Inorg. Chem. **1992**, *31*, 1148-1151

Contribution from the Department of Chemistry, University of California, Davis, California 95616,
and Institute of Chemistry, University of Wrocław, Wrocław 50383, Poland

Geometric and Electronic Structure of Paramagnetic Tetraarylporphyrin Complexes of Chromium

Alan L. Balch,*[†] Lechosław Latos-Grażyński,[‡] Bruce C. Noll,[†] Marilyn M. Olmstead,[†]
and Edward P. Zovinka[†]

Received August 1, 1991

$(TPP)Cr^{III}(OPh)(THF)$ (TPP is the dianion on *meso*-tetraphenylporphyrin; THF is tetrahydrofuran) crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.583$ (5) Å, $b = 11.473$ (7) Å, $c = 11.504$ (6) Å, $\alpha = 63.90$ (4)°, $\beta = 91.04$ (4)°, $\gamma = 77.29$ (4)°, and $Z = 1$ at 130 K. Refinement of 151 parameters and 2125 reflections yields $R = 0.082$, $R_w = 0.076$. The structure consists of a six-coordinate chromium located at the center of the planar porphyrin with axial phenoxide (Cr–O distance 1.943 (10) Å) and THF (Cr–O distance 2.069 (10) Å) ligands which are disordered about the chromium. The ^2H NMR spectra of deuterated-pyrrole Cr(III) and Cr(II) complexes have been examined in solution, and the hyperfine shifts are interpreted in terms of their electronic structures. Axial ligand resonances have also been observed for $(TPP\text{-}d_8)Cr^{III}(OPh\text{-}d_5)(THF)$. The reaction of *tert*-butyl hydroperoxide with $(TPP)Cr^{III}Cl$ has been monitored by ^2H NMR and electronic spectroscopy. An unstable isoporphyrin complex is formed.

Introduction

Chromium porphyrins have been found to have a number of remarkable properties. The axial ligands in chromium(III) porphyrins are unusually labile for complexes with a d^3 electronic configuration.[1] Oxochromium porphyrin complexes have been shown to be active oxygen atom transfer reagents.[2] Chromium porphyrins have been found to form unusually stable nitrido complexes.[3] Remarkably facile transfer of the nitrido ligand from manganese porphyrins to chromium(III) porphyrins has been observed.[4]

In this article, we are concerned with utilizing NMR spectroscopy as a structural probe for characterization of the paramagnetic states of symmetric chromium tetraarylporphyrins, particularly for chromium in the oxidation states III (d^3) and II (d^4). Previous work at 100 MHz had shown that the ^1H NMR spectra of $(TPP)Cr^{III}Cl$ and $(TTP)Cr^{III}Cl$ (TPP is the dianion of tetraphenylporphyrin, and TTP is the dianion of tetra-*p*-tolylporphyrin) exhibited broad resonances for the phenyl and *p*-methyl groups which were near their expected diamagnetic position and that there was a negligible contact shift.[5] The resonances of the pyrrole and the phenyl ortho hydrogens were apparently too broad to detect. Since the pyrrole protons of paramagnetic porphyrins have been shown to be particularly diagnostic of changes in spin, oxidation, and ligation states, we undertook an investigation of these resonances.[6] To do so, we employed ^2H NMR spectroscopy utilizing specifically deuterated porphyrins. In the limit of electronic–nuclear dipolar relaxation, the linewidths for the deuterium resonances are theoretically predicted to be 42 times smaller than those of the corresponding proton resonances.[7] This narrowing has been observed experimentally for many paramagnetic species and renders ^2H NMR spectroscopy particularly useful in detecting those paramagnetically broadened resonances that are not accessible in ^1H NMR spectra.[8]

Results and Discussion

Synthesis and Structure of $(TPP)Cr^{III}(OPh)(THF)$. In order to produce a chromium(III) complex with an axial ligand suitable for monitoring by NMR spectroscopy, a complex with a phenoxy ligand was prepared. Treatment of $(TPP)Cr^{III}Cl$ with lithium phenoxide in tetrahydrofuran produced a solution from which blue crystals were obtained that were suitable for study by X-ray diffraction.

A view of the complex is shown in Figure 1. Atomic positional parameters are given in Table I. Table II contains selected bond distances and angles. The asymmetric unit consists of half of the complex molecule. The chromium ion sits at a center of symmetry. There is disorder in the positions of the two different axial ligands.[9] Each axial site above and below the porphyrin plane is occupied by half of a phenoxide ion and half of a THF ligand. Figure 1 shows the complete molecule, but the same site is equally occupied by a molecule with a THF ligand above the porphyrin plane and a phenoxide ligand below it.

Because of the crystallographic symmetry, the chromium ion is at the center of the porphyrin ring. The two Cr–N distances (2.035 (5), 2.038 (7) Å) are effectively equivalent. These Cr–N distances are similar to those found in high-spin ($S = 2$) $(TPP)Cr^{II}$ (2.032 (3), 2.034 (3) Å),[10] in low-spin ($S = 1$) $(TPP)Cr^{II}(py)_2$ (2.012 (8)–2.044 (8) Å),[12] and in diamagnetic $(TPP)Cr^{IV}O$ (2.028 (8), 2.031 (7) Å).[12] No other chromium(III) porphyrin structure is available for comparison. The two Cr–O distances are significantly different. The Cr–O(1) distance (1.943 (10) Å) to the phenoxide ligand is shorter than the Cr–O(2) distance (2.069 (10) Å) to the THF ligand.

The phenoxy and THF ligands are arranged so that the O–Cr–N angles are nearly 90°. The O(1)–Cr–O(2) angle is 170.0

[†] University of California.
[‡] University of Wrocław.

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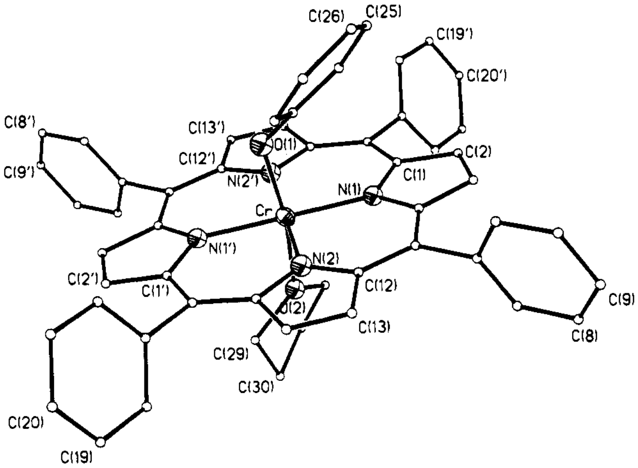

Figure 1. Perspective view of (TPP)Cr^{III}(OPh)(THF) showing 50% thermal contours for Cr, N, and O and uniform, arbitrarily sized circles for C. The disorder has been omitted.

Table I. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for (TPP)Cr^{III}(OPh)(THF)

	x	*y*	*z*	*U*[a]
Cr	5000	5000	5000	19 (1)
N(1)	3698 (5)	6585 (5)	5272 (5)	20 (1)
N(2)	6188 (5)	5037 (5)	6099 (5)	22 (1)
O(1)	3606 (14)	3746 (12)	6632 (13)	27 (4)
O(2)	6567 (13)	6097 (11)	3115 (12)	22 (3)
C(1)	2496 (7)	7183 (6)	4814 (6)	24 (2)
C(2)	1783 (7)	8183 (6)	5334 (6)	28 (2)
C(3)	2535 (7)	8178 (6)	6093 (7)	28 (2)
C(4)	3738 (7)	7183 (6)	6052 (6)	24 (2)
C(5)	4792 (7)	6891 (6)	6715 (6)	23 (1)
C(6)	4694 (7)	7716 (6)	7458 (6)	22 (1)
C(7)	5369 (8)	8875 (7)	6755 (8)	37 (2)
C(8)	5268 (8)	9658 (7)	7439 (8)	43 (2)
C(9)	4495 (7)	9243 (6)	8843 (7)	31 (2)
C(10)	3804 (8)	8067 (7)	9567 (8)	40 (2)
C(11)	3915 (8)	7311 (7)	8871 (7)	36 (2)
C(12)	5920 (7)	5875 (6)	6730 (6)	22 (1)
C(13)	6967 (7)	5542 (6)	7461 (7)	32 (2)
C(14)	7837 (7)	4495 (6)	7265 (6)	26 (2)
C(15)	7360 (7)	4168 (6)	6422 (6)	25 (2)
C(16)	7967 (7)	3132 (6)	6011 (6)	23 (1)
C(17)	9145 (7)	2231 (6)	6565 (6)	22 (1)
C(18)	10612 (8)	2605 (7)	6126 (7)	38 (2)
C(19)	11674 (9)	1761 (7)	6683 (8)	48 (2)
C(20)	11246 (8)	550 (7)	7687 (7)	41 (2)
C(21)	9785 (8)	149 (7)	8149 (8)	42 (2)
C(22)	8752 (8)	983 (6)	7570 (7)	32 (2)
C(23)	2796 (14)	3821 (12)	7847 (13)	24 (3)
C(24)	1348 (19)	4462 (16)	8136 (18)	45 (4)
C(25)	436 (18)	4337 (14)	9500 (16)	47 (4)
C(26)	980 (18)	3653 (14)	10562 (17)	49 (4)
C(27)	2461 (16)	3054 (13)	10241 (15)	36 (4)
C(28)	3367 (18)	3132 (15)	8930 (16)	36 (4)
C(29)	8185 (17)	5673 (15)	2473 (16)	36 (4)
C(30)	8853 (16)	6787 (13)	1139 (14)	36 (4)
C(31)	7373 (21)	7284 (18)	664 (19)	57 (5)
C(32)	6077 (17)	7153 (14)	1985 (15)	39 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table II. Selected Bond Lengths (Å) and Angles (deg) for (TPP)Cr^{III}(OPh)(THF)

Bond Lengths			
Cr–N(1)	2.035 (5)	Cr–N(2)	2.038 (7)
Cr–O(1)	1.943 (10)	Cr–O(2)	2.069 (10)
Bond Angles			
N(1)–Cr–N(1A)	180.0 (1)	N(2)–Cr–O(1)	92.3 (5)
O(1)–Cr–N(1A)	85.1 (4)	N(2)–Cr–O(1)	93.1 (5)
N(1)–Cr–N(2A)	90.1 (2)	N(1)–Cr–O(1)	94.9 (4)
O(1)–Cr–N(2A)	87.7 (5)	N(1)–Cr–O(2)	93.5 (4)
N(1)–Cr–O(1A)	85.1 (4)	O(1)–Cr–O(2)	170.0 (7)
N(1)–Cr–O(2A)	86.5 (4)	N(2)–Cr–N(2A)	180.0 (1)
Cr–O(1)–C(23)	127.8 (12)	O(2)–Cr–N(2A)	86.9 (5)
Cr–O(2)–C(32)	122.1 (9)	N(2)–Cr–N(1A)	87.7 (5)
N(1)–Cr–N(2)	89.9 (2)	Cr–O(2)–C(29)	125.6 (8)

Table III. ^{2}H Chemical Shifts for Chromium Porphyrins

compd[a]	δ_{pyrr}, ppm	*T*, °C	line width, Hz
(TPP-d_8)Cr^{III}(OPh)(THF)	−13.4	24	125
	−20.0	−40	
(TPP-d_8)Cr^{III}(OH)(THF)	−12.3	23	103
(TPP-d_8)Cr^{III}Cl(THF)	−16.7	25.5	145
	−23.9	−40	300
(TPP-d_8)Cr^{III}Br(THF)	−15.7	23	
(TPP-d_8)Cr^{II}	−34.9	24	107 (1540)[c]
	−58	−60	
(TPP-d_8)Cr^{II}(py)$_2$[b]	12.8	23	61 (163)[c]
	16.2	−40	122
(TPP-d_8)Cr^{IV}=O	9	23	

[a] Solvent is THF unless noted otherwise. [b] Solvent is dichloromethane. [c] Line width for the ^{1}H NMR spectrum is in parentheses; ^{1}H NMR solvent is benzene-d_6.

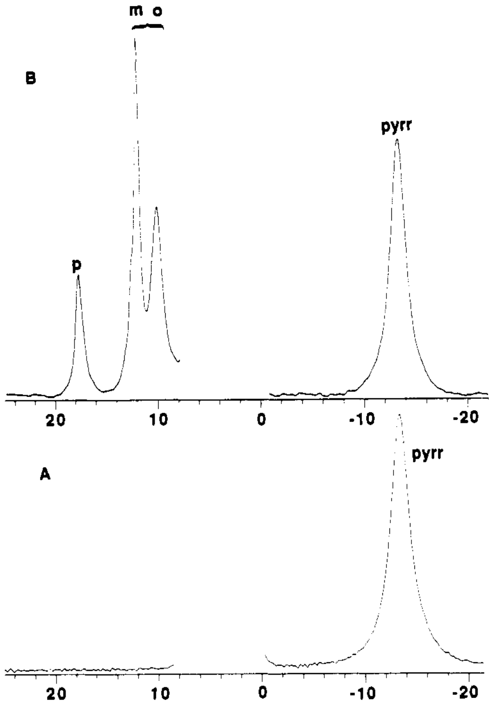

Figure 2. 46.0-MHz ^{2}H NMR spectra of (A) (TPP-d_8)Cr^{III}(OPh)(THF) and (B) (TPP-d_8)Cr^{III}(OPh-d_5)(THF) in THF solution at 24 °C. Resonance assignments: pyrr, pyrrole deuterons; o, m, p = ortho, meta, para deuterons of the phenoxy ligand.

(7) Å. The phenoxide ligand is bent so that the Cr–O(1)–C(23) angle is 127.8 (12)°. Other aspects of the coordination geometry are entirely regular for a metalloporphyrin. The structure emphasizes the ability of a poorly coordinating solvent (THF) to bind to this chromium porphyrin as an axial ligand. A related phenoxide complex, (OEP)Cr^{III}(OPh)·HOPh, was previously described.[13] The phenol may be acting as a sixth ligand as the THF does in (TPP)Cr^{III}(OPh)(THF).

^{2}H NMR Spectra. Cr(III) Complexes. Representative data are collected in Table III. Figure 2 shows ^{2}H NMR spectra of (TPP-d_8)Cr^{III}(OPh)(THF). Trace A shows a sample of material with specific deuteration of the pyrrole protons. The pyrrole resonance occurs at −13.4 ppm at 24 °C. Trace B shows a sample with the pyrrole and phenoxide groups deuterated. The three resonances in the 10–20 ppm region are due to the phenoxide

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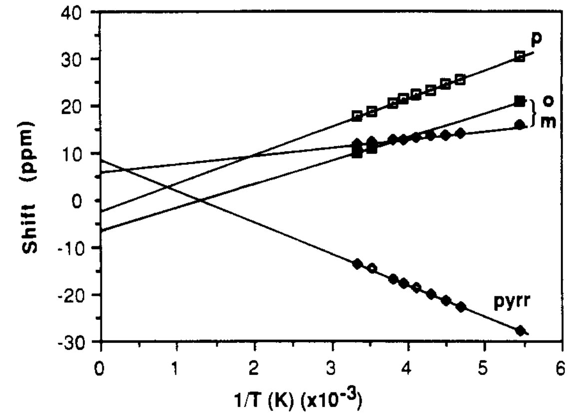

Figure 3. Curie plot for (TPP-d_8)Cr^{III}(OPh-d_5)(THF) in THF solution. Resonance labels follow those in Figure 2.

deuterons. The lowest field resonance can be assigned to the para phenoxide deuteron on the basis of its intensity. The other two resonances then are due to the ortho and meta phenoxide deuterons. A Curie plot for these resonances is shown in Figure 3. Each resonance displays Curie behavior with the extrapolated shifts at infinite temperature relatively near the anticipated diamagnetic reference positions.

The pyrrole resonances of several other chromium(III) porphyrins with different anionic axial ligands have been observed in tetrahydrofuran solution (Table I). There is a clear effect of the anionic ligand on the pyrrole chemical shift, with the phenoxy and hydroxy groups producing less negative shifts than the bromo and chloro ligands. Observation of the temperature dependency of the pyrrole resonances shows that each complex obeys the Curie law. The effect of solvent on the spectrum of (TTP-d_8)Cr^{III}Cl has been monitored. The pyrrole chemical shift is −17.5 ppm in both dichloromethane and chloroform. This slight difference from the value seen in THF may reflect the differences in the axial ligation by the solvents. Addition of successive amounts of imidazole (Im) to a dichloromethane solution of (TPP-d_8)Cr^{III}Cl causes an upfield shift of the pyrrole resonance to a limiting value of −23 ppm at 23 °C. We ascribe this shift to the formation of the adduct (TPP-d_8)Cr^{III}Cl(Im). The electronic spectrum of this solution shows a Soret peak at 456 nm, which is consistent with previous observations on (TPP)Cr^{III}Cl with axial ligation by nitrogen donors.[14]

Cr(II) Complexes. Solutions of (TPP-d_8)Cr^{II} in THF exhibit a pyrrole resonance at −34.9 ppm at 24 °C that is shifted further upfield than any of the resonances of the chromium(III) porphyrins that we have observed. The temperature dependence of the pyrrole resonance is linear in plots of the chemical shift versus T^{-1} with an intercept at infinite temperature of 12 ppm.

Addition of an excess of pyridine to (TPP-d_8)Cr^{II} in dichloromethane results in a downfield shift of the pyrrole resonance to 12.8 ppm at 23 °C. A Curie plot of the temperature dependence of the chemical shift for this resonance is linear with an extrapolated shift at infinite temperature of 2 ppm. The magnetic susceptibility of this chromium complex has been determined by the Evans method.[15] The magnetic moment at 23 °C is 2.9 (2) μ_B based on the formulation (TPP)Cr^{II}(py)$_2$. A similar downfield pyrrole shift is seen when imidazole is added to a dichloromethane solution of (TPP)Cr^{II}.

Oxidation of (TPP-d_8)Cr^{III}Cl with *tert*-Butyl Hydroperoxide. In order to demonstrate the feasibility of ^{2}H NMR spectroscopy monitoring a chemical reaction that involves chromium porphyrins, the reaction of *tert*-butyl hydroperoxide with (TPP-d_8)Cr^{III}Cl in dichloromethane solution was examined. The ^{2}H NMR spectral results are shown in Figure 4. Trace A shows the spectrum of (TPP-d_8)Cr^{III}Cl at −40 °C. Trace B shows the effect of adding 2 equiv of *tert*-butyl hydroperoxide to the sample. The resonance of the starting complex decreases in intensity and broadens while a new resonance at 9.2 ppm appears. The latter is indicative of the formation of diamagnetic (TPP-d_8)Cr^{IV}=O. On warming, however, the resonance at 9.2 ppm decreases in intensity while a new set of resonances in the −10 to −30 ppm region appear as seen in trace C at −10 °C. Trace D shows these resonances for another sample at 25 °C. Four distinct pyrrole resonances are observed. Deconvolution of the spectrum shows that the four have equal intensity but that their line widths vary. The electronic spectrum of the sample is shown in Figure 5. While the sample has sufficient stability for these spectral measurements, further purification of the product through chromatography or crystallization has not been successful. Nevertheless, it is clear that the product contains a chromium isoporphyrin complex, **1** (where R is either *t*-BuOO or *t*-BuO). Isoporphyrins have been obtained from the reactions of *tert*-butyl hydroperoxide with cobalt and

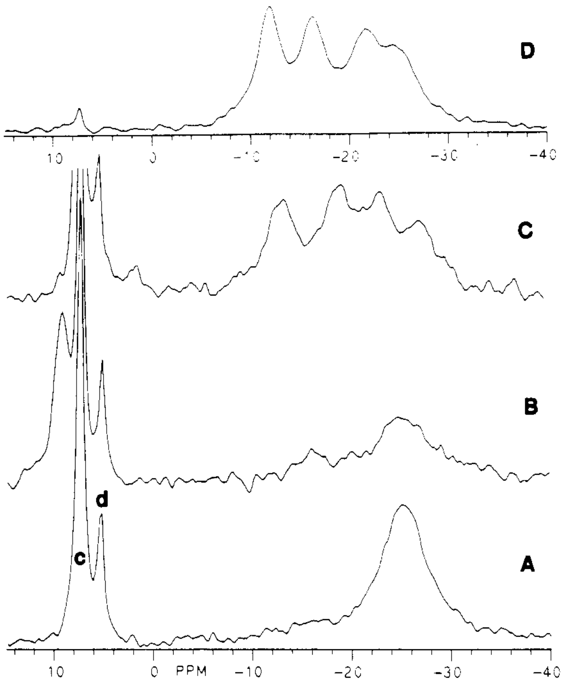

Figure 4. ^{2}H NMR spectra of a sample of (TPP-d_8)Cr^{III}Cl in dichloromethane: (A) initial spectrum at −40 °C; (B) spectrum after the addition of 2.0 equiv of *tert*-butyl hydroperoxide at −40 °C; (C) spectrum after warming to −10 °C. Trace D shows the spectrum of another sample at 23 °C in chloroform. The peaks labeled c and d are due to chloroform-d_1, added as a standard, and dichloromethane, respectively.

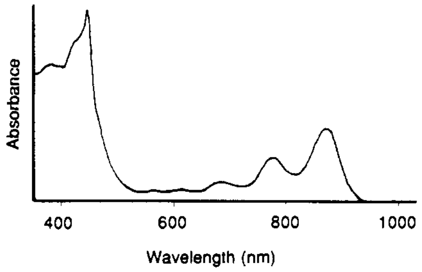

Figure 5. Electronic spectrum of a solution of (TPP-d_8)Cr^{III}Cl in dichloromethane after the addition of 2 equiv of *tert*-butyl hydroperoxide.

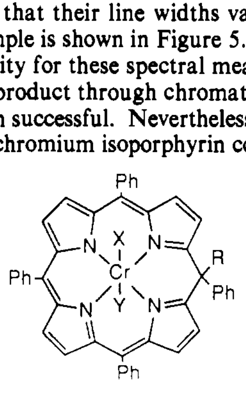

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Table IV. Crystallographic Data for (TPP)Cr^{III}(OPh)(THF)

$C_{54}H_{41}N_4O_2Cr$	fw = 829.95
a = 9.583 (5) Å	$P\bar{1}$ (No. 2), triclinic
b = 11.473 (7) Å	T = 130 K
c = 11.504 (6) Å	λ(Mo Kα) = 0.71069 Å
α = 63.90 (4)°	μ(Mo Kα) = 3.16 cm^{-1}
β = 91.04 (5)°	d_{calcd} = 1.334 Mg·m^{-3}
γ = 77.29 (4)°	transm factors = 0.85–0.93
V = 1033 (1) Å^3	$R(F_o)$ = 0.082
Z = 1	$R_w(F_o)$ = 0.076

iron tetraarylporphyrins,[16,17] and a chromium isoporphyrin has been obtained from the reaction of chromium tetraarylporphyrin with styrene ozonide.[18] The observation of four equally intense pyrrole resonances in trace D of Figure 4 is consistent with isoporphyrin formation, as is the observation of strong absorption features at 684 and 775 nm in the electronic spectrum (Figure 5).[19] The position of the pyrrole resonances in Figure 4 is consistent with the presence of Cr(III) in the unstable product. A plot of line widths of these four pyrrole resonances versus the square of the contact shift is linear. The fact that this plot has a significant slope indicates there is a prominent contribution of scalar relaxation to the line widths of the pyrrole resonances.

^{1}H NMR Data. The ^{2}H NMR data presented above give an unambiguous assignment of pyrrole resonances for these chromium complexes. Knowing the location of these resonances, we sought to locate the corresponding resonances in the ^{1}H NMR spectra of undeuterated complexes. Some data regarding these line widths are given in Table III.

Analysis of Pyrrole Shifts. The data available in Table III show that the spin and ligation states of paramagnetic chromium(III) and chromium(II) porphyrins can be identified by characteristic pyrrole resonances in the ^{2}H NMR spectra of suitably deuterated compounds.

For the Cr(III) complexes with the $d_{xy}{}^1$, $d_{xz}{}^1$, $d_{yz}{}^1$ configuration, the **g** tensor is isotropic and the zero-field splitting is small. Consequently, the dipolar contribution to the isotropic shift is expected to be negligible. Thus, the observation of negligible paramagnetic shifts for the phenyl resonances of (TPP)Cr^{III}Cl and significant upfield shifts for the pyrrole resonances is fully consistent with porphyrin to chromium(III) charge transfer. This places spin density in the filled $3e_g$ porphyrin orbital. A similar, but larger, upfield shift for the pyrrole resonances of the high-spin (S = 2) chromium(II) porphyrin with orbital occupancy $d_{xy}{}^1$, $d_{yz}{}^1$, $d_{xz}{}^1$, $d_{z^2}{}^1$ similarly suggests dominant porphyrin $3e_g$ to chromium(II) $d\pi$ charge transfer. The situation here resembles that seen for the isoelectronic manganese(III) porphyrins which also exhibit marked upfield pyrrole shifts. The alternative electronic configuration $d_{xy}{}^1$, $d_{yz}{}^1$, $d_{xz}{}^1$, $d_{x^2-y^2}{}^1$ should produce a downfield contribution to the isotropic shift of the pyrrole resonance, since there would be a σ-contact contribution to the delocalization pathway.

Addition of pyridine or imidazole to (TPP)Cr^{II} produces a marked downfield shift of the pyrrole resonance, which is indicative of a change in electronic structure. Crystals of (TPP)Cr^{II}(py)$_2$, which were obtained from THF/pyridine/water mixtures and recrystallized from toluene, are low-spin (S = 1) with a $(d_{xy}, d_{xz}, d_{yz})^4$ orbital occupancy.[11] The measured magnetic moment 2.9 (2) μ_B for our sample is consistent with the presence of the bis(pyridine) adduct. Thus, a spin-state change to form six-coordinate, low-spin (TPP-d_8)Cr^{II}(py)$_2$ is responsible for the downfield shift of the pyrrole resonance that is observed upon pyridine addition. However, it is difficult to account for the direction of this shift unless there is an unusual dipolar contribution that operates for such a low-spin d^4 species. Low-spin d^4 complexes generally have upfield pyrrole chemical shifts.[20,21]

Experimental Section

Materials. H$_2$TPP-d_8,[20] H$_2$TTP-d_8,[20] (TPP)Cr^{III} (X = Cl, Br),[12] (TPP)Cr^{III}OH,[23] (TPP)Cr^{II},[24] and (TPP)Cr^{IV}O[2] were prepared by standard methods. Tetrahydrofuran was deoxygenated by three freeze–pump–thaw cycles and stored over sodium metal under a purified dinitrogen atmosphere. Phenol-d_6 was purchased from Aldrich.

(TPP-d_8)Cr^{III}(OPh)(THF). Lithium phenoxide was prepared by the addition of a THF solution of *n*-butyllithium to a THF solution of phenol under a dinitrogen atmosphere. The white precipitate was collected and dried under vacuum. A solution of 12.2 mg (0.117 mmol) of lithium phenoxide was added to a solution of 69 mg (0.097 mmol) of (TPP-d_8)Cr^{III}Cl in 7 mL of THF. The solution was stirred for 15 min, and then the solvent was removed under vacuum. The solid was redissolved in a minimum volume of THF. Slow addition of hexane produced blue crystals of (TPP-d_8)Cr^{III}(OPh)(THF).

Instrumentation. ^{2}H NMR spectra were recorded on Nicolet NT-500 and General Electric QE-300 Fourier transform spectrometers. The spectra were collected over a 30-kHz bandwidth with 4K data points. Between 500 and 25000 transients were accumulated with a delay time of 50 ms. ^{1}H NMR spectra were recorded at 300 MHz on a General Electric QE-300 FT spectrometer. Electronic spectra were obtained by using a Hewlett-Packard 9122 diode array spectrometer and a Hitachi U-2000 spectrophotometer. Infrared spectra were obtained as films by using an IBM IR32 infrared spectrometer.

X-ray Data Collection for (TPP)Cr^{III}(OPh)(THF). Blue blocks were formed by slow diffusion of hexane into a solution of (TPP)Cr^{III}(OPh)(THF) in THF. The air-sensitive crystals were quickly coated with a light hydrocarbon oil to prevent degradation. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the 130 K dinitrogen stream of a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low-temperature apparatus. A triclinic unit cell was obtained by indexing 11 reflections from a rotation photograph and verified by examination of the axial photographs. Two check reflections remained stable throughout the collection. The data were corrected for Lorentz and polarization effects. Crystal data and collection parameters are given in Table IV.

Solution and Structure Refinement of (TPP)Cr^{III}(OPh)(THF). Calculations were performed on a Data General MV/10000 computer with SHELXTL version 5.1 software. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[25] The structure was solved in the space group $P\bar{1}$ by placing the chromium on an inversion center ($^1/_2$, $^1/_2$, $^1/_2$), followed by successive cycles of least-squares refinement and calculation of difference Fourier maps. The asymmetric unit consists of half of the complex with a THF group and a phenoxy group at 50% occupancy in the alternate positions above the below the porphyrin. Hydrogen atom positions were calculated using a riding model with C–H vectors fixed at 0.96 Å and thermal parameters fixed at 1.2 times those of the bonded carbons. An absorption correction was applied. The chromium atom was assigned anisotropic thermal parameters. Refinement converged at R = 8.2% (R_w = 7.6%) with 151 least-squares parameters and 2125 reflections. The goodness-of-fit was 1.44; the mean shift/esd was 0.006, with a maximum of 0.023 for the overall scale. The largest unassigned peak in the final difference map had a density of 0.727 electron/Å^3. This peak was 0.76 Å from C(19). An attempt was made to refine the structure in the noncentrosymmetric space group $P\bar{1}$, but the disorder between THF and phenoxy groups was not removed.

Acknowledgment. We thank the NIH (Grant GM26226) for financial support and Ms. E. Fung for valuable assistance with the X-ray crystallography.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal data for (TPP)Cr^{III}(OPh)(THF) (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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