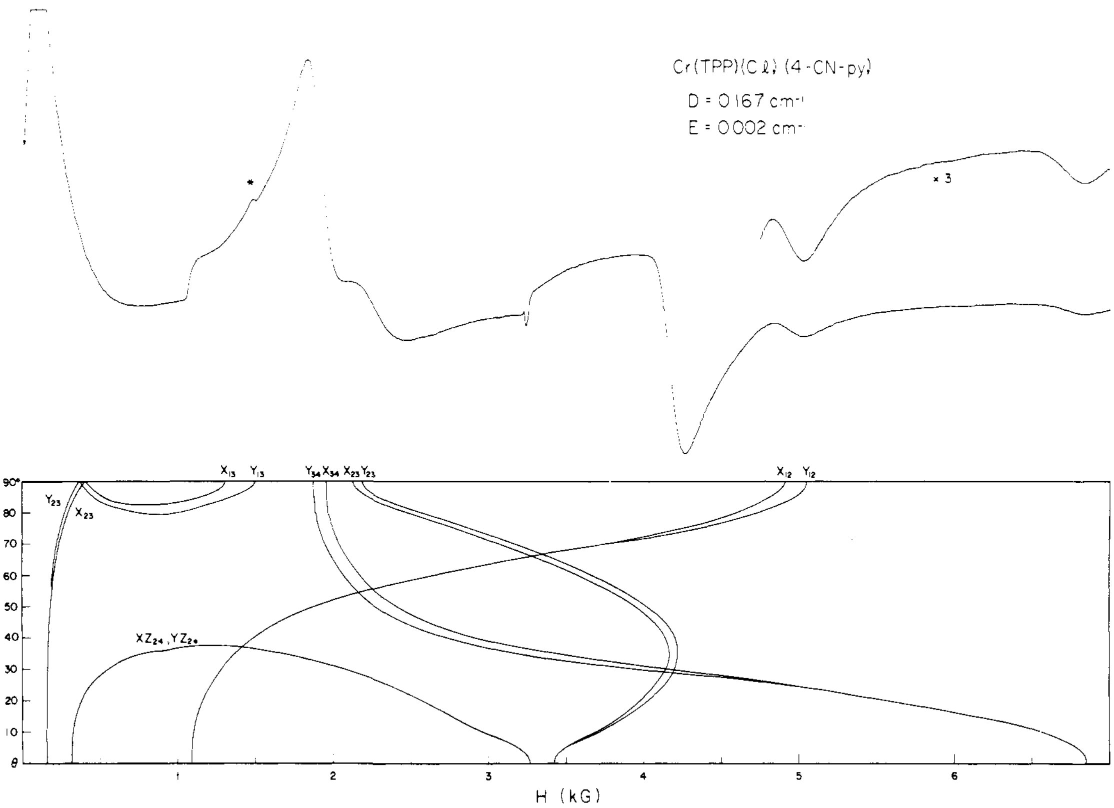


Figure 3. Top: X-band EPR spectrum of Cr(TPP)(Cl)(4-cyanopyridine) in ~1 M solution of 4-cyanopyridine in toluene. "*" indicates signal from rhombic iron in quartz. Bottom: The calculated resonance positions as a function of orientation of the magnetic field in the *xz* and *yz* planes. θ represents the angle between the *z* axis and the magnetic field vector. The subscripts 1-4 refer to the energy levels involved in the transition in order of decreasing energy.

dine or piperidine.[19] Other anomalous effects of the imidazole ligand have been observed for O_2 and CO bonding to metalloporphyrin and metallophthalocyanin complexes.[20-23]

In the bisimidazole complexes of some Fe(III) porphyrins (the bisimidazole hemichromes), the imidazole ligand has been implicated as a π donor from Mössbauer data[24] and as a π acceptor from NMR studies compared with Hückel calculations.[25] It is therefore of interest to examine our equilibrium data for the binding of nitrogen bases to Cr(TPP)(Cl).

A plot of log K for the equilibrium

$$\mathrm{Cr(TPP)(Cl)(acetone)} + \mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{Cr(TPP)(Cl)(L)} + \mathrm{acetone}$$

vs. the basicity (pK_a for LH^+) of the N-donor ligand L is shown in Figure 5. 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.

For a d^3 ion in a tetragonal environment the ground state is the $(t_{2g})^3$, $S = {}^3\!/_2$ configuration and the spin Hamiltonian takes the form given above in eq 2. In the absence of a magnetic field, the four states of the $S = {}^3\!/_2$ manifold split into two Kramer's doublets which are separated in energy by the zero-field splitting, $\Delta = 2(D^2 + 3E^2)^{1/2}$. On application of an external magnetic field, the Kramer's doublets are also split. The energies of the resulting states are given by McGarvey[12] for the field oriented along the *x*, *y*, and *z* axes. For the condition where $\Delta \gg h\nu_0$ (where ν_0 is the frequency of the microwave quantum) only intradoublet transitions are observed at accessible field strengths, and we have previously given expressions for the observed *g* values.[19] For Cr(TPP)(Cl)(L), $\Delta \approx h\nu_0$, interdoublet transitions are observable, and the spectra are in general more complex than for the previous case.[10,11]

A casual visible inspection of the EPR spectra of the frozen solutions of the Cr(TPP)(Cl) adducts reveals that on the basis of general appearance alone the spectra can be divided into two classes. The spectra obtained from the adducts with the weaker oxygen and sulfur donors all had the same general appearance as did the spectra obtained from the stronger nitrogen donors. Typical spectra from each of these two classes are produced in Figures 3 and 4. The values calculated for $|D|$ and $|E|$ are consistent with the similarities observed in the spectra (Table IV). Thus the weaker O- and S-donors all have $|D|$ values in the range 0.232 ± 0.004 cm^{-1} while the N-donors exhibited $|D|$ values in the range 0.156 ± 0.012 cm^{-1}. The only exception was for the adduct Cr(TPP)(Cl)(CH_3CN) that gave a value for $|D|$ of 0.207 cm^{-1}.

A second similarity shared by all complexes is the relatively small size of $|E|$ (Table IV). Although in many of the complexes it is unambiguously clear that $|E| > 0$, in no case is the rhombic distortion, measured by $|E/D|$, greater than 0.066. Moreover, through spectra of Cr(TPP)(Cl)(py) oriented in the liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-butylaniline we have verified that the unique axis is, as expected, normal to the molecular plane.[26] Thus, the environment experienced by the Cr^{III} ion in Cr(TPP)(Cl)(L) and Cr(OEP)(Cl)(L) is almost purely tetragonal, with the pyrrole nitrogens of the porphinato ring providing the basic fourfold coordination geometry. In the three features, relatively small values of $|D|$, small $|E/D|$, and fourfold coordination by nitrogen ligands, the chromic porphyrin complexes resemble $Cr(NH_3)_4(X)(Y)$ and $Cr(py)_4(X)(Y)$ complexes.[11] This is demonstrated by the value of $|D|$ and $|E|$ for representative examples as listed in Table IVB.

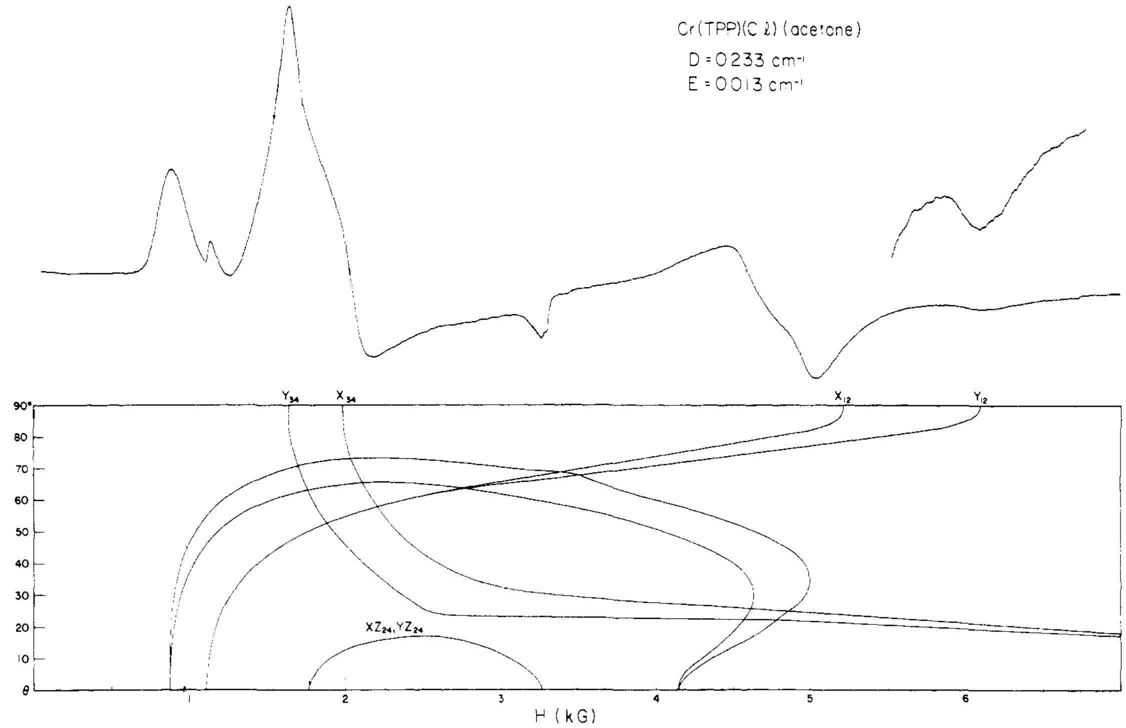


Figure 4. Top: X-band EPR spectrum of Cr(TPP)(Cl)(acetone) in 20% acetone/toluene at 78 K. Bottom: The calculated resonance positions as a function of orientation of the magnetic field in the *xz* and *yz* planes. θ represents the angle between the *z* axis and the magnetic field vector. The subscripts 1-4 refer to the energy levels involved in the transition in order of decreasing energy.

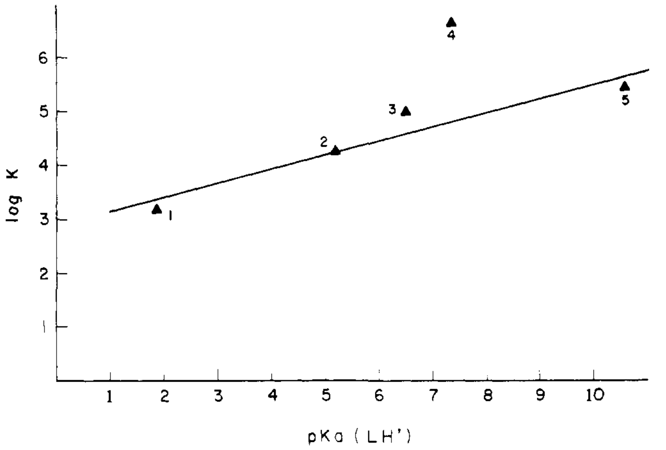


Figure 5. Correlation between pK_a for the conjugate acids (LH^+) and log *K* for the reaction Cr(TPP)(Cl)(acetone) + L $\rightleftharpoons$ Cr(TPP)(Cl)(L) + acetone in 60% acetone in toluene at 23 °C. Ligands (L) are 1 = 4-cyanopyridine; 2 = pyridine; 3 = 3,4-lutidine; 4 = 1-methylimidazole; 5 = *sec*-butylamine.

In these simple Werner-type chromic complexes it has been found that the magnitude of $|D|$ can in general be rationalized from second-order perturbation theory on a crystal field model, considering spin-orbit coupling between the $^4A_{2g}$ ground state and components of the $^4T_{2g}$ excited state.[11,28,29] Because of the similar behavior for the chromic porphyrins, we shall discuss them within the same framework. This amounts to assuming that the low-lying excitations which are primarily porphyrin in character (so-called tripquartets and singquartets[2]) contribute minimally. It also emphasizes that porphyrin deformations from fourfold symmetry must indeed be small, for the unusually large values of $|D|$ and $|E|$ in $[Cr(en)_2Cl_2]^+$ (Table IV) have been shown by McGarvey to occur because of small deviations from the anticipated symmetry.[27]

For a purely tetragonal d^3 ion, the perturbation-theory crystal field model gives rise to the expression

$$D = \frac{35\lambda^2 D_t}{(\Delta E)^2}$$

where λ is the spin-orbit coupling constant, ΔE is the average energy of the $^4T_{2g}$ level, and D_t is the tetragonal field distortion parameter which is the coefficient of $V_4{}^0$.[29,30] In first order, the $^4T_{2g}$ state is split by the tetragonal perturbation into B_{2g} and E_g states, with $E(B_{2g}) - E(E_g) = 35D_t/4$. For axial ligand fields weaker than equatorial ("axial elongation") $D_t > 0$ and thus $D > 0$.

Within this framework we can understand why $|D|$ for the stronger field ligands is less than that for the weaker ligands. If we assume that for both classes the "ligand-field strength" of the porphinato macrocycle exceeds that of the Cl^- and L, combined, then $D_t > 0$ and $D > 0$. In this case increasing the axial ligand field strength, say by going from THF to pyridine, would decrease *D* by decreasing D_t, that is, by reducing the "elongation".[31] Since the sign of *D* is not directly determined, it is even conceivable that the distortion, and therefore *D*, changes sign, with $D_t > 0$ ("elongation") for the weak-field ligands but $D_t < 0$ ("compression") for the strong-field ligands.

One observation we made during the EPR studies bears on our previous discussion of the difficulties which may arise from minor impurities in apparently pure compounds which are to be used as axial ligands.[32] The EPR spectrum of Cr(TPP)(Cl) in THTP/toluene had an unassignable resonance centered at $g \sim 1.63$. The relative intensity of the resonance was found to vary with the concentration of the THTP. Distillation of the tetrahydrathiophene resulted in a diminution in the intensity of the band. However, no EPR spectrum of a solution of the porphyrin in a THTP toluene mixture was ever obtained in which the resonance was entirely absent. An EPR spectrum of Cr(TPP)(Cl) in toluene containing 20% by volume tetrahydro-1-thiapyran also showed the presence of the bothersome band. A toluene solution of the metalloporphyrin containing 20% by volume of a forerun cut from a vacuum distillation of

THTP gave an EPR spectrum unlike that previously observed for the Cr(TPP)(Cl)(THTP) derivative. The spectrum showed a large resonance at $g = 1.63$ and was similar to, but not identical with, the spectra obtained from the adducts of Cr(TPP)(Cl) with the N-donors listed in Table IV. While we have not identified this impurity, we have estimated from the equilibrium results in Table II that were the impurity pyridine, the intensity of the $g = 1.63$ resonance observed in the spectrum taken in the presence of THTP would arise if the neat THTP input contains a pyridine impurity at 10^{-3} M.

It is interesting to compare the results obtained from this study on the Cr(III) porphyrin complexes with the behavior of metalloporphyrin complexes of some of the other first-row transition elements. In doing so, it is significant to note that no x-ray structural data have been reported for a Cr(III) porphyrin complex. The d^3 electronic configuration of Cr(III) is similar to that of the low-spin Fe(II), Fe(III), and Co(III) porphyrin complexes in that the d electrons occupy only the π-bonding d_{xy}, d_{yz}, and d_{xz} orbitals, leaving vacant the $d_{x^2-y^2}$ and d_{z^2} orbitals. These empty orbitals are completely available for σ binding, both with the porphyrin macrocycle and with axial ligands. Thus for the low-spin six-coordinate metalloporphyrin complexes of Fe(II), Fe(III), and Co(III), the metal ion is found to lie essentially in the plane defined by the four core nitrogen atoms. This is true not only for the bisamine adducts, e.g., $\mathrm{Fe^{II}(TPP)(pip)_2}$,[33] $\mathrm{[Fe^{III}(TPP)(Im)_2]^+Cl^-}$,[34] and $\mathrm{[Co^{III}(TPP)(Im)_2]^+OAc^-}$,[35] but also for the complexes $\mathrm{Fe^{III}(TPP)(N_3)(py)}$[36] and $\mathrm{Co^{III}(TPP)(NO_2)(3,5\text{-}lut)}$[37] that have both anionic and neutral ligands in the axial positions. On this basis we might anticipate that a complete structural analysis of the six-coordinate adducts of Cr(TPP)(Cl) will show the Cr(III) ion lying essentially in the plane of the ring.

An examination of the ionic radius of Cr(III) also shows that it would have no intrinsic difficulty in adopting this configuration. Buchler[38] has pointed out that a metal ion having an ionic radius between 0.60 and 0.69 Å may produce a metalloporphyrin having an essentially planar $\mathrm{MN_4}$ conformation. The value reported[39] for the ionic radius of Cr(III) of 0.62 Å fits well within these limits.

However, a strictly planar $\mathrm{CrN_4}$ moiety for compounds of the type Cr(TPP)(Cl)(L) is unlikely because of repulsive interactions between the pyrrole nitrogen atoms of the porphyrin and the coordinated chloride anion. For the high-spin, d^4 manganese(III) porphyrins, $\mathrm{Mn^{III}(TPP)(Cl)(acetone)}$ and $\mathrm{Mn^{III}(TPP)(Cl)CHCl_3)}$, it has been shown that even with an average displacement of the Mn(III) of 0.27 Å from the plane of the four nitrogen atoms toward the chloride ion, the distance between the chloride ion and the core nitrogen atoms is still less than the sum of the van der Waals radii of the two atoms. A similar argument holds for the complexes Mn(TPP)(Cl)(py) and $\mathrm{Mn(TPP)(N_3)(CH_3OH)}$.[40] A comparison of the Cr–Cl bond length from $\mathrm{CrCl_3}$ (2.34 Å)[41] with the above analysis for the Mn(III) porphyrin complexes indicates that a planar $\mathrm{CrN_4}$ moiety for the complexes Cr(TPP)(Cl)(L) would also result in repulsive interactions between the chloride ion and the ring nitrogen atoms. Thus the Cr(III) ion is likely to be removed slightly from the plane to minimize this repulsive energy term.

These considerations of geometry may offer an explanation of an apparent anomaly. Our EPR results do not show the ground-state electronic structure of the Cr(III) ion of Cr(TPP)(Cl)(L) to be significantly different from that in tetrapyridyl or even tetraammine Werner-type complexes, yet the axial ligand is anomalously labile in the Cr(III) porphyrins.[4,5] Substitution reactions on Cr(III) complexes are believed in general to occur by dissociative processes. Although the axial ligand affinities in the chromic porphyrins are high, it may be that the anticipated steric repulsions with the pyrrole nitrogens cause atypical rates of axial ligand dissociation.

The empty d_{z^2} orbital on the Cr(III) is available for σ bonding with axial ligands, as indicated by the strong affinity we have observed by the five-coordinate Cr(TPP)(Cl) for a sixth ligand. As noted above, we are unable to put absolute values on the affinities of Cr(TPP)(Cl) toward coordinating bases. However, even using the values in Table II as lower limits for the affinities of Cr(TPP)(Cl) for a sixth ligand, then these equilibrium constants establish that the tendency of Cr(TPP)(Cl) toward binding a sixth ligand is larger than the affinity of any metalloporphyrin complex yet examined toward binding a single ligand to a vacant coordination site.

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(42) Abbreviations: TPP, dianion of *meso*-tetraphenylporphin; OEP, dianion of octaethylporphyrin; py, pyridine; DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran; 1-MeIm, 1-methylimidazole; Me_2SO, dimethyl sulfoxide; THTP, tetrahydrothiophene; *sec*-$BuNH_2$, *sec*-butylamine; 3,4-Lut, 3,4-lutidine (3,4-dimethylpyridine); 3,5-Lut, 3,5-lutidine; 4-CN-py, 4-cyanopyridine; Pip, piperidine.

Structural Evidence for Xenon–Chlorine Bonding: Neutron and X-Ray Diffraction Determinations of the Structure of Cesium and Rubidium Trioxodichloroxenate(VI) Chloride, $Cs_9(XeO_3Cl_2)_4Cl$ and $Rb_9(XeO_3Cl_2)_4Cl$[1]

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Abstract: The compounds $XeO_3 \cdot 2.25CsCl$ and $XeO_3 \cdot 2.25RbCl$ have been structurally characterized as cesium and rubidium trioxodichloroxenate(VI) chloride, $M_9(XeO_3Cl_2)_4Cl$, using single-crystal counter diffraction methods. The crystals are body-centered tetragonal, point group $4/m$, with a = 16.56 Å and c = 7.10 Å for the Cs salt and a = 15.97 Å and c = 6.91 Å for the Rb salt, and contain eight $XeO_3 \cdot 2.25MCl$ formula units per unit cell. The structures have been refined in the space group $I\bar{4}$ to R factors of 8.3% for the Cs compound using neutron data and 10.4% for the Rb compound using x-ray data. The crystal structures contain infinite chains, parallel to c, of XeO_3Cl^- units linked by nearly linear chlorine bridges. The metal cations and one-ninth of the chlorine atoms are separated from the repeating polymeric unit $XeO_3Cl_2{}^{2-}$ by nonbonding distances. The xenon coordination is octahedral (distorted) with three terminal oxygen neighbors (in the Cs salt) at 1.77 Å, one terminal Cl neighbor at 2.96 Å, and two bridging Cl neighbors at 2.95 and 2.97 Å.

We wish to report the first conclusive demonstration of the existence of stable Xe–Cl bonding at normal temperatures. Stable chemical compounds of xenon with the strongly electronegative elements fluorine and oxygen are well known. Since chlorine is nearly as electronegative as oxygen, it is to be expected that Xe–Cl bonds may exist. Perlow and Perlow[2] have shown through Mossbauer studies that $XeCl_2$ and $XeBr_2$ are formed at 4 K by the radioactive decay of the corresponding iodine compounds. Attempts to synthesize $XeCl_2$ or $XeCl_4$ by chemical means have not been successful, but recently RbCl and CsCl salts of XeO_3 have been isolated.[3] Although they are of different stoichiometry from the potassium fluoride salt of XeO_3, $K(XeO_3)F$,[4] these chloride salts might also be expected to contain halogen bridges.

Indeed, LaBonville, Ferraro, and Spittler,[3] although they formulated them as $XeO_3 \cdot 2MCl$, have observed vibrational transitions in the far IR for these compounds which they assigned as Xe–Cl stretching modes. Thus in order to shed further light on the existence of Xe–Cl bonds at ambient temperature, we have solved the crystal structures and found the specimens selected to have the stoichiometry $XeO_3 \cdot 2.25MCl$ and to be structurally $M_9(XeO_3Cl_2)_4Cl$.

Structure Determination

Samples of both a rubidium and a cesium chloride addition compound with XeO_3, prepared by reacting RbCl and CsCl in a 2:1 ratio with XeO_3,[3] were studied. The crystals selected were well-shaped tetragonal prisms with a = 16.56 and c = 7.10 Å for Cs and a = 15.97 and c = 6.91 Å for Rb. The crystal densities were greater than that of methylene iodide (3.32 g cm^{-3}), hence not measured; ρ_{calcd} = 3.40 and 3.81 for Rb and Cs, respectively, on the assumption that Z = 8. Precession photographs established the systematic extinctions to be $h + k + l = 2n + 1$ and the possible space groups $I4/m$ and $I\bar{4}$ for both compounds.

It was subsequently discovered that smaller amounts of a second phase existed in both Rb and Cs samples. These were identified by X-ray photography as triclinic phases with cell parameters a = 10.10, b = 12.77, c = 10.00 Å α = 91.30, β = 92.22, and γ = 100.64° for the Rb compound. The density of the second Rb phase was less than 3.32 and was measured as 3.19 g cm^{-3}. This value leads to possible stoichiometries of $(RbCl)_{1.87} \cdot XeO_3$ or $RbCl \cdot XeO_3$ for assumed Z = 6 and 8, respectively, for the triclinic phase. All further structural work was concentrated on the tetragonal phase. The above findings, however, cast doubt on the initial assumed stoichiometry of $(RbCl)_2 \cdot XeO_3$ for the tetragonal phase.

Since both salts exhibited very severe decomposition upon exposure to the x-ray beam, peak-height data were collected using an automated GE diffractometer. A total of 1095 reflections were collected for the Cs salt and 1102 for the Rb salt. In each case, it was necessary to use three crystals in order to complete the data collection. The distribution of intensities was indicative of an acentric structure.[5]

The main heavy atom (Xe, 2M) positions, indicated by the formula $XeO_3 \cdot 2MCl$, were readily located using both the Patterson function and direct methods. However, extra peaks found in high symmetry positions on subsequent Fourier maps were eventually attributed to extra M^+ and Cl^- ions requiring a reformulation of the stoichiometry to $XeO_3 \cdot 2.25MCl$. In-

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