"semibridging" leads to the following electronic reorganization: (a) some electron density is transferred from W(1) to W(2) and (b) some electron density is transferred from W(2) to Ir(1). The net result of these two transfers is that W(1) becomes slightly "electron poor" and Ir(1) becomes slightly "electron rich". This appears to be compensated by direct transfer of electron density from Ir(1) to W(1). Thus, the Ir(1)–W(1) bond length of 2.796 (1) Å is substantially shorter than any of the other Ir–W bond lengths in the molecule [viz, Ir(1)–W(2) = 2.863 (1), Ir(2)–W(1) = 2.833 (1), Ir(2)–W(2) = 2.847 (1) Å].

Our suggestion would clearly extend the range of M···CO contacts that have customarily been regarded as yielding significant bonding interactions. The "semibridging" carbonyl ligands in this complex would appear principally to relieve steric stress in the molecule.

Other distances in the molecule are within the expected ranges: C–O = 1.125 (20)–1.182 (19), W–C(cyclopentadienyl) = 2.293 (16)–2.381 (14),[16] and C–C(cyclopentadienyl) = 1.335 (22)–1.433 (20) Å.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and anisotropic thermal parameters (15 pages).

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Synthesis, Characterization, and Molecular Structure of Oxo(porphyrinato)chromium(IV) Complexes

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The reaction of chloro(5,10,15,20-tetraphenylporphyrinato)chromium(III) [Cr(TPP)Cl] with iodosylbenzene and base (*tert*-butyl hydroperoxide, *m*-chloroperoxybenzoic acid, or sodium hypochlorite) produced the corresponding oxochromium(IV) complex (**2**). This diamagnetic compound had an intense band in the IR at 1025 cm^{-1}, which shifted to 981 cm^{-1} upon ^{18}O substitution. The visible spectrum showed bands at 430 and 544 nm. The oxochromium(IV) complex reacted with triphenylphosphine to give triphenylphosphine oxide and chromium(II), which reacted with methylene chloride to give Cr(TPP)Cl or with **2** to give a μ-oxo chromium(III) dimer, **5**. Crystallization of oxo(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(IV) from benzene–hexane gave diffractable single crystals: space group $P2_1/c$, $Z = 4$, $a = 17.342$ (6) Å, $b = 16.964$ (7) Å, $c = 15.804$ (6) Å, $\beta = 112.52$ (3), $V = 4295$ (3) $Å^3$. Least-squares refinement based on 2309 observed data with $I > 3\sigma(I)$ gave $R_1 = 0.068$, $R_2 = 0.072$. The Cr–O bond length was 1.572 (6) Å, the average Cr–N distance was 2.032 (7) Å and the chromium cation was 0.469 Å above the average pyrrole nitrogen plane. The porphyrin ring was distinctly saddle shaped with the pyrrole β-carbons displaced 0.340 and 0.568 Å above and below the mean pyrrole nitrogen plane.

Introduction

Transition-metal oxo complexes are useful reagents for the oxidation of organic molecules.[1] There are relatively few examples of such species in ligand encinctures which may control the electronic and steric environment of the high-valent metal center. While oxo–metalloporphyrin complexes of titanium(IV),[2] vanadium(IV),[3] molybdenum(IV),[4] and molybdenum(V)[5] have been prepared and structurally characterized, these compounds have not been shown to be effective oxidizing agents. In 1979 we demonstrated that chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) [Fe(TPP)Cl] was an effective catalyst for oxygen transfer from iodosylbenzene to organic substrates.[6] An oxo–iron intermediate was proposed as the oxygen-transfer agent.[7,8] Cr(TPP)Cl[9] and Mn(TPP)Cl[10,11] were also shown to be active catalysts, and in the case of the chromium porphyrin, a reactive intermediate was formed which we have characterized as a chromium(V) porphyrinate (**1**).[12] On standing, **1** decomposed to an unusually stable, oxochromium(IV) complex,[13] the synthesis, structure, and characterization of which we describe herein.

Experimental Section

General Data. Thiophene-free benzene was distilled from potassium. Tetrahydrofuran was distilled from LAH/triphenylmethane, and alkane solvents were purified by treatment with sulfuric acid followed by distillation from potassium. Methylene chloride was distilled from P_2O_5 and filtered through solid potassium carbonate. Deuteriochloroform (100% Merck) was treated with solid potassium carbonate prior to use to remove acidic impurities. Elemental analyses were performed by Spang Microanalytical Laboratory. Mass spectra were obtained on a Finnegan Model 4021 GC mass spectrometer. Infrared spectra were determined by a Beckmann Model 4240. NMR spectra were obtained on JEOL FX-90Q and Bruker WM 360 NMR spectrometers. Visible spectra were determined on a Cary-17 or a Varian/Cary 219 spectrophotometer. Magnetic susceptibility mea-

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surements were performed on a Cahn Ventron R100 Faraday balance.

Synthesis of Chromium(III) Tetraarylporphyrinates. The free porphines H_2TPP and H_2TTP (para) were prepared according to the method of Adler.[14] Chlorin impurities were removed by refluxing the free base with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in benzene following the procedure of Smith.[15] Tetramesitylporphyrin, H_2TMP, was prepared by the condensation of pyrrole and mesitaldehyde according to the method of Badger, Jones, and Laslett.[16] The intermediate zinc porphyrinate was demetalated with concentrated HCl. Column chromatography of the crude product on silica, oxidation with DDQ, and subsequent chromatography gave an overall yield of 4% of H_2TMP. Cr(TPP)Cl was synthesized and purified as previously described.[17,18]

Synthesis of Chloro(5,10,15,20-tetramesitylporphyrinato)chromium(III) [Cr(TMP)Cl]. Metalation of chlorine-free H_2TMP was conducted under nitrogen with 500 mg (0.64 mmol) of the porphyrin in refluxing dimethylformamide (250 mL). Upon dissolution of the H_2TMP, anhydrous chromium(II) chloride (2.05 g) was added in three portions over 30 min. Thin-layer chromatography (alumina) indicated no free base at this point. The solution was cooled and added to an equal volume (250 mL) of cold, saturated sodium chloride solution. The dull green precipitate was filtered and washed with water until the filtrate no longer appeared green. The resulting solid was air-dried and applied to a 12-in. × 1-in. alumina column (Woelm neutral activity II) as a methylene chloride solution. Elution with methylene chloride afforded a trace of the free base (<1 mg), which was followed by a somewhat slower red band (<4 mg), the visible spectrum of which was identical with that of CrO(TMP) (**4**). A slow moving green band as well as the bulk of a dark green-brown material which remained at the origin was eluted with 3% methanolic methylene chloride. Both metalated fractions were combined and treated with 5 mL of concentrated hydrochloric acid with stirring overnight. The dark green solution was evaporated to dryness and vacuum-dried to give 400 mg (0.46 mmol) of Cr(TMP)Cl in 72% yield. This material was found to change in time due to apparent formation of the corresponding chromium(III) hydroxide so that a satisfactory analysis could not be obtained.[18]

Vis (CH_2Cl_2) λ_{max} (log ϵ): 397.5 (4.61), 451.5 (5.32), 525 (3.81), 567 (4.01), 606 (3.99). Mass spectrum (EI 70 eV) *m/e* (relative intensity scanned from 530 to 930 *m/e*): 872 (0.86), 871 (3.00), 870 (6.96), 869 (13.68 $^{52}Cr^{37}ClM^+$), 868 (15.62), 867 (24.39, $^{52}Cr^{35}Cl$ M^+), 836 (3.22), 835 (14.82), 8.34 (40.23), 833 (20,14), 832 (100, $52CrM^+ - Cl$), 831 (6.96), 8.30 (7.24, $50CrM^+ - Cl$). Anal. Calcd for $C_{56}H_{52}N_4$: C, 77.47; H, 6.04; N, 6.45; Cl, 4.08. Found: C, 73.98; H, 6.15; N, 6.19; Cl, 6.21.

Synthesis of Chloro(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(III) [Cr(TTP)Cl]. Metalation of H_2TTP was conducted in a manner identical with that previously described for the metalation of H_2TMP with one exception. H_2TTP was very insoluble even in refluxing dimethylformamide. As a result, 1.40 g (1.79 mmol) of free base was metalated in 1 L of refluxing dimethylformamide. Aqueous sodium chloride workup and chromatography on neutral Woelm activity II alumina followed by aqueous hydrochloric acid treatment and vacuum drying afforded a 76% yield of Cr(TTP)Cl. Recrystallization from dry methylene chloride and hexane provided an analytical sample which was vacuum-dried (125 °C (10^{-5} mm). The sample was found to occlude methylene chloride, and no satisfactory analysis was obtained.

Vis (CH_2Cl_2) λ_{max} (log ϵ): 393.5 (4.58), 448 (5.48), 524 (3.76), 565.5 (4.09), 605 (4.14). Anal. Calcd for $C_{48}H_{36}NCrCl$: C, 76.23; H, 4.80; N, 7.41; Cl, 4.61). Found: C, 73.02; H, 5.27; N, 6.90; Cl, 6.01).

Synthesis of Oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV) [CrO(TPP)] (2) with Iodosylbenzene. In a typical reaction, 140 mg (200 μmol) of Cr(TPP)Cl and 150 mg (735 μmol) of iodosylbenzene are stirred vigorously in 10 mL of methylene chloride at 25 °C for 5 min. Powdered potassium hydroxide (0.5 g, 8.9 mmol) was added, and the mixture was stirred for 5 min. The resulting orange-red solution was directly transferred to an alumina column (activity grade 4 basic Woelm) and was eluted with potassium carbonate-treated methylene chloride. A rapidly moving, cherry red band was eluted and concentrated under vacuum to give small, dark lavender crystals. This material was filtered and washed with 25 mL of acetone to remove iodobenzene. Vacuum drying gave 94 mg (69%) of CrO(TPP) (**2**): IR (CH_2Cl_2) 1026 s (Cr=O), 999; IR (KBr): 1025 s (Cr=O), 997 s; ^1H NMR ($CDCl_3$) δ 9.080 (8 H, s), 8.285 (4 H, m), 8.163 (4 H, m), 7.784 (12 H, m); mass spectrum (EI, 70 eV) *m/e* (relative intensity) 683 (1.77), 682 (23.73), 681 (70.89), 680 (100, $^{52}Cr^{16}OM^+$), 679 (1.52), 678 (2.18), 666 (8.48), 665 (39.11), 664 (52.4, $^{52}CrM^+ - O$), 663 (0.89), 662 (3.65, $^{50}CrM^+ - O$), 586 (9.95, $^{52}CrM^+ - O - H - Ph$), 508 (8.27, $^{52}CrM^+O - Ph - 2H$); Vis [$\lambda_{max}{}^{THF}$ (log ϵ)] 375 (4.37), 432.5 (5.39), 548 (4.14), 595 (3.70); $\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ) 379.5 (4.54), 430 (5.29), 544 (4.29). Anal. Calcd for $C_{44}H_{28}OCr$: C, 77.64; H, 4.14; N, 8.23; Cr, 7.64; O, 2.35. Found: C, 77.38; H, 4.16; N, 8.23; Cr, 7.55.

Oxidation of Cr(TPP)Cl with Sodium Hypochlorite or *m*-Chloroperoxybenzoic Acid. Cr(TPP)Cl (110 mg, 157 μmol) was dissolved in 15 mL of methylene chloride. Sodium hypochlorite (7 mL, 0.74 N Clorox bleach) was added, and the mixture was stirred for 4 min. The color of the reaction mixture turned from green to red. Concentrated sodium hydroxide (3 mL of a 50% solution) was added to the reaction mixture. After, the two-phase mixture was shakened in a separatory funnel, 25 mL of water was added. The organic layer was removed and dried over potassium carbonate. Chromatography on basic alumina yielded 23 mg (34 μmol) of CrO(TPP) (**2**), which was crystallized and vacuum-dried to analytical purity.

In a similar experiment, oxidation of 100 mg (143 μmol) of Cr-(TPP)Cl with 74 mg (429 μmol) of *m*-chloroperoxybenzoic acid produced 11 mg (16.2 μmol) of CrO(TPP) after chromatography on basic alumina.

Oxidation of Triphenylphosphine by CrO(TPP) (2). CrO(TPP) (7.39 mg, 10.9 μmol) and triphenylphosphine (3.15 mg, 12.0 μmol), which was free of triphenylphosphine oxide, were added to a 1-mL conical vial equipped with a magnetic stirrer and a Teflon septum. The vial was purged with nitrogen and 500 μL of methylene chloride, which had been treated with potassium carbonate and purged with nitrogen was added. After 15 min at room temperature, VPC analysis (6-ft × $^1/_8$-in. 1% SP-1240 DA on Supelcoport 100/120 column at 260 °C) indicated 100% conversion (on the basis of CrO(TPP)) of triphenylphosphine to triphenylphosphine oxide. The visible spectrum of the resulting solution indicated the presence of Cr(TPP)Cl. The identical reaction in benzene gave 60 ± 5% triphenylphosphine oxide and **5**, which was insoluble in benzene.

Synthesis of Oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV) (2) with *t*-BuOOH. Cr(TPP)Cl (100 mg, 143 μmol) was dissolved in 15 mL of CH_2Cl_2, and 98% *t*-BuOOH (120 mg, 1.13 μmol; Lucidol) was added. Stirring was commenced under nitrogen. After 1 min, 85 mg of powered KOH was added and the resulting reddish brown solution was extracted with 25 mL of water after 2 min of additional stirring. The methylene chloride phase was quickly stirred over solid potassium carbonate to remove excess water and was directly applied to an alumina column (Woelm Basic IV). The red solution of **2** was collected, the solvent removed under vacuum, and the remaining solid washed with acetone to give 50 mg of **2** after vacuum drying: 51%; IR (KBr) 1026 s (Cr=O). Anal. Calcd for $C_{44}H_{28}N_4OCr$: C, 77.64; H, 4.14; N, 8.23; Cr, 7.64. Found: C, 77.31; H, 4.22; N, 7.98; Cr, 7.67.

Synthesis of ^{18}O-Labeled Iodosylarenes. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate (Aldrich Chemical Co.) according to the method of Saltzman and Sharefkin.[19] The oxidation titre of iodosylbenzene was determined by iodimetry to be in excess of 99%. Care was taken to keep this yellow, explosive (210 °C) compound cold to avoid disproportionation to the inactive iodoxybenzene.

^{18}O-labeled iodosylbenzene was synthesized from hydrolysis of the iodobenzene dichloride with $H_2{}^{18}O$. Potassium hydroxide (56.1 mg,

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2.95 mmol) was dissolved in 1 mL of $H_2{}^{18}O$ content 85%; Merck). Iodobenzene dichloride (395 mg, 1.48 mmol) was added to this solution with rapid stirring, and the reaction was maintained under nitrogen during the course of hydrolysis and workup. The bright yellow, needle-shaped crystals of the dichloride gave rise to a milky yellow-white suspension after 45 min of stirring. Stirring was stopped, and the reaction flask was stoppered and allowed to stand at 5 °C for 10 h. The suspension was then filtered onto a small frit. The crude iodosylbenzene was vacuum-dried, washed with a small amount of chloroform, and vacuum-dried to give 290 mg of iodosylbenzene, mp 209 °C (explosive dec). The ^{18}O content of this material was found to be in excess of 70% as determined by Cr^{III}(TPP)Cl/iodosylbenzene (labeled) epoxidation of norbornylene.[9]

Synthesis of $Cr^{18}O$(TPP) (2-^{18}O). Solid Cr(TPP)Cl (50 mg) was dissolved in 5 mL of dry methylene chloride under nitrogen and added to excess iodosylbenzene on an airless frit. After 2 min, the mixture was filtered into a precooled receiver at −78 °C. The solution was degassed, and ca. 1 mL of *tert*-butylamine was distilled in. The mixture was warmed to −20 °C for 10 min, and hexane was gradually added until solid began to separate. The mixture was allowed to stand for 3 h at −40 °C. Additional hexane was added, and the mixture was allowed to stand overnight at −40 °C. Solid **2**-^{18}O was isolated by filtration and washed with acetone to give an 80–90% yield: mass spectrum (EI, 70 eV) *m*/*e* (relative intensity) 684 (2.99), 683 (15.69), 682 (28.06 $^{52}Cr^{18}OM^+$), 681 (9.68), 680 (16.14, $^{52}Cr^{16}OM^+$), 681 (9.68), 680 15.14, $^{52}Cr^{16}OM^+$), 666 (4.23), 665 (17.27), 664 (31.90, $^{52}CrM^+ - O$), 662 (1.67, $^{50}CrM^+ - O$), 586 (7.01), 508 (3.74), 332 (12.23, 664 doubly charged), 250 (100); IR (KBr) 982 cm^{-1} (Cr=^{18}O).

Synthesis of Oxo(5,10,15,20-tetra-*p*-tolylporphinato)chromium(IV) (3) from Cr(TTP)Cl and Iodosylbenzene. Cr(TTP)Cl (200 mg, 264 μmol) and iodosylbenzene (94 mg, 427 μmol) were stirred for 20 min in 10 mL of dry benzene. When the reaction was judged complete by visible spectroscopy (20 min), the mixture was filtered directly onto a short alumina column (Woelm Basic IV). The resulting solution was evaporated, and the dark lavender crystals were washed with petroleum ether and vacuum-dried to give 140 mg (190 μmol) of CrO(TTP) in 72% yield. An analtyical sample was prepared by dissolving the material in benzene and allowing slow pentane diffusion to effect crystallization. Crystals suitable for X-ray diffraction were obtained over a 10-day period at 25 °C with this slow diffusion technique: IR (KBr) 1020 cm^{-1} (Cr=O); ^{1}H NMR ($CDCl_3$, K_2CO_3 treated) δ 9.093 (8 H, s), 8.154 (4 H, m), 8.049 (4 H, m), 7.560 (8 H, m), 2.701 (12 H, m); Vis [$\lambda_{max}{}^{CH_2Cl_2}$ (log ε)] 379.5 (4.57), 432.5 (5.29), 503 sh (3.66), 545 (4.32), 578.5 (3.63). Anal. Calcd for $C_{48}H_{38}N_4OCr$: C, 78.24; H, 4.93; N, 7.60. Found: C, 78.25; H, 5.11; N, 7.53.

Synthesis of Oxo(5,10,15,20-tetra-2,4,6-mesitylporphinato)chromium(IV) (4). Cr^{III}(TMP)Cl (90 mg, 103 μmol) and iodosylbenzene (170 mg, 773 μmol) were stirred in 4 mL of methylene chloride for 10 min, followed by chromatography of this solution on alumina (Woelm Basic IV). The combined fractions were concentrated, and the resulting purple microcrystals were washed sparingly with hexane to give 80 mg (94 μmol) of product, which contained a trace of iodobenzene after vacuum drying. The yield was 92%. An analytical sample was prepared by recrystallization from benzene/pentane: IR (KBr) 1023 cm^{-1} (Cr=O); ^{1}H NMR (K_2CO_3 treated $CDCl_3$) δ 8.837 (8 H, s), 7.308 (4 H, s), 7.263 (4 H, s), 2.631 (12 H, s), 1.965 (12 H, s), 1.735 (12 H, s); Vis [$\lambda_{max}{}^{CH_2Cl_2}$ (log ε)] 377.5 (4.50), 431.5 (5.27), 501 sh (3.59), 545 (4.25), 579 sh, 607 (3.10). Anal. Calcd for $C_{56}H_{52}N_4OCr$: C, 79.22; H, 6.17; N, 6.60. Found: C, 78.84; H, 6.04; N, 6.52.

Synthesis of CrO(TMP) from Cr(TMP)Cl and *tert*-Butyl Hydroperoxide. Cr(TMP)Cl (43 mg, 49.5 μmol) was placed in a vial containing 100 mg of powdered potassium hydroxide. Methylene chloride (5 mL) containing Lucidol *tert*-butyl hydroperoxide (83 mg, 98%, 904 μmol) was added, and the mixture was shaken vigorously for 5 min. Direct application of the solution to a 4-in. × $^1/_4$-in. alumina column (Basic Woelm Activity II) afforded CrO(TMP) on elution, which gave 38 mg (44.9 μmol) of product on concentration after drying (90% yield).

Synthesis of μ-Oxo-bis((5,10,15,20-tetraphenylporphyrinato)chromium(III)) from Cr(TPP)Cl and Sodium Hydroxide. Cr(TPP)Cl (200 mg, 285 μmol) was dissolved in 50 mL of methylene chloride, and an equal portion of 50% sodium hydroxide was added; the mixture was stirred for 24 h. The resulting purple emulsion was left to stand for 120 h, after which it was extracted with 10 100-mL portions of water. The methylene chloride phase including solid at the interface was evaporated and dried under vacuum: Vis (THF) [λ_{max} (log ε)] 395 sh, 433 (5.41), 518 (3.70), 556 (4.08), 593 (3.95), 622.5 (3.720). Anal. Calcd as hydrate of dimer $C_{44}H_{30}N_4O_2Cr$: C, 77.52; H, 4.20; N, 8.33. Found: C, 77.59; H, 4.21; N, 8.23.

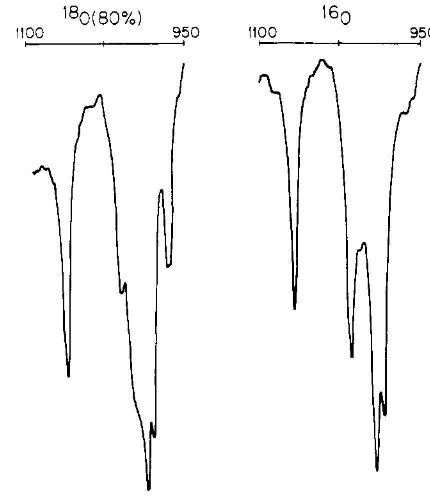

Figure 1. Infrared spectra of CrO(TPP) (**2**) and **2**-^{18}O (cm^{-1}).

Solution and Refinement of CrO(TPP) (3). Crystals of CrO(TTP) (3) were obtained by diffusion of pentane into a benzene solution. A crystal was mounted on a Syntex $P2_1$ automatic diffractometer and the space group determined to be $P2_1/c$ with $Z = 4$, $a = 17.342$ (6) Å, $b = 16.964$ (7) Å, $c = 15.804$ (6) Å, $\beta = 112.52$ (3)°, $V = 4295$ (3) Å, and d (calcd) = 1.26 g/cm^3. Data were collected with graphite-monochromated Mo Kα radiation. There were 6475 reflections collected with $2\theta > 45°$. The absorption coefficient was 2.95, and no absorption correction was necessary. The data were reduced by methods previously described.[20]

The structure contains one molecule of CrO(TTP) (3) and one molecule of benzene/asymmetric unit and was solved by direct methods using the MULTAN crystallographic program. Least-squares refinement based on 2309 observed data with $I > 3\sigma(I)$ and with anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.081$ and $R_2 = 0.087$. Hydrogen atomic positions were calculated and added as fixed contributions to the structure factors with the assumption of a bond distance of 1.00 Å and an isotropic temperature parameter of 1.1 times the thermal parameter of the atom to which the hydrogen is attached. Refinement to convergence gave $R_1 = 0.068$ and $R_2 = 0.072$.

Results

Treatment of Cr(TPP)Cl in methylene chloride with iodosylbenzene and potassium hydroxide followed by chromatography on basic alumina led to the isolation of a crystalline, red material, **2**, in 69% yield. The same compound could be isolated from the reaction of the TPP–Cr(V) species (**1**) we have recently described with *tert*-butylamine or Cr(TPP)Cl. *tert*-Butyl hydroperoxide, *m*-chloroperoxybenzoic acid, and potassium hypochlorite oxidation of Cr(TPP)Cl also produced **2**. Similarly, the iodosylbenzene oxidation of chloro(5,10,15,20-tetra-*p*-tolylporphinato)chromium(III) [Cr(TTP)Cl] and chloro(5,10,15,20-tetramesitylporphinato)chromium(III) [Cr(TMP)Cl] produced **3** and **4**, analogous to **2**. Elemental analyses of crystalline samples of **2–4** were consistent with compounds for the formula oxochromium porphyrinate. Spectral and physical characterization indicated that **2–4** were diagmagnetic, oxochromium(IV) complexes.

The infrared spectrum of **2** determined in a potassium bromide mull showed a strong band at 1025 cm^{-1}. Preparation of **2**-^{18}*O* from [^{18}*O*]iodosylbenzene gave material with a weak band at 1025 cm^{-1} and a new absorbance at 981 cm^{-1} (Figure

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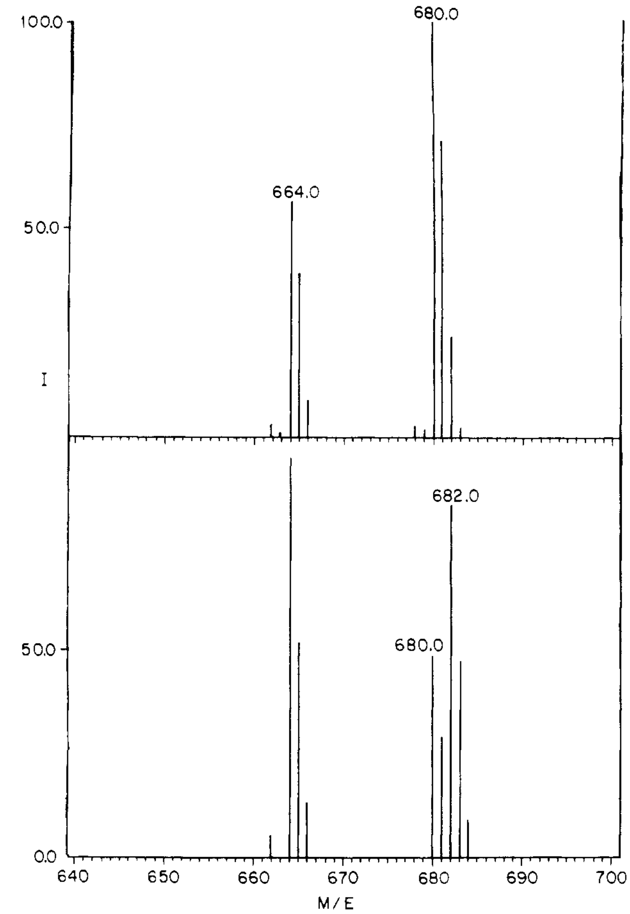


Figure 2. Mass spectra of **2** (upper trace) and **2**-^{18}O (lower trace).

Table I. ^1H NMR Spectra of Oxochromium(IV) Porphyrins

	β-pyrrole H	ortho	meta	para
CrO(TPP) (2)	9.085[a]	8.163, 8.285	7.78	
CrO(TTP) (3)	9.093	8.049, 8.154	7.56	2.70[b]
CrO(TMP) (4)	8.847	1.735,[b] 1.975[b]	7.31	2.63[b]

[a] δ values in $CDCl_3$ at 30 °C. [b] Methyl resonance.

1). This shift is close to the value calculated by reduced mass considerations for a Cr–O vibration.[21] The two complexes, **2** and **2**-^{18}O, gave mass spectra with prominent parent and parent-O peaks. Comparison of the parent regions of the mass spectra of **2** and **2**-^{18}O indicated 64% ^{18}O incorporation (Figure 2). The oxochromium(IV) phthalocyanine complex reported by Wasgestian[22] from the autoxidation of the corresponding chromium(II) complex has a similar ^{18}O-shifted Cr–O stretch (1041 cm^{-1}). Curiously, though, this material was found to be dimeric and paramagnetic in contrast to **2**.

Consistent with their diamagnetism, **2–4** gave well-resolved ^1H NMR spectra (Table I). Chemical shift assignments were made on the basis of comparisons with the known Ni^{2+}, Zn^{2+}, VO^{2+}, and MoO^{2+} systems.[23]

The ortho phenyl protons in **3** appeared as two broad singlets at 25 °C that sharpened to two doublets (J = 7.3 and 7.8 Hz) at −20 °C (Figure 3). This observation is indicative of chemical exchange of the nonequivalent ortho hydrogens via rotation about the phenyl–porphyrin bond. Coalescence of the ortho phenyl protons was observed at 37 °C, which indicated a rotational barrier for ring rotation of 15.7 ± 0.3 kcal/mol in toluene-d_8. Phenyl rotation at similar rates has been reported for Fe(TTP)Cl and TiO(TPP) derivatives.[24]

Pure, recrystallized samples of CrOTPP (**2**) were bright red and showed bands at 379.5 (log ε 4.54), 430 (log ε 5.29), and 544 nm (log ε 4.29). Addition of iodosylmesitylene to methylene chloride solutions of **2** led to the smooth conversion of **2** to the paramagnetic chromium(V) complex **1** (418 nm, log ε 5.03) we have recently described.[9,12] On standing, **1** slowly decomposed back to **2**. Indeed, great care was necessary to prepare samples of **1** which were free of **2**. The visible spectra

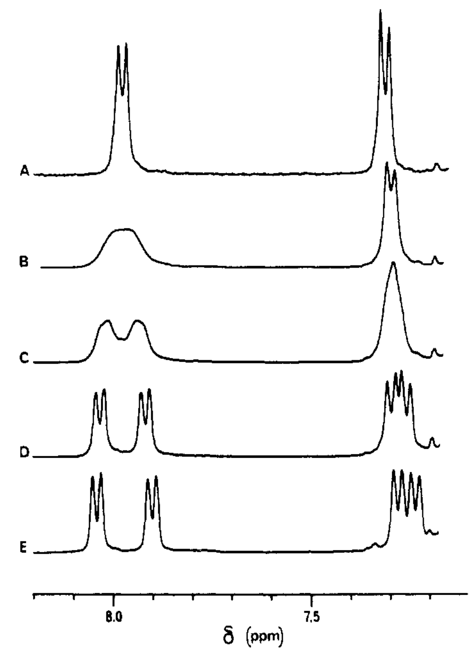


Figure 3. ^1H NMR spectra of CrO(TTP) (**3**) in $CDCl_3$ at 360 MHz: A, 65 °C; B, 37 °C; C, 25 °C; D, 0 °C; E, −20 °C.

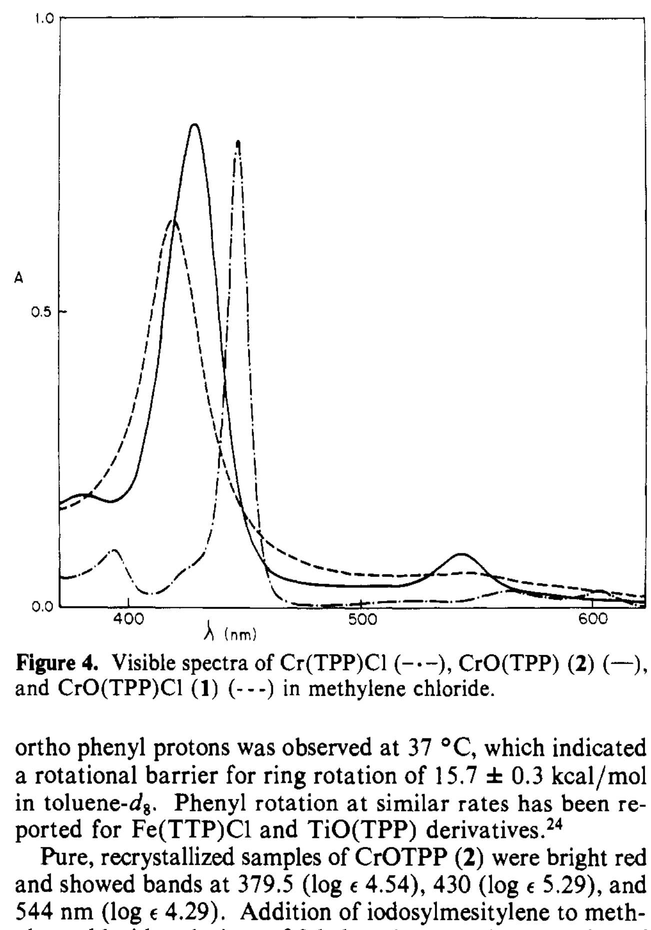


Figure 4. Visible spectra of Cr(TPP)Cl (–·–), CrO(TPP) (**2**) (—), and CrO(TPP)Cl (**1**) (---) in methylene chloride.

(21) The weak CrO absorptions we had ascribed to **1** were due to small amounts of **2** in these solutions; cf. ref 9. The chromyl band of **1**-perchlorate has now been located at 972 cm^{-1}: Takahashi, T., unpublished results.
(22) Nill, K. H.; Wagestian, F.; Pfeil, A. *Inorg. Chem.* **1979**, *18*, 564.
(23) LaMar, G. N.; Walker, F. A. *Porphyrins* **1979**, *4*, 61.
(24) (A) Eaton, S. S.; Eaton, G. R. *J. Chem. Soc., Chem. Commun.* **1974**, 576. (b) *J. Am. Chem. Soc.* **1975**, *97*, 3660. (c) Walker, F. A.; LaMar, G. N. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 328.

Table II. Molecular Bond Lengths (Å) and Angles (Deg) for CrO(TTP) (3)

Bond Lengths

Cr-O	1.572 (6)	N3-C34	1.384 (11)	C54-C55	1.384 (14)	C42-C43	1.341 (12)
Cr-N1	2.028 (8)	N3-C31	1.401 (11)	C54-C5M	1.510 (14)	C43-C44	1.431 (12)
Cr-N2	2.031 (7)	C31-C32	1.427 (12)	C55-C56	1.396 (13)	C44-C8	1.364 (12)
Cr-N3	2.032 (7)	C32-C33	1.345 (12)	N2-C21	1.381 (11)	C8-C81	1.512 (13)
Cr-N4	2.037 (8)	C33-C34	1.435 (12)	N2-C24	1.383 (10)	C81-C86	1.373 (13)
N1-C14	1.378 (11)	C34-C7	1.400 (12)	C21-C22	1.419 (12)	C81-C82	1.387 (13)
N1-C11	1.397 (10)	C7-C41	1.388 (12)	C22-C23	1.357 (12)	C82-C83	1.379 (14)
C11-C8	1.406 (12)	C7-C71	1.482 (13)	C23-C24	1.436 (13)	C83-C84	1.374 (15)
C11-C12	1.430 (12)	C71-C72	1.386 (13)	C24-C6	1.396 (12)	C84-C85	1.365 (15)
C12-C13	1.344 (12)	C71-C76	1.410 (13)	C6-C31	1.365 (12)	C84-C8M	1.519 (14)
C13-C14	1.436 (12)	C72-C73	1.385 (12)	C6-C61	1.504 (12)	C85-C86	1.392 (14)
C14-C5	1.398 (12)	C73-C74	1.362 (14)	C61-C62	1.381 (14)	C91-C92	1.368 (16)
C5-C21	1.372 (12)	C74-C75	1.382 (14)	C61-C66	1.384 (15)	C91-C96	1.420 (17)
C5-C51	1.516 (13)	C74-C7M	1.505 (13)	C62-C63	1.403 (14)	C92-C93	1.367 (17)
C51-C56	1.387 (13)	C75-C76	1.385 (14)	C63-C64	1.355 (17)	C93-C94	1.420 (18)
C51-C52	1.392 (13)	N4-C41	1.393 (11)	C64-C65	1.369 (17)	C94-C95	1.351 (18)
C52-C53	1.388 (13)	N4-C44	1.400 (10)	C64-C6M	1.523 (15)	C95-C96	1.373 (17)
C53-C54	1.399 (14)	C41-C42	1.425 (12)	C65-C66	1.388 (16)		

Bond Angles

O-Cr-N1	104.5 (4)	C64-C65-C66	126.3 (13)	C52-C53-C54	121.9 (11)	C7-C41-C42	125.1 (10)
O-Cr-N2	100.6 (4)	C61-C66-C65	115.6 (12)	C55-C54-C53	117.1 (10)	N4-C41-C42	110.2 (9)
O-Cr-N3	105.7 (4)	C34-N3-C31	105.6 (8)	C55-C54-C5M	120.9 (12)	C43-C42-C41	107.4 (9)
O-Cr-N4	102.5 (4)	C6-C31-N3	126.3 (9)	C53-C54-C5M	122.0 (12)	C42-C43-C44	108.3 (9)
N1-Cr-N2	86.6 (3)	C6-C31-C32	124.7 (10)	C54-C55-C56	121.8 (11)	C8-C44-N4	125.2 (10)
N1-Cr-N3	149.7 (3)	N3-C31-C32	108.8 (9)	C51-C56-C55	120.0 (11)	C8-C44-C43	125.6 (10)
N1-Cr-N4	87.5 (3)	C33-C32-C31	108.6 (9)	C21-N2-C24	105.7 (8)	N4-C44-C43	109.2 (9)
N2-Cr-N3	87.5 (3)	C32-C33-C34	107.0 (9)	C5-C21-N2	124.9 (9)	C44-C8-C11	124.3 (9)
N2-Cr-N4	156.9 (3)	N3-C34-C7	125.8 (9)	C5-C21-C22	124.5 (10)	C44-C8-C81	119.6 (9)
N3-Cr-N4	86.4 (30	N3-C34-C33	109.9 (9)	N2-C21-C22	110.4 (9)	C11-C8-C81	116.0 (9)
C14-N1-C11	105.1 (8)	C7-C34-C33	124.3 (10)	C23-C22-C21	107.0 (9)	C86-C81-C82	117.8 (10)
N1-C11-C8	124.8 (9)	C41-C7-C34	122.9 (10)	C22-C23-C24	107.4 (9)	C86-C81-C8	122.0 (10)
N1-C11-C12	109.9 (9)	C41-C7-C71	119.5 (10)	N2-C24-C6	125.3 (10)	C82-C81-C8	120.2 (10)
C8-C11-C12	125.3 (9)	C34-C7-C71	117.7 (9)	N-C24-C23	109.4 (9)	C83-C82-C81	119.9 (11)
C13-C12-C11	107.1 (9)	C72-C71-C76	116.7 (11)	C6-C24-C23	125.1 (10)	C84-C83-C82	122.2 (11)
C12-C13-C14	107.8 (9)	C72-C71-C7	120.3 (10)	C31-C6-C24	123.1 (9)	C85-C84-C83	118.0 (10)
N1-C14-C5	125.8 (9)	C76-C71-C7	122.9 (11)	C31-C6-C61	118.5 (10)	C85-C84-C8M	121.7 (13)
N1-C14-C13	109.9 (9)	C73-C72-C71	120.5 (11)	C24-C6-C61	118.3 (10)	C83-C84-C8M	120.3 (13)
C5-C14-C13	124.3 (10)	C74-C73-C72	122.9 (11)	C62-C61-C66	120.2 (10)	C84-C85-C86	120.4 (12)
C21-C5-C14	122.9 (10)	C73-C74-C75	117.5 (11)	C62-C61-C6	120.1 (11)	C81-C86-C85	121.6 (11)
C21-C5-C51	119.9 (10)	C73-C74-C7M	122.8 (13)	C66-C61-C6	119.7 (11)	C92-C91-C96	122.8 (14)
C14-C5-C51	117.1 (10)	C75-C74-C7M	119.8 (12)	C61-C62-C63	120.9 (12)	C93-C92-C91	120.4 (15)
C56-C51-C52	119.2 (11)	C74-C75-C76	120.9 (11)	C64-C63-C62	120.5 (13)	C92-C93-C94	116.2 (15)
C56-C51-C5	119.6 (11)	C75-C76-C71	121.3 (11)	C63-C64-C65	116.4 (12)	C95-C94-C93	123.6 (16)
C52-C51-C5	121.2 (10)	C41-N4-C44	105.0 (8)	C63-C64-C6M	121.9 (15)	C94-C95-C96	120.3 (16)
C53-C52-C51	119.8 (11)	C7-C41-N4	124.4 (10)	C65-C64-C6M	121.6 (15)	C95-C96-C91	116.4 (15)

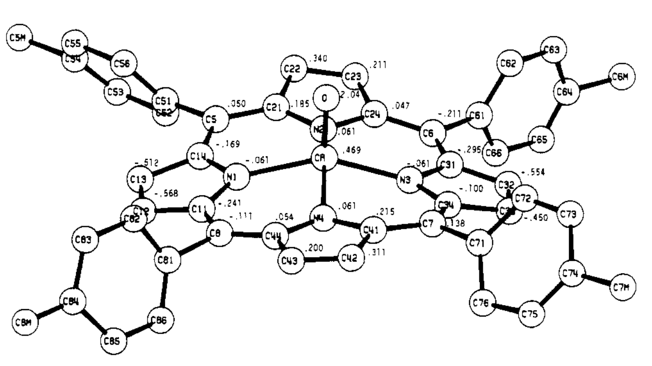


Figure 5. Structure and numbering scheme for CrO(TTP) (**3**). Superscripted numbers are deviations in Å of ring atoms from the least-squares plane of the pyrrole nitrogens ($0.02332X - 0.9891Y - 0.04034Z + 2.19768 = 0$).

of **1**, **2**, and Cr(TPP)Cl are compared in Figure 4.

Pure CrO(TPP) (**2**) reacted with triphenylphosphine in dry, degassed methylene chloride to produce 1 molar equiv of triphenylphosphine oxide and Cr(TPP)Cl. By contrast, the same reaction in benzene or THF produced only a 60% yield of triphenylphosphine and a new, insoluble chromium porphyrin species (**5**). This chromium species was determined to be a (μ-O)CrTPP dimer by the following observations. Treatment of **5** with hydrogen chloride or even halogenated solvents which had not been rigorously purified converted **5** to Cr(TPP)Cl. Likewise, treatment of Cr(TPP)Cl with sodium hydroxide also produced **5**.

Taken together, these results for the reduction of CrO(TPP) (**2**) with triphenylphosphine indicate the initial production of triphenylphosphine indicate the initial production of triphenylphosphine oxide and Cr(TPP) (**6**). Reduction of or-

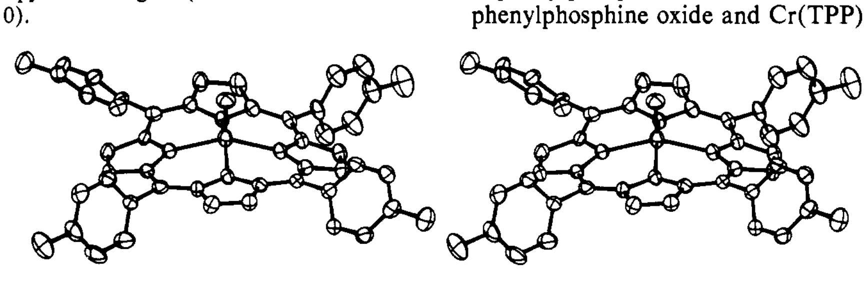


Figure 6. Stereoscopic view of CrO(TTP) (**3**) with 30% probability ellipsoids.

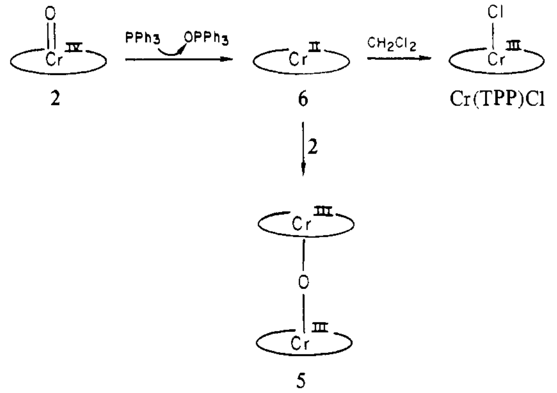
Table III. Positional Parameters for the Nonhydrogen Atoms of CrO(TTP) (3)

atom	*x*	*y*	*z*
Cr	0.2999 (1)	0.1038 (1)	0.1250 (1)
O	0.3002 (4)	0.0112 (3)	0.1225 (5)
N1	0.1903 (4)	0.1320 (4)	0.1356 (5)
C11	0.1128 (6)	0.1438 (6)	0.0644 (7)
C12	0.0508 (6)	0.1601 (6)	0.1012 (8)
C13	0.0882 (7)	0.1537 (7)	0.1928 (7)
C14	0.1744 (6)	0.1346 (6)	0.2146 (8)
C5	0.2321 (7)	0.1193 (6)	0.3030 (7)
C51	0.1990 (8)	0.1153 (6)	0.3788 (9)
C52	0.2242 (7)	0.1695 (7)	0.4504 (8)
C53	0.1895 (8)	0.1668 (7)	0.5163 (8)
C54	0.1286 (7)	0.1114 (8)	0.5127 (7)
C55	0.1054 (6)	0.0576 (7)	0.4415 (9)
C56	0.1406 (7)	0.0583 (7)	0.3756 (7)
C5M	0.0877 (8)	0.1109 (9)	0.5816 (8)
N2	0.3542 (5)	0.1232 (5)	0.2620 (5)
C21	0.3162 (6)	0.1124 (7)	0.3236 (7)
C22	0.3771 (7)	0.1008 (8)	0.4133 (7)
C23	0.4529 (7)	0.1105 (8)	0.4082 (7)
C24	0.4390 (6)	0.1238 (6)	0.3138 (7)
C6	0.5011 (6)	0.1420 (6)	0.2810 (7)
C61	0.5889 (6)	0.1535 (8)	0.3493 (7)
C62	0.6414 (7)	0.0894 (8)	0.3800 (8)
C63	0.7239 (8)	0.0991 (10)	0.4424 (9)
C64	0.7547 (8)	0.1719 (11)	0.4715 (9)
C65	0.7005 (10)	0.2336 (9)	0.4388 (10)
C66	0.6176 (8)	0.2286 (8)	0.3788 (9)
C6M	0.8454 (7)	0.1850 (10)	0.5348 (10)
N3	0.4092 (4)	0.1380 (5)	0.1171 (5)
C31	0.4857 (6)	0.1505 (6)	0.1901 (7)
C32	0.5474 (6)	0.1688 (6)	0.1540 (8)
C33	0.5118 (6)	0.1658 (6)	0.0621 (8)
C34	0.4261 (6)	0.1441 (6)	0.0385 (7)
C7	0.3686 (6)	0.1325 (5)	−0.0512 (7)
C71	0.4016 (7)	0.1260 (7)	−0.1246 (8)
C72	0.4606 (7)	0.0691 (7)	−0.1196 (7)
C72	0.4919 (7)	0.0631 (7)	−0.1878 (8)
C74	0.4695 (7)	0.1130 (8)	−0.2608 (7)
C75	0.4109 (8)	0.1703 (7)	−0.2671 (8)
C76	0.3784 (6)	0.1779 (7)	−0.1999 (9)
C7M	0.5060 (7)	0.1080 (8)	−0.3330 (7)
N4	0.2453 (5)	0.1324 (4)	−0.0102 (5)
C41	0.2832 (6)	0.1269 (6)	−0.0734 (7)
C42	0.2215 (7)	0.1237 (7)	−0.1642 (7)
C43	0.1466 (7)	0.1282 (7)	−0.1580 (7)
C44	0.1595 (6)	0.1330 (6)	−0.0631 (7)
C8	0.0983 (6)	0.1398 (6)	−0.0293 (7)
C81	0.0079 (6)	0.1432 (7)	−0.0947 (7)
C82	−0.0437 (7)	0.0784 (7)	−0.1049 (8)
C83	−0.1266 (7)	0.0825 (7)	−0.1626 (8)
C84	−0.1611 (7)	0.1496 (9)	−0.2112 (8)
C85	−0.1107 (8)	0.2137 (8)	−0.2005 (9)
C86	−0.0264 (7)	0.2098 (7)	−0.1441 (8)
C8M	−0.2530 (7)	0.1516 (9)	−0.2731 (9)
C91	0.1203 (9)	0.5713 (8)	0.3506 (10)
C92	0.1075 (9)	0.5738 (8)	0.2597 (10)
C93	0.1737 (11)	0.5777 (10)	0.2332 (11)
C94	0.2542 (11)	0.5734 (9)	0.3043 (12)
C95	0.2674 (10)	0.5713 (9)	0.3943 (11)
C96	0.2011 (10)	0.5714 (9)	0.4215 (10)

ganohalogen compounds by chromium(II) complexes is known to be fast[25] and thus explains the production of Cr(TPP)Cl in methylene chloride solvent. In benzene or tetrahydrofuran, the initially formed CrTPP must dimerize with starting CrO(TPP) to give the μ-oxo dimer **5** (Scheme I).[26]

(25) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 137.

Scheme I



Description of the Structure of CrO(TPP) (3)

The crystal structure of **3** consisted of one CrO(TTP) molecule and one benzene molecule per asymmetric unit and was isomorphous to the MoO(TTP) structure reported recently by Weiss.[4] There were no unusual nonbonded interactions evident. The chromium–oxygen bond length was 1.572 Å, very close to the Cr–O distance reported for oxodiperoxo(pyridine)chromium(VI).[27] The average Cr–N distance was 2.032 Å. The chromium cation in **3** was displaced 0.469 Å above the mean plane of the four pyrrole nitrogens. The porphyrin ring was distinctly nonplanar.[28] Pyrrole rings 1 and 3 (Figure 5) were tilted away from the chromyl oxygen atom while pyrrole rings 2 and 4 were tilted toward the oxygen atom. The result of this distortion is a saddle-shaped porphyrin with a vertical displacement of 0.9 Å from C-12 to C-22. Bond lengths and bond angles for **3** are presented in Table II according to the numbering scheme in Figure 5. Superscripted numbers in Figure 5 are deviations in Å of all porphyrin ring atoms from the mean plane of the pyrrole nitrogens. A stereoview of **3** is shown in Figure 6.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged (Grant CHE-8106064). The National Science Foundation provided funds for the purchase of a GC mass spectrometer and a 360-MHz NMR spectrometer. We also thank Professor J. W. Buchler for an exchange of information regarding chromium(IV) porphyrins prior to publication.

Registry No. **2**, 78833-34-8; **2**-^{18}O, 80584-25-4; **3**-C_6H_6, 80584-27-6; **4**, 80584-28-7; **5**, 80593-65-3; Cr(TPP)Cl, 28110-70-5; Cr(TMP)Cl, 80584-29-8; Cr(TTP)Cl, 43145-39-7; iodosylbenzene, 536-80-1; [^{18}O]-iodosylbenzene, 80572-92-5; iodobenzene dichloride, 932-72-9.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and thermal parameters for **3** (11 pages). Ordering information is given on any current masthead page.

(26) The reaction of CrO(TPP) with Cr^{II}TPP to form the μ-oxo dimer **6** has also been proposed by West (cf. ref 13). This paper reported the spontaneous oxygenation of **6** to regenerate CrO(TPP). In our hands, this change occurs only with concomitant autoxidation of the solvent toluene. Thus, we ascribe the reoxidation of **6** to the formation of benzyl hydroperoxide; cf.: Baccouche, M.; Ernst, J.; Fuhrhop, J.-H.; Schlözer, R.; Arzoumanian, H. *J. Chem. Soc., Chem. Commun.* **1977**, 821.

(27) Stromberg, R. *Ark. Kemi* **1964**, *22*, 29.

(28) A preliminary structure of CrO(TPP), **2**, based on 346 reflections, has been reported in which the porphyrin ring was planar, presumably due to the tetragonal space group of these disordered crystals (cf. ref 13).