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Oxochromium Compounds. 2. Reaction of Oxygen with Chromium(II) and Chromium(III) Porphyrins and Synthesis of a μ-Oxo Chromium Porphyrin Derivative

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The reaction of oxygen with Cr(II) porphyrin complexes in solution has been found to result in the formation of $Cr^{IV}O(P)$ compounds when oxygen is in excess. Solid $Cr^{II}(P)$ also react irreversibly with oxygen, and the products dissolve in toluene to form $Cr^{IV}O(P)$. The complex (TPP)CrOCr(TPP) has been isolated from the reaction of CrO(TPP) and $Cr^{II}(TPP)$ and shown to undergo further reaction with oxygen to give CrO(TPP). The complex shows an IR absorption at 860 cm^{-1}, considered to indicate the presence of the CrOCr linkage, and has $\mu_{eff} = 1.61\ \mu_B$ per Cr at 300 K, indicating substantial antiferromagnetic coupling. Similar μ-oxo complex formation has been demonstrated spectroscopically between other CrO(P)/Cr(P′) combinations where P and P′ may be the same or different. (P)CrOCr(P) complexes can be detected as intermediates in the reaction of $Cr^{II}(P)$ with oxygen when the amount of oxygen is restricted. $Cr^{III}(P)Cl$ also reacts with oxygen in chloroform in the presence of HCl to give intermediates that are converted to $Cr^{IV}O(P)$ in the presence of basic alumina. A Cr–porphyrin π-cation radical is proposed as the intermediate.

Introduction

In contrast to the extensive studies carried out on the reaction of oxygen with porphyrin and Schiff-base complexes of Fe(II) and Co(II),[1] analogous compounds of Cr(II) have received relatively little attention. Thus, a β-keto imino Cr(II) complex has been reported[2] to react with oxygen although the product could not be unambiguously defined.

Reed et al.[3] have studied the reaction of the solid porphyrin complex $Cr^{II}(TPP)(py)_2$[4] with oxygen and provided spectroscopic and magnetic evidence to support the constitution of the product as a superoxo complex $Cr(O_2)(TPP)py$. [The dianions of 5,10,15,20-tetraarylporphyrins employed in this study are represented by the following abbreviations: TPP, tetraphenylporphyrin; TTP, tetra-*p*-tolylporphyrin; TXP, tetra-3,5-xylylporphyrin; TMP, tetrakis(*p*-methoxyphenyl)porphyrin; TCP, tetrakis(*p*-chlorophenyl)porphyrin; TFP, tetrakis(*p*-fluorophenyl)porphyrin; TMesP, tetramesitylporphyrin; TFMP, tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin; TPFP, tetrakis(pentafluorophenyl)porphyrin. OEP represents the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, salen, the dianion of *N*,*N′*-ethylenebis(salicylaldimine), and TPyEA, tris(2-pyrazol-1-ylethyl)amine.] The reaction was stated to be irreversible. The product formed when oxygen reacts with Cr(II) phthalocyanine (Cr(Pc)) has, however, been considered to be a dimeric form of $Cr^{IV}O(Pc)$.[5]

Subsequently it was demonstrated[6] that $Cr^{II}(TPP)$ in toluene solution reacts with oxygen to form the chromyl $Cr^{IV}O(TPP)$ in high yield. The resultant complex was characterized by an X-ray crystallographic study. Alternative routes to $Cr^{IV}O(P)$ derivatives (P = TPP, TTP, TMesP, OEP) by oxidation of $Cr^{III}(P)Cl$ with iodosylbenzene, sodium hypochlorite, *m*-chloroperoxybenzoic acid, or *tert*-butyl hydroperoxide have been reported.[7,8]

This reaction is in sharp contrast to the behavior of most Fe(II) porphyrin derivatives that readily form μ-oxo complexes, $[Fe(P)]_2O$, upon exposure to oxygen in solution.[9] The oxoiron(IV) compounds FeO(P) are extremely reactive species and have only been detected spectroscopically in solution at low temperatures when $Fe^{II}(P)$ react with oxygen in the presence of a Lewis base.[10] The $Fe^{IV}O$ compounds nevertheless are considered to be fundamentally implicated in the formation of $[Fe(P)]_2O$ via the following sequence of reactions:[11]

$$2Fe^{II}(P) + O_2 \rightleftharpoons (P)Fe^{III}\text{–O–O–}Fe^{III}(P)$$

$$(P)Fe\text{–O–O–}Fe(P) \rightarrow 2Fe^{IV}O(P)$$

$$Fe^{IV}O(P) + Fe^{II}(P) \rightarrow (P)Fe^{III}\text{–O–}Fe^{III}(P)$$

Analogous Cr(III) μ-oxo porphyrin complexes have not previously been isolated by an unambiguous synthetic route although some evidence for their existence has been reported.

Thus, visible spectral evidence has indicated[6] that a μ-oxo complex was formed when $Cr^{II}(TPP)$ reacted with a limited amount of oxygen but rapidly converted to CrO(TPP) when oxygen was in excess. It has been further reported that such a complex was formed when CrO(TPP) reacted with triphenylphosphine, and its preparation was claimed to result from the reaction of Cr(TPP)Cl and NaOH[7] but no other detailed properties were presented.

Few μ-oxo chromium(III) complexes with any ligands have been described previously, $[[(NH_3)_5Cr]_2O]Br_4$[12,13] and $[[Cr(NCS)(TPyEA)]_2O](BPh_4)_2$[14] being the only compounds to have been characterized by complete X-ray studies with linear Cr–O–Cr bonds being found in each compound. Both complexes have infrared spectral bands ascribed to Cr–O–Cr asymmetric stretching vibrations in the region 850–870 cm^{-1} and show magnetic coupling between the Cr(III) centers, with moments of 1.29 and 1.63 μ_B per Cr, respectively, being found at room temperature.

Similar IR and magnetic data have supported the constitution of the complex $[Cr(salen)]_2O$.[15]

The reactions of $Cr^{IV}O(P)$ complexes with various $Fe^{II}(P)$ derivatives have led to the isolation and characterization of stable, μ-oxo heterometallic compounds $(P)Cr^{III}OFe^{III}(P')$ where P and P′ may be the same or different porphyrins.[16,17]

This paper reports a study of similar reactions between various $Cr^{IV}O(P)$ and $Cr^{II}(P)$ complexes that has led to the isolation of the extremely air-sensitive $[(TPP)Cr]_2O$ derivative and spectral identification of several other related μ-oxo species in solution.

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Some further studies on the reactions of $Cr^{II}(P)$ compounds with oxygen in both solution and the solid state are also described.

The CrO(P) derivatives have, for the most part, been prepared by an unusual reaction involving aerial oxidation of Cr(P)Cl derivatives in toluene or chloroform solution in the presence of aqueous hydrochloric acid. Some evidence for the likely mechanism of this reaction is presented.

Experimental Section

Materials. Anhydrous conditions were essential for all phases of this work, and the general techniques used were as previously described.[17] Aluminum oxide, basic, activity II (Ajax Chemicals), and Celite (BDH) were used for chromatography. Amalgamated zinc for reduction of Cr(P)Cl was prepared by treatment of granulated zinc with dilute, aqueous mercuric chloride and washing the product with water, alcohol, and ether before drying under vacuum. Vacuum drying of samples was accomplished by continuous pumping at 10^{-3} torr for appropriate periods at either room or elevated temperatures.

Air-sensitive solids were handled in a nitrogen-filled glovebag or Dri-Lab (Vacuum Atmosphere) handling box.

Instrumentation. Spectra were recorded as follows: ^1H and ^{19}F NMR, Bruker WH90; visible, Varian Super Scan 3; infrared, PE180. Magnetic susceptibilities were measured as previously described.[17]

Porphyrins. Tetraarylporphyrins were prepared[18] and purified[19] by literature methods. Octaethylporphyrin was purchased from EGA.

Chromium(III) Porphyrin Chlorides. The complexes Cr(P)Cl where P = TPP, TTP, TXP, TMP, TCP, TFP, TFMP, TPFP, and OEP were prepared by the reaction of chromium hexacarbonyl with the porphyrin in refluxing dimethylformamide.[20] When all the porphyrin had reacted, the mixture was cooled to 50 °C and poured into ice-cold 2 M hydrochloric acid solution. The resulting precipitate was filtered and washed with 2 M HCl before drying at 100 °C for 2–3 h. The crude products contained an impurity absorbing in the region of 635 nm and were purified by a modification of the method of Basolo et al.[21] used for Cr(TPP)Cl. Thus, the crude chloro complex was dissolved in chloroform containing concentrated HCl (1 mL/10 mL of $CHCl_3$) and the mixture stirred overnight. The solution was then evaporated to dryness under reduced pressure and the residue redissolved in $CHCl_3$. This solution was extracted twice with water then dried over anhydrous sodium sulfite (Na_2SO_3). The solution was reduced in volume (ca. 25 mL) and applied to a dry, basic alumina (activity II) column. Any traces of residual porphyrin or CrO(P) complex were rapidly removed as a reddish band with the solvent front, and the Cr(P)Cl complex was finally eluted by a $CHCl_3$/MeOH mixture (1:1). The complex was precipitated from the concentrated eluate by addition of hexane. Cr(TPP)Cl,[21] Cr(TTP)Cl,[7] and Cr(OEP)Cl[21] have previously been reported. Their measured UV/visible spectra agreed with the published values.

Yield of Cr(TXP)Cl: 55%. Anal. Calcd for $C_{52}H_{44}ClCrN_4\cdot 0.8CHCl_3$: C, 69.8; H, 4.98; N, 6.81. Found: C, 69.9; H, 5.66; N, 6.38. UV (benzene) λ_{max}, nm (log ϵ): 397 (4.49), 448 (4.64), 522 (3.74), 567 (3.90), 605 (3.85).

Yield of Cr(TCP)Cl: 81%. Anal. Calcd for $C_{44}H_{20}Cl_5CrN_4\cdot H_2O$: C, 61.8; H, 3.07; N, 6.55; Cl, 20.7. Found: C, 61.3; H, 3.06; N, 6.41; Cl, 19.5. UV (benzene) λ_{max}, nm (log ϵ): 393 (4.04), 447 (4.65), 517 (2.49), 564 (3.51), 602 (3.47), 690 (3.13), 753 (3.02).

Yield of Cr(TMP)Cl: 81%. Anal. Calcd for $C_{48}H_{36}ClCrN_4O_4\cdot 2CHCl_3$: C, 56.7; H, 3.62; N, 5.29. Found: C, 56.7; H, 4.81; N, 5.56. UV (benzene) λ_{max}, nm (log ϵ): 399 (4.48), 451 (5.11), 523 (3.74), 566 (4.00), 607 (4.03).

Yield of Cr(TFP)Cl: 50%. Anal. Calcd for $C_{44}H_{20}ClCrF_4N_4\cdot CHCl_3$: C, 60.6; H, 2.83; N, 6.29. Found: C, 61.1; H, 3.63; N, 6.19. UV ($CHCl_3$) λ_{max}, nm (log ϵ): 394 (4.30), 447 (5.14), 522 (3.64), 563 (4.05), 601 (3.36), 710 (3.0).

Yield of Cr(TPFP)Cl: 55%. Anal. Calcd for $C_{44}H_8ClCrF_{20}N_4$: C, 49.9; H, 0.76; N, 5.29. Found: C, 49.8; H, 1.85; N, 5.37. UV ($CHCl_3$) λ_{max}, nm: 439, 555.

Yield of Cr(TFMP)Cl: 61%. Anal. Calcd for $C_{48}H_{24}ClCrF_{12}N_4$: C, 59.3; H, 2.49; N, 5.76; F, 23.5. Found: C, 58.4; H, 2.58; N, 5.71; F, 23.3. UV ($CHCl_3$) λ_{max}, nm: 392, 447, 562, 598.

Preparation of $Cr^{II}(P)$ Complexes. The toluene solvate $Cr(TPP)\cdot 2CH_3C_6H_5$ was prepared following the method of Reed[3] by the reduction of Cr(TPP)Cl (400 mg, 0.6 mmol) with chromium(II) acetylacetonate ($Cr_2(acac)_4$) (850 mg, 3.4 mmol) in toluene (50 mL) and ethanol (1 mL). The mixture was heated until it had turned brown. Excess $Cr_2(acac)_4$ was removed by filtration, ethanol (60 mL) added to the filtrate, and the solution allowed to crystallize. The resulting purple solid was filtered and washed with ethanol before recrystallization from toluene/heptane. It was stored under nitrogen until required. UV λ_{max}, nm: (toluene) 421, 541; (lit.[3] in THF) 402, 421, 460, 516, 601, 655 nm.

$Cr(TPP)(py)_2$ was also synthesized by the method of Reed,[4] Cr(TPP)Cl (1 g, 1.4 mmol) being reduced with amalgamated zinc (2 g) in a mixture of tetrahydrofuran (100 mL), pyridine (10 mL), and water (15 mL) over 24 h, under nitrogen.

The resulting blue-black solid was collected by filtration, washed with a 1:1 mixture of THF/water (30 mL), dried, and then redissolved in hot toluene, and the solution was again filtered and the complex precipitated by addition of heptane. The black microcrystalline solid was washed with heptane and dried under vacuum; yield 0.6 g (50%). UV λ_{max}, nm: (toluene) 421, 542; (lit.[4] in THF) 420, 530, 675.

All subsequent operations involving manipulation of the isolated solid Cr(II) complexes were carried out in a nitrogen-filled handling box.

Other Cr(II) complexes required for oxygenation studies in solution or in the solid state were similarly prepared by reduction of the appropriate Cr(P)Cl complex in tetrahydrofuran using amalgamated zinc. The final reduced solution was filtered under nitrogen and solvent removed by vacuum pumping. The solid residue of $Cr^{II}(P)$ complex could then be reacted directly with oxygen in the reaction vessel or redissolved in fresh toluene for studying reactions in solution.

Reactions of $Cr^{II}(P)$ with Oxygen in Solution. (a) Preparation of Oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV), [CrO(TPP)]. Cr(TPP)Cl (200 mg, 0.286 mmol) was reduced by stirring in tetrahydrofuran solution with amalgamated zinc (2 g) under nitrogen for 4 h. The resulting brown solution of $Cr^{II}(TPP)$ was evaporated to dryness under reduced pressure and the residue extracted with degassed toluene (50 mL). The extract was filtered and dry oxygen bubbled through the solution that rapidly turned burgundy red in color. It was added to a Celite column (30 × 2.5 cm) and the red complex further eluted by toluene. Addition of hexane to the eluate yielded the red, microcrystalline CrO(TPP) that was dried in vacuo; yield 65 mg (33%). The crystals contained toluene of crystallization, which was detected by its ^1H NMR spectrum in $CDCl_3$.

(b) Other Preparations. Similarly, CrO(TMP) and CrO(TFMP) were isolated in 30% and 25% yields, respectively, after similar procedures. CrO(TXP), CrO(TCP), CrO(TPFP), CrO(TFP), and CrO(OEP) were formed in solution by this method but not isolated. All complexes were identified by comparison of their visible absorption spectra with those of authentic samples. In several instances samples of toluene were distilled from the reaction mixtures and subjected to GLC analysis, but no evidence for any volatile compound other than toluene was found. Reaction of $Cr^{II}(TPP)$ with oxygen was also found to occur as readily in benzene as in toluene.

(c) Detection of μ-Oxo Formation. Samples of $Cr^{II}(P)$ (P = TPP, TCP) were prepared by zinc amalgam reduction of Cr(P)Cl in tetrahydrofuran, and the solution was evaporated to dryness under vacuum. The residue was dissolved in a small volume of deoxygenated toluene under nitrogen, and the solution was filtered and diluted to a concentration of the order of 10^{-5} M and a sample placed in a spectroscopic cell under nitrogen. Toluene saturated with oxygen was then added in successive drops by means of a hypodermic syringe and the spectrum measured between each addition of oxygen.

Reactions of Solid $Cr^{II}(P)$ with Oxygen. (a) Preparation of Oxo(5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrinato)chromium(IV), [CrO(TMP)]. Cr(TMP)Cl (200 mg, 0.24 mmol) was reduced by amalgamated zinc (2 g) in tetrahydrofuran (40 mL) and the solution filtered and evaporated to dryness under reduced pressure. The reaction flask was finally completely evacuated and dry oxygen admitted to 1 atm pressure. After 15 min the color of the purple solid had changed to red. Reaction was allowed to continue for 24 h. The red microcrystalline solid was then extracted with toluene, and the extract was applied to a Celite column. The red complex was eluted by toluene and precipitated from the eluate by slow addition of hexane; yield 50 mg (26%). (Amalgamated zinc could be left in the system until after reaction with oxygen and extraction of the solid with toluene before being removed without apparently affecting the yield of CrO(TMP).)

(b) Other Preparations. Similar reactions were carried out with samples of $Cr^{II}(P)$ (P = TPP, TTP, TXP, TCP, TPFP, TFMP, OEP) prepared as discussed above. Visible absorption spectra of the solid products formed after 24 h of reaction were obtained either by smearing a sample of the finely ground product onto translucent tracing paper and placing

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(18) (a) $(TPP)H_2$, $(TTP)H_2$, $(TXP)H_2$, $(TMP)H_2$, $(TCP)H_2$, $(TFP)H_2$, $(TFMP)H_2$: Adler, A. D.; Longo, F. R.; Finarelli, R. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) $(TPFP)H_2$: Longo, F. R.; Finarelli, M. G.; Kim, J. B. *J. Heterocycl. Chem.* **1969**, *6*, 927.

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the paper sample in the light beam of the spectrophotometer with a standard sample of paper in the reference beam or by mulling the solid with Nujol and placing a smear of the mull on tracing paper in the light beam. The solid products were also dissolved in toluene and the spectra of the solutions measured.

Synthesis of CrO(P) by Oxidation of Cr(P)Cl with Air in Acid Solution. Oxo(5,10,15,20-tetra-3,5-xylylporphyrinato)chromium(IV), [CrO(TXP)]. The preparation of CrO(TXP) serves as a general description of the method. Concentrated hydrochloric acid (6 mL of 12 M, CP grade) was added to a solution of Cr(TXP)Cl (1.75 g, 2.28 mmol) in chloroform (50 mL) and the mixture stirred in contact with air. Samples of solution were removed from time to time and their visible spectra recorded to follow the rise of a new Soret band at 426 nm. (A band close to this wavelength occurs in all cases examined.) Stirring was discontinued when the intensity of this band no longer increased. The time involved varied somewhat with the particular batch of concentrated HCl used, but a maximum yield of product was generally observed after 2–3 days. Addition of small amounts of $FeCl_3$ to the reaction mixtures caused the maximum concentration of intermediate to be reached after 24 h of stirring rather than several days. The chloroform solution was then extracted twice with water and dried over anhydrous Na_2SO_4 before being poured onto a dry column of basic alumina (20 × 2.5 cm). The mixture was eluted with dry chloroform. (The whole chromatographic procedure was carried out under a nitrogen atmosphere to prevent entry of water to the system since a number of the chromyl derivatives were sensitive to hydrolytic action.) Any residual Cr(TXP)Cl remained at the top of the column while a red band due to CrO(TXP) eluted with the solvent front. Dry hexane was added to the eluate to precipitate the complex that was then dried under vacuum; yield 0.34 g (20%). Analysis indicated that $CHCl_3$ was retained in the crystals of this and several other complexes. Unreacted Cr(TXP)Cl could be recovered by elution with a 1:1 mixture of $CHCl_3$/MeOH.

A similar procedure allowed the isolation of CrO(TPP) (50% yield), CrO(TTP) (42%), CrO(TMP) (20%), CrO(TFP) (25%), and CrO(TCP) (30%).

Cr(TFP)Cl forms the intermediate in low yield during 1–2 days reaction, but on continued stirring the compound decomposes and the starting material is re-formed. Cr(TPFP)Cl does not react at all under these conditions.

Attempted Isolation of the Reaction Intermediate. Concentrated HCl (6 mL) was added to a chloroform solution (50 mL) of Cr(TPP)Cl (1.5 g, 2.14 mmol) and the mixture stirred in air for 2 days. The mixture was then washed twice with water and the chloroform layer dried over Na_2SO_4. Addition of hexane to the chloroform solution precipitated a green solid that was filtered and dried under vacuum at 20 °C.

Reaction of Gaseous HCl with CrO(TPP). Dry hydrogen chloride gas was passed through a stirred solution of complex in dry toluene in a flask from which the air had been initially displaced by a stream of nitrogen. Samples of solution were diluted with dry toluene and their visible spectra recorded.

Oxo(5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato)chromium(IV), [CrO(TPP)]. Cr(TPFP)Cl (200 mg, 0.187 mmol) and iodosylbenzene (440 mg, 2.24 mmol) were placed in a flask that was carefully purged with nitrogen. Dichloromethane (30 mL), previously deoxygenated, was transferred to the vessel and the mixture stirred for 20 min. Spectral examination at this stage indicated considerable conversion to the oxo derivatives. The deep red solution was transferred to a dry basic alumina column and elution commenced with CH_2Cl_2. CrO(TPFP) was eluted as a red-purple band with the fast moving solvent front while unreacted Cr(TPFP)Cl remained on the column. The eluate was evaporated under reduced pressure to 2–3-mL volume and dry heptane slowly added (up to 15 mL total). The product separated as a pink-purple solid and was filtered and washed with heptane; yield 36 mg (18%). Longer reaction times than 20 min or increased iodosylbenzene did not increase the yield in experiments on this scale. The complex is quite sensitive to water, and despite several purification steps the magnetic moment could not be reduced below $\mu_{eff} = 0.96\ \mu_B$ at 294 K. The moment is considered due to traces of Cr(III) impurities.

Oxo(5,10,15,20-tetrakis(*p*-(trifluoromethyl)phenyl)porphyrinato)chromium(IV), [CrO(TFMP)]. The method used was analogous to that for CrO(TPFP), with benzene replacing CH_2Cl_2 as the solvent since oxidation occurs only to a limited extent in CH_2Cl_2. The molar ratio of iodosylbenzene to Cr(III) complex for maximum yield was found to be 20:1 with a reaction time of 30 min; yield 14%. The complex was very sensitive to moisture, and despite repeated preparations totally adequate microanalytical data were not obtained for the samples. Each successive purification resulted in a lower magnetic moment for the sample, but the lowest magnetic susceptibility value obtained, $\mu_{eff} = 1.2\ \mu_B$, suggested there was still considerable contamination by Cr(III) impurities.

Synthesis of μ-Oxo Chromium Derivatives. (a) (μ-Oxo)bis(5,10,15,20-tetraphenylporphyrinato)dichromium(III), $[(TPP)]_2O$. CrO(TPP) (57.5 mg, 0.85 mmol) and $Cr(TPP)(py)_2$ (68.4 mg, 0.85 mmol) were dissolved in dry toluene (15 mL) under nitrogen, and the mixture was stirred for 2 h. After 30 min the initial brown solution had turned orange. Dry hexane was added slowly to the mixture, cooled in an ice bath, yielding a blue precipitate. It was filtered and dried under vacuum for 12 h; yield 60 mg (53%). Purification was achieved by chromatography of a toluene solution of the complex on Celite, with careful exclusion of air. Anal. Calcd for $C_{88}H_{56}Cr_2N_8O\cdot 0.5C_6H_5CH_3$: C, 79.0; H, 4.40; N, 8.05. Found: C, 78.9; H, 4.70; N, 7.91.

(b) Other Syntheses. Similar synthetic scale reactions were carried out between the pairs CrO(TMP) and Cr(TMP), CrO(TCP) and Cr(TPP), CrO(TCP) and Cr(TPP), and CrO(TMP) and Cr(TPP). However, the final purification steps involving chromatography on Celite columns disclosed the presence of substantial amounts of the various CrO(P) species in each case, together with further products having Soret bands in the region of 450 nm as well as the desired μ-oxo compounds, and satisfactory analytical and spectroscopic purity of the μ-oxo complexes could not be obtained.

(c) Spectroscopic Studies on the Reactions between CrO(P) and Cr^{II}(P) Compounds. A quantity of a Cr^{I}(P) component was first prepared in a flask by reduction of Cr(P)Cl (ca. 50 mg) with zinc amalgam in tetrahydrofuran followed by evaporation of solvent, resolution in toluene, and filtration. An equimolar amount of CrO(P) was then added by syringe and the resulting mixture stirred for 1 h. It was diluted to an appropriate concentration (ca. 10^{-5} M) for spectral examination.

Synthesis of Hydroxochromium Complexes. (a) The procedure of Groves[7] (reported to give a hydrated μ-oxo Cr(TPP) complex) gave a solid that was dried under vacuum for 24 h. Anal. Calcd for $C_{44}H_{29}CrN_4O\cdot 3H_2O$: C, 71.8; H, 4.8; N, 7.6. Found: C, 71.5; H, 4.5; N, 7.5.

(b) A mixture of $Cr(CO)_6$ and $(TCP)H_2$ was refluxed in dimethylformamide for 7 h. The solution was then cooled, allowed to stand for 2 h, and then passed down a basic alumina column. The product was eluted with $CHCl_3$, the solvent evaporated, and the complex dried at 100 °C under vacuum. This procedure was similar to that reported by Fleischer et al.[20] to yield $[Cr(TPP)(H_2O)_2]OH$. Anal. Calcd for $C_{44}H_{25}Cl_4CrN_4O\cdot 2H_2O$: C, 61.7; H, 3.54; N, 6.54. Found: C, 61.1; H, 3.24; N, 6.93.

(c) The reaction reported by Buchler[22] whereby Cr(TPP)Cl reacts with NaOH in a mixture of CH_2Cl_2 and MeOH gave a product that was dried at 100 °C under vacuum. The compound is insoluble in toluene and soluble in CH_2Cl_2. Anal. Calcd for $C_{44}H_{29}CrN_4O\cdot 2H_2O$: C, 70.3; H, 4.70; N, 7.54. Found: C, 70.1; H, 4.42; N, 7.58.

Results and Discussion

1. Formation of (TPP)Cr–O–Cr(TPP) and Other μ-Oxo Chromium(III) Derivatives. It has been proposed[6] that μ-oxo chromium(III) porphyrin complexes can form by the reaction

$$Cr^{IV}O(P) + Cr^{II}(P) \rightarrow (P)Cr^{III}–O–Cr^{III}(P)$$

The reaction between $Cr^{IV}O$(TPP) and Cr^{II}(TPP) has now been carried out in toluene in the absence of oxygen, resulting in the isolation of the expected product, (TPP)CrOCr(TPP), as a blue microcrystalline solid. The complex appears to be indefinitely stable in the solid state in dry air but does undergo hydrolysis in the presence of moisture. It has a main (Soret) visible absorption band at 412 nm compared to that for CrO(TPP) at 431 nm and Cr(TPP)Cl at 447 nm.

In solution, under anhydrous conditions, the complex rapidly reacts with further oxygen to form the chromyl CrO(TPP), confirming the earlier postulate[6] (Figure 1). It also reacts with aqueous HCl under nitrogen to form 2 equiv of Cr(TPP)Cl.

The magnetic moment of the complex at 300 K (μ_{eff}) was found to be 1.61 μ_B per Cr atom. Similar low moments have been reported at room temperatures for the two structurally characterized μ-oxo complexes $[[(NH_3)_5Cr]_2O]Cl_4$[12] (1.29 μ_B per Cr) and $[[Cr(NCS)(TPyEA)]_2O](BPh_4)_2$[14] (1.6$_3$ μ_B per Cr) as well as $[Cr(salen)]_2O$[15] (2.2 μ_B per Cr), indicating a considerable degree of coupling between the Cr centers. The variation with temperature of the magnetic susceptibility of the $[[(NH_3)_5Cr]_2O]^{4+}$ ion has been adequately explained by antiferromagnetic coupling between Cr(III) ions each having $S = {}^3/_2$ and leads to a predicted

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(22) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879.

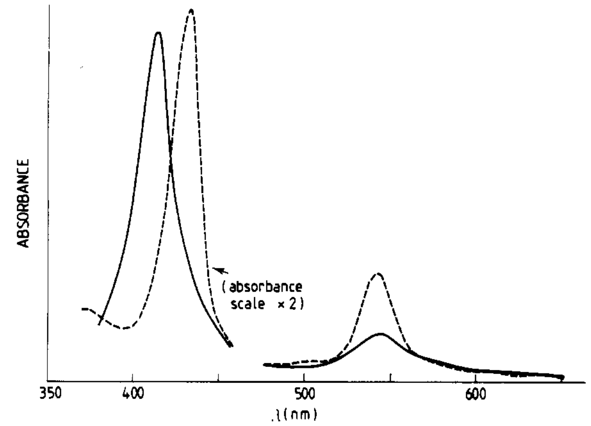

Figure 1. Reaction of (TPP)CrOCr(TPP) with oxygen in toluene solution: (—) (TPP)CrOCr(TPP) under nitrogen; (---) CrO(TPP) formed after complete reaction with oxygen.

zero value for susceptibility at or close to 0 K.[12] A study of the variation of susceptibility and moment with temperature of a sample of $[(TPP)Cr]_2O$ down to 4.2 K showed the overall behavior typical of an antiferromagnetically coupled system. However, the sample showed a residual magnetic moment of 0.82 μ_B at 4.2 K that contrasts with the essentially zero values found experimentally (and predicted by the theoretical treatment of coupled $S = {}^3/_2$ centers) for the pure $[[(NH_3)_5Cr]_2O]X_4$ halide complexes.[12] Earlier reports of residual paramagnetism[23] at low temperatures for the decammine compounds have been explained due to contamination by hydroxy-bridged species[12] such as $[(NH_3)_5Cr-OH-Cr(NH_3)_4OH]^{4+}$, which show much lower degrees of coupling. In the light of the reactivity of the (TPP)CrOCr(TPP) complex with moisture it is considered that the sample used in the temperature/susceptibility study had undergone some degree of hydrolysis and that contaminating Cr(III)–OH species are causing the residual moment at liquid-helium temperatures. The general magnetic behavior of the μ-oxo compound nevertheless indicates strong internuclear antiferromagnetic coupling between the Cr(III) centers.

Infrared bands at 854 and 870 cm^{-1} have been suggested to arise from the CrOCr linkage in $[[(NH_3)_5Cr]_2O]Cl_4$,[23] and similar bands have been reported for $[Cr(salen)]_2O$[15] at 858 and 870 cm^{-1}. $[(TPP)Cr]_2O$ also shows medium–strong bands at 847.8 and 860.1 cm^{-1}. A single infrared-active band due to the asymmetric stretching vibration of a linear MOM system is expected for linear CrOCr compounds, and this has been allocated to the absorption at 873 cm^{-1} for $[[(NH_3)_5Cr]_2O]Cl_4$[24] and 830 cm^{-1} for $[[Cr(NCS)(TPyEA)]_2O](BPh_4)_2$[14] on the basis of isotopic substitution experiments. This suggests that the 860.1-cm^{-1} band arises from the CrOCr asymmetric (ν_3) stretching vibration in $[(TPP)Cr]_2O$.

Under rigorously controlled anhydrous and anaerobic conditions in a spectroscopic cell it was possible to demonstrate the formation of μ-oxo complexes by reactions between a range of CrO(P) and Cr(P′) complexes, where P and P′ were the same or different porphyrin anions. The resulting complexes each showed a visible spectrum similar to that of $[(TPP)Cr]_2O$ (Table I). In the presence of oxygen the complexes rapidly converted to CrO(P) species, the mixed complexes (P)CrOCr(P′) yielding both CrO(P) and CrO(P′). Attempts to isolate the mixed-ligand complexes (TPP)CrOCr(TMP) and (TPP)CrOCr(TCP) by reactions between CrO(TMP) and Cr(TPP) or CrO(TPP) and Cr(TCP) were not successful. The μ-oxo complexes were formed in solution as evidenced by the spectra of such reaction mixtures, but the solid products finally isolated failed to give adequate microanalytical data. The air and moisture sensitivity of the μ-oxo complexes is believed to be responsible for these difficulties. The mixed-ligand heterobinuclear complexes (P)CrOFe(P′) have been obtained with considerably less difficulty.[17]

Table I. Visible Spectra of Cr(III) Porphyrin μ-Oxo Species in Toluene

compd	conditions^a	λ_{max}, nm (log ϵ)	
(TPP)CrOCr(TPP)	A	412 (4.88)	542 (3.79)
	A*	421	572
(TMP)CrOCr(TMP)	B	415	546
(TCP)CrOCr(TCP)	B	415	541
(TCP)CrOCr(TPP)	B	414	542
(TMP)CrOCr(TPP)	B	414	543
(TXP)CrOCr(TXP)	C	414	541
(TTP)CrOCr(TTP)	C	414	543
(TFP)CrOCr(TFP)	C	412	542
(TPFP)CrOCr(TPFP)	C	410	544
(OEP)CrOCr(OEP)	C	390	556

^{a} Key: A, isolated $[(TPP)Cr]_2O$ redissolved in toluene; A*, isolated $[(TPP)Cr]_2O$ redissolved in pyridine; B, recorded after reaction of CrO(P) and Cr^{II}(P′); C, measured after addition of small amounts of oxygen-saturated toluene to a solution of Cr^{II}(P).

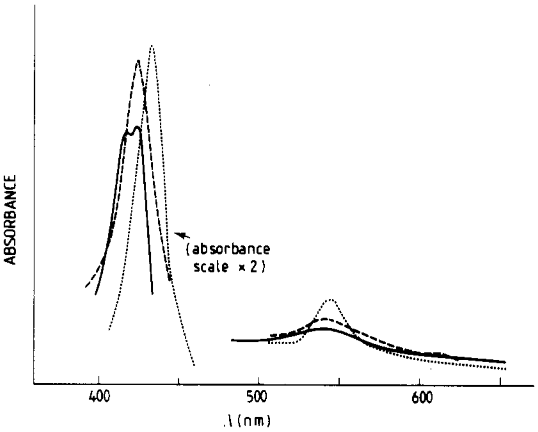

Figure 2. Reaction of Cr^{II}(TCP) with oxygen: (---) Cr^{II}(TCP) in toluene under nitrogen; (—) same solution after addition of a small volume of toluene, saturated with air; (···) same solution after addition of excess oxygen, i.e. the spectrum of CrO(TCP).

A previous report[7] has described the preparation of a compound suggested to be the hydrated μ-oxo chromium porphyrin derivative (TPP)CrOCr(TPP) by treatment of the corresponding halide with hydroxide ions. In our hands the reaction of Cr(TPP)Cl in methylene chloride with 50% sodium hydroxide solution gave a product having a visible spectrum similar to that previously reported, but the solid showed no infrared bands in the 800–900-cm^{-1} region as expected for an authentic (TPP)CrOCr(TPP) species.

It did, however, show a sharp band at 3620 cm^{-1} indicative of a metal hydroxide species.[25] The microanalytical data for this product indicated a composition close to $Cr(TPP)OH\cdot3H_2O$. A solution of (TPP)CrOCr(TPP) in THF exposed to moist air rapidly gave the same visible spectrum as the product formed by alkaline hydrolysis of Cr(TPP)Cl.

2. Reactions of Cr^{II}(P) with Oxygen. (a) Solution Reactions. Treatment of a toluene solution of Cr^{II}(TCP) under nitrogen with small volumes of toluene saturated with oxygen caused the Soret band at 421 nm due to Cr^{II}(TCP) to decrease in intensity as that due to (TCP)CrOCr(TCP) began to grow at 415 nm (Figure 2).

Addition of further oxygen caused the gradual evolution of a band at 433 nm due to the presence of CrO(TCP). Eventually, when excess oxygen was present, this band alone was observed. Corresponding changes occurred in the Cr^{II}(TCP) band at 541 nm that was eventually replaced by the CrO(TCP) peak at 545 nm.

A range of other Cr^{II}(P) derivatives (P = TTP, TXP, TFP, TFMP, TPFP, TMP, OEP) have been prepared in situ and found

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(23) Earnshaw, A.; Lewis, J. *J. Chem. Soc.* **1961**, 396.
(24) Hewkin, D. J.; Griffith, W. P. *J. Chem. Soc. A* **1966**, 472.
(25) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 82.

Table II. Solid-State UV/Visible Spectra of the Superoxo Complex $Cr(O_2)(TPP)(py)$ and CrO(TPP)

compd and med	condition	λ_{max}, nm		
$Cr(O_2)(TPP)(py)$	Nujol mull	440	573	607
CrO(TPP)	Nujol mull	438	545	574 (sh)

to react with excess oxygen in toluene or benzene solution to form the appropriate CrO(P) complexes.

In several other instances, the addition of small volumes of oxygen-saturated toluene to the solution of a $Cr^{II}(P)$ allowed the Soret band for the appropriate (P)CrOCr(P) complex to be distinguished together with the corresponding (reduced) band due to the $Cr^{II}(P)$ compound. The addition of further oxygen eventually transformed the spectrum completely to that of the appropriate CrO(P).

This confirms the original suggestion[6] that μ-oxo complexes are formed in the reactions of $Cr^{II}(P)$ complexes at low concentrations of oxygen. The yields of chromyl derivatives were essentially quantitative. The complexes CrO(TTP), CrO(TMP), and CrO(TFMP) were prepared and isolated from solution by this procedure. It is however a less useful procedure for general synthesis of CrO(P) compounds than the oxidation of $Cr^{III}(P)Cl$ by air in acid solution (see section 3) or iodosylbenzene because the sensitivity to moisture of a number of the complexes requires much greater attention to experimental detail to achieve satisfactory levels of purity when using the $Cr^{II}(P)/O_2$ route.

The presence of pyridine reduced the rate of autoxidation of $Cr^{II}(P)$ derivatives, suggesting that oxygen must compete with pyridine for coordination to Cr(II) as a first step in the oxidation process. $Mn^{II}(TPP)$ has also been reported[26] to react rapidly with oxygen in noncoordinating solvents and very slowly when pyridine or another coordinating ligand is present. The μ-oxo complex (TPP)CrOCr(TPP) reacts with oxygen more slowly in pyridine than in toluene. The absorption spectrum of the complex in pyridine shows shifts in the positions of its absorption maxima (Table I), likely indicating coordination of the heterocycle to the Cr atoms.

The reduced activity with oxygen may therefore be due to the restricted dissociation of the pyridine μ-oxo complex $[(py)(TPP)Cr]_2O$ to CrO(TPP) and $Cr^{II}(TPP)$ or solely to the associated formation of the pyridine $Cr^{II}(TPP)$ complex.

The Cr(II) autooxidation reactions proceed as readily in benzene as in toluene, and no evidence was obtained from GLC examination of toluene samples from reaction mixtures that oxidation products of toluene were being formed during the reaction.[7]

(b) Solid-State Reactions. The reaction of oxygen with solid $Cr^{II}(TPP)(py)_2$ reported by Reed et al.[3] to yield a superoxo complex $Cr(O_2)(TPP)(py)$ has been repeated as part of the present study. The product formed after a reaction period of 24 h under 1 atm pressure of dry oxygen was found to have an IR band at 1142 cm^{-1}, confirming that described by Reed (1142 cm^{-1}) and allocated to an O–O stretching vibration.[3] When the oxygen atmosphere was displaced by nitrogen and the product dissolved in toluene, the UV/visible spectrum observed was that of CrO(TPP). The UV/visible spectrum of the solid obtained by transmission through a Nujol mull differs from that of CrO(TPP) (Table II). Moreover, CrO(TPP) has an infrared band at 1020 cm^{-1} due to a Cr=O stretch (Table IV). These observations indicate that $Cr(O_2)(TPP)(py)$ formed in the solid state must be converted rapidly in solution to CrO(TPP). The rate of reaction between oxygen and solid $Cr(TPP)(py)_2$ is not rapid. Thus, when contact between solid and oxygen was limited to a 2-h reaction period, the absorption spectrum of the solution of the product obtained under nitrogen showed mainly CrO(TPP) together with a small proportion of (TPP)CrOCr(TPP). The toluene solvate $Cr(TPP)\cdot 2C_6H_5CH_3$ also reacts with oxygen in the solid state. After 24 h of reaction time at 1 atm pressure of oxygen, the IR and visible spectra of the resultant solid are similar to those obtained for the $Cr(TPP)(py)_2O_2$ reaction product, the IR spectrum showing a band at 1145 cm^{-1}, appropriate to an O–O stretching frequency. The product dissolved in toluene to give the spectrum of CrO(TPP). The rate of reaction between oxygen and the solid toluene solvate is somewhat faster than for the pyridinate since, after an exposure time of 2 h, CrO(TPP) was the sole product detected by its absorption spectrum in solution. Both the solid "toluene" and "pyridine" oxygenated products are susceptible to moisture, the "toluene" product being the more rapidly attacked. The products of such hydrolytic reactions give similar spectra in toluene to that of the hydroxochromium species formed when CrO(TPP) hydrolyzes. This latter reaction is discussed later in this paper.

Other solid $Cr^{II}(P)$ derivatives (P = TTP, TXP, TMP, TFMP, TFP, TPFP, OEP) also showed similar behavior when reacted with oxygen in the solid state for 24 h. Each "oxygenated" product when dissolved in toluene under nitrogen gave solely the spectrum of the CrO(P) derivative. Isolation of a solid sample of a chromyl by this route was only undertaken for CrO(TMP).

(c) Possible Mechanism for Autoxidation. The foregoing experiments, whether involving oxygen reacting with $Cr^{II}(P)$ in solution or the solid state, are generally consistent with a mechanism that parallels that proposed for the autoxidation of $Fe^{II}(P)$.[11] Thus

$$Cr^{II}(P) + O_2 \rightleftarrows Cr^{III}(O_2)(P) \qquad (i)$$

$$Cr^{III}(O_2)P + Cr^{II}(P) \rightarrow (P)Cr^{III}\text{–}O_2\text{–}Cr^{III}(P) \qquad (ii)$$

$$(P)Cr^{III}\text{–}O_2\text{–}Cr^{III}(P) \rightarrow 2Cr^{IV}O(P) \qquad (iii)$$

$$Cr^{IV}O(P) + Cr^{II}(P) \rightleftarrows (P)Cr^{III}\text{–}O\text{–}Cr^{III}(P) \qquad (iv)$$

There is as yet no direct evidence for the formation and fission of the peroxo complexes (steps ii and iii), but steps i and iv now appear reasonably well established. It appears necessary to postulate that partial dissociation of the superoxo species occurs when dissolved in toluene in order that some free $Cr^{II}(P)$ is available for steps ii and iii to take place. If a solid sample of $Cr^{II}(P)$ is exposed to insufficient oxygen to allow complete conversion to $Cr(O_2)(P)$, there will still be $Cr^{II}(P)$ available to produce the μ-oxo species by reaction iv when the product is dissolved in toluene. If oxygenation is carried out in solution, this latter step will occur as long as there is sufficient $Cr^{II}(P)$ available. The disproportionation equilibrium of the μ-oxo complex will allow $Cr^{II}(P)$ to be continuously converted to CrO(P) via steps i–iii so that in the presence of excess oxygen complete conversion to CrO(P) occurs.

The relative reactivities of CrO(P) and (P)CrOCr(P) are thus opposite to those of the analogous FeO(P) and (P)FeOFe(P) compounds. The equilibrium for Fe compounds represented by reaction iv must be displaced so far in favor of Fe–O–Fe products that the highly reactive FeO(P) species cannot readily be detected at room temperature.

3. Oxidation of Cr(P)Cl in Air. Solutions of Cr(P)Cl in toluene or chloroform (P = TPP, TTP, TXP, TMP, TCP, TFP, TFMP, OEP) containing aqueous hydrochloric acid, after stirring in contact with air for periods up to 48 h, develop new absorption bands at very similar wavelengths, viz. 425 and 532 nm, in addition to those due to any unreacted Cr(P)Cl (Figure 3). The solutions may then be extracted with water to remove excess acid without altering their spectral characteristics and either chromatographed on basic alumina or shaken with solid Na_2CO_3, to yield the chromyl complexes, CrO(P), in yields varying from 20% (TMP) to 50% (TPP).

A similar intermediate species is formed during the first 1–2 days of reaction of Cr(TFP)Cl, as shown by a spectral change, but continued stirring of the mixture results in the gradual disappearance of the spectrum of this species and reversion to that of Cr(TFP)Cl.

Cr(TPFP)Cl shows no reaction in the presence of air and HCl even after reaction periods up to 6 days. The complex CrO(TPFP) can nevertheless be synthesized conveniently by the reaction of Cr(TPFP)Cl with iodosylbenzene.

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[26] Gonzalez, B.; Kouba, J.; Yee, S.; Reed, C. A.; Kerner, J. F.; Scheidt, W. R. *J. Am. Chem. Soc.* **1975**, *97*, 3247.

Table III. Elemental Analyses and Yields

compd	% calcd C	% calcd H	% calcd N	% calcd Cl/F	% found C	% found H	% found N	% found Cl/F	% yield
$CrO(TPP)\cdot 0.18CHCl_3$	75.56	4.02	7.98	2.73	75.84	4.07	7.96	3.2	50
$CrO(TPP)\cdot 0.3C_6H_6$[a]	78.11	4.27	7.96		77.98	4.47	7.74		50
$CrO(TPP)\cdot 1.0CHCl_3$	68.73	4.36	6.54	12.41	68.52	4.7	6.8	12.2	42
$CrO(TMP)\cdot 0.3CHCl_3$	69.33	4.4	6.7		69.27	4.95	6.49		17
$CrO(TXP)\cdot 0.5CHCl_3$	73.96	5.27	6.51		74.15	5.44	6.29		10
$CrO(TFP)\cdot 0.3CHCl_3$	67.04	3.0	7.05		66.91	3.48	7.07		20
CrO(TCP)	64.56	2.96	6.80	17.3	64.29	2.87	6.50	17.2	25
CrO(TFMP)[b]	60.51	2.54	5.88	23.93	57.23	2.55	5.36	24.10	14
CrO(TPFP)[b]	50.78	0.78	5.39	36.52	49.2	1.50	5.08	36.60	18

[a] Prepared in benzene by aerial oxidation of Cr(TPP)Cl in the presence of HCl(aq). [b] Prepared by iodosylbenzene oxidation of Cr(P)Cl.

Table IV. UV/Visible and Infrared Spectral Data for CrO(P) Complexes

compd[a]	λ_{max}, nm (log ϵ)[b]	$\nu_{M=O}$, cm^{-1}
CrO(TPP)	372 (4.28), 431 (5.17), 503 (3.43) 544 (4.14), 575 (sh, 3.38), 680, 750	1020[d]
CrO(TTP)	374 (4.27), 433 (5.25), 504 (3.49) 545 (4.23), 580 (sh, 3.40), 640, 680	1020[c]
CrO(TXP)	375 (4.04), 433 (5.32), 507 (3.59) 545 (4.26), 580 (sh, 3.59), 646	1023[d]
CrO(TFP)	373 (4.15), 430 (5.18), 503 (3.08) 543 (4.07), 577 (sh)	1027[c]
CrO(TCP)	372 (4.52), 433 (5.23), 502 (3.64) 545 (4.2), 576 (sh, 3.56)	1019[d]
CrO(TMP)	375 (4.25), 435 (5.24), 507 (3.40) 546 (4.19), 585 (sh)	1016[d]
CrO(OEP)	413 (5.15), 532 (4.09), 570 (4.50)	1018[d]
CrO(TFMP)	370 (4.26), 431 (5.28), 542 (4.18) 577 (3.31)	1027[c]
CrO(TPFP)	424 (5.46), 541 (4.39), 577 (4.21)	1026[c]
CrO(TmesP)		1027[d]

[a] Data previously reported for CrO(TPP), CrO(TTP), and CrO(TmesP) in ref 7 and CrO(TTP) and CrO(OEP) in ref 8 are in general agreement with the values reported here. [b] All spectra determined in toluene. [c] Spectra run as Nujol mulls. [d] KBr disk.

In the absence of acid the chromyl derivatives are sensitive to moisture in varying degrees depending on the porphyrin ligand, and it was found advisable to protect the solutions after chromatography from contact with moist air. The method, although requiring longer reaction times than when using iodosylbenzene, has an advantage when preparing compounds such as CrO(TCP), which are particularly sensitive to attack by water since the intermediates formed in acid solution are not apparently water sensitive and hence anhydrous conditions need not be applied until the final desorption of chromyl from an alumina column.

The microanalytical data and UV/visible and infrared spectral bands for the complexes prepared by this route are given in Tables III and IV.

Chemical shifts observed in the ^1H and ^{19}F NMR spectra of the compounds and magnetic moments are given in Table V.

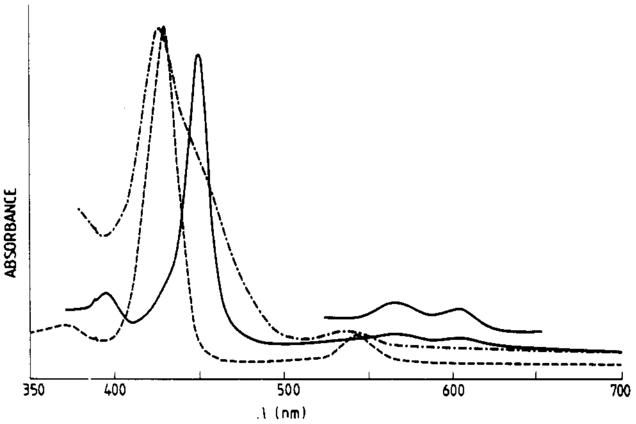


Figure 3. Visible spectra in toluene: (a) Cr(TPP)Cl, —; (b) Cr(TPP)Cl after prolonged treatment with aqueous HCl in contact with air, -·-; (c) CrO(TPP), ---.

The NMR spectra of the chromyl derivatives are unaffected by the presence of paramagnetic Cr(P)Cl, and hence the chromyls can be readily detected in mixtures containing both species, the Cr(III) complexes giving only very broad absorptions. The sensitivity to hydrolysis of a number of the chromyls has led to residual paramagnetism being detected in most of the new compounds isolated due to Cr(III)–OH species. The sharp ^1H NMR spectra observed in all cases nevertheless indicate the essential diamagnetism of the compounds.

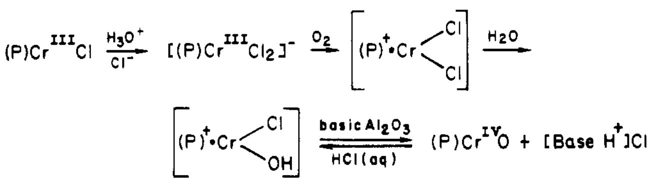
Constitution of the Intermediate Formed in the Oxidation of Cr(III) in Acid Solution. The species formed when oxygen reacts with Cr(P)Cl in the presence of acid are also produced, as judged by the appearance of appropriate spectral bands, when concentrated aqueous HCl is added to toluene solutions of CrO(P) in contact with air. CrO(TPFP) is however an exception to the general observation in that it reacts with aqueous HCl in air to form Cr(TPFP)Cl without an intermediate complex being observed comparable with those formed by other porphyrin derivatives. Thus, for CrO(TPP), after treatment with acid, the visible absorption bands due to CrO(TPP) can no longer be observed but peaks due to Cr(TPP)Cl at 447 and 563 nm can be recognized

Table V. NMR and Magnetic Data for Oxochromium(IV) Porphyrin Complexes[a]

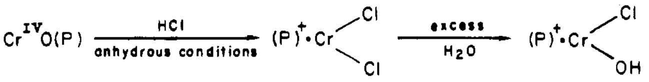
compd	^1H NMR pyrrole H	^1H NMR phenyl gp o-H	^1H NMR phenyl gp m-H	^1H NMR phenyl gp p-H	^1H NMR methyl	^{19}F NMR	μ_{eff}(293 K), μ_B
CrO(TPP)	9.09 (s)	8.21 (s)	7.78 (m)				0
CrO(TTP)	9.09 (s)	8.06 (d)	7.6–7.5 (m)		2.70 (s)		0
CrO(TXP)	9.09 (s)	7.78 (m)		7.41 (s)	2.59 (s)		0.8
CrO(TMP)	9.11 (s)	8.17, 8.08 (m)	7.34 (s)		4.08 (m)		0.3
CrO(TFP)	9.07 (s)	8.17 (s)	7.47 (t)			−114.81 (m)	0.4
CrO(TCP)	9.08 (s)	8.11 (m)	7.81–7.72 (m)				0.5
CrO(TFMP)	9.04 (s)	8.33 (s)	8.11–8.02			−62.69 (s)	1.2
MoO(TPFP)	9.14 (s)	. . .				−139 (m)	0.96

[a] Conditions: ^1H NMR in $CDCl_3$, reported in δ relative to Me_4Si; ^{19}F NMR in $CDCl_3$ reported in δ relative to $CFCl_3$. Key: s = singlet, t = triplet, m = multiplet, d = doublet.

Scheme I



Scheme II



together with those due to the intermediate. The ^{1}H NMR spectrum of the solution shows only broad resonances, indicating that the intermediate is paramagnetic or that magnetic exchange is now possible between Cr(III) and $Cr^{IV}O$.

Extraction of the solution with water to remove excess acid does not change the new visible spectral bands, and treatment of this solution with Na_2CO_3 or passage through a basic alumina column brings about the reappearance of the absorption spectrum of CrO(TPP).

An attempt was made to isolate the "intermediate" complex by addition of hexane to the final acid-free solution, resulting in precipitation of a green solid. This product contained some Cr(TPP)Cl as evidenced by its absorption spectrum in chloroform, but the infrared spectrum of the impure solid showed an absorption band at 1280 cm^{-1}, close to the band at 1285 cm^{-1} proposed[27] to arise from a π-cation radical $(TPP)^{+\cdot}$ in the complex [Cr(TPP)Cl]($SbCl_6$). The visible spectrum reported for the ion formed on oxidation of Cr(TPP)Cl with phenoxathiin hexachloroantiomonate(V)[28] is also very similar to that of the intermediate formed in the present experiments. It is thus concluded that oxygen can bring about this type of oxidation of the porphyrin ring in the presence of acid.

The Cr intermediate species was found to be formed at a faster rate when ferric chloride was added to the concentrated HCl used for the aerial oxidation reaction, the rate increasing with the amount of $FeCl_3$ added. The formation of Fe(III) porphyrin π-radical cation species by the reaction of (TPP)FeCl with iron(III) perchlorate has been observed.[29] Although the overall rate of oxidation of Cr(P)Cl species in air is slow, some variation was observed between different batches of hydrochloric acid used and traces of Fe(III) in the acid may well account for this variation.

A comparable sequence of reactions to those involving $Cr^{IV}O(P)$ species has been observed in the reaction of Fe(TMesP)Cl with peroxy acids or iodosylbenzene.[30] The Fe porphyrin π-radical cation prepared by reaction of Fe(TMesP)Cl with a peroxybenzoic acid can be converted by treatment with base to a species postulated as an oxoiron(IV) derivative. The reaction is reversed by addition of acid. A possible scheme for the Cr(III) → Cr(IV) reaction is given in Scheme I. The passage of dry HCl through a toluene solution of CrO(TPP) (under nitrogen) for a brief time results in a visible spectral change to a species having λ_{max} = 426, 565, and 600 nm; i.e., the Soret band appears at the same wavelength shown by the intermediate formed in air, but significant differences occur in the remaining α and β bands. If moisture and oxygen are then admitted to the system, a further change occurs in those latter bands, resulting finally in the appearance of the spectrum of the proposed intermediate. This sequence may be seen as the reverse of the previous reaction, with the further π-radical-cation-containing species $[(P)^{+}\cdot CrCl_2]$ being the source of the initial absorptions and showing a similar Soret band at 426 nm to that of the final intermediate formed when water is present (Scheme II). Differences in the positions of the α and β bands could arise because of the different axial substituents.

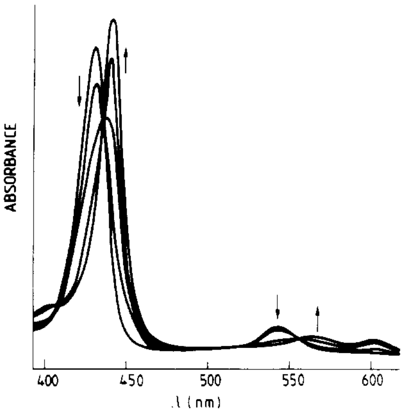


Figure 4. Reaction of CrO(TPP) with pyridine in toluene solution (spectra recorded at various intervals over 1 h).

In a chemically similar reaction $Mo(TPP)Cl_2$ has been prepared by reaction of dry HCl with MoO(TPP),[31] and it is plausible that a similar reaction occurs in the case of CrO(TPP) in the first instance in the absence of significant amounts of water.

Reaction of CrO(P) with Pyridine. The coordination of Lewis bases to oxometalloporphyrins has been studied for the case of piperidine reacting with $V^{IV}O(TTP)$, the 6-coordinate complex VO(TTP)(pip) being formed.[32] Similarly, the coordination of *N*-methylimidazole was a necessary requirement in stabilizing an $Fe^{IV}O(P)$ complex at low temperatures.[10]

The FeO(P) complex[33] and CrO(TPP)[7] react with triphenylphosphine, however, by oxygen transfer to form triphenylphosphine oxide and the M(II) porphyrin complexes.

It has now been established that pyridine can react with several CrO(P) complexes (P = TPP, TMP, TFMP) to form labile monopyridine adducts CrO(P)(py). Thus, when pyridine is added in large excess (10^4) to a toluene solution of CrO(TPP), the absorption spectrum changes with time to give a new series of absorption maxima, isosbestic points being observed when spectra were measured at various time intervals (Figure 4). This infers a coordination reaction

$$\mathrm{CrO(TPP)} + \mathrm{py} \rightleftharpoons \mathrm{CrO(TPP)(py)}$$

Treating the reaction as a first-order process in the presence of a large excess of pyridine gave a reaction half-life of 15 min for the reaction with the concentration of CrO(TPP) of 10^{-5} M. Corresponding half-lives for the reactions of CrO(TMP) and CrO(TFMP) were 25 and 13 min, respectively.

The pyridine adduct with CrO(TPP) is still diamagnetic since there is little change to the sharply defined ^{1}H NMR spectrum of CrO(TPP) in benzene-d_6 when pyridine-d_5 is added. Attempts were made to isolate an example of the pyridine adduct by adding hexane to a solution of CrO(TMP) in pyridine. The final product, however, contained both pyridine and chloroform, the latter arising from the presence of solvent in the samples of CrO(TMP) used. The analytical figures for the products of several experiments have therefore been treated with caution but indicate the presence of close to 1 mol of pyridine/mol of CrO(TMP). The pyridine ligand is quite labile since a solution of the pyridinate in toluene at the concentration suitable for visible spectral examination (ca. 10^{-5} M) was found to show only the spectrum of the parent CrO(TMP). The ^{1}H NMR spectrum of such a solution in benzene-d_6

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Table VI. UV/Visible Spectra of Cr(P)OH Compounds

method	compd	solvent	λ_{max}, nm	μ_{eff}(293 K), μ_B
		Type A		
hydrolysis of CrO(P)	$Cr O(TPP)OH\cdot 3H_2O$	toluene	449, 562, 599	3.84
		Type B		
$Cr(CO)_6/(TPP)H_2$	$Cr(TPP)OH\cdot 2H_2O$[20]	$CHCl_3$	397, 449, 557, 590, 664	
	$Cr(TPP)OH\cdot 2H_2O$	toluene[a]	449, 562, 599	3.91
		Type C		
$Cr(TPP)Cl/OH^-$	$Cr(TTP)OH\cdot 2H_2O$[22]	CH_2Cl_2	435, 561, 600	
	$Cr(TPP)OH\cdot 4H_2O$	CH_2Cl_2[b]	435, 561, 600	3.93

[a] No additional bands observed. [b] The product prepared by this route is insoluble in toluene.

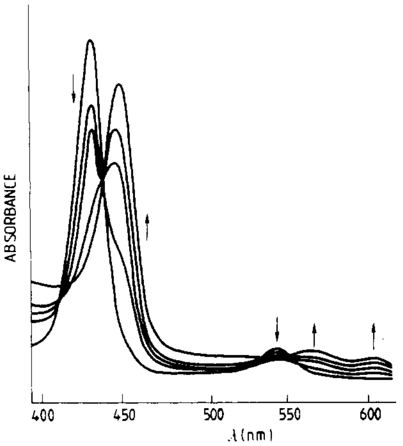

Figure 5. Reaction of CrO(TCP) with water in toluene (spectra recorded at various intervals over 4 h).

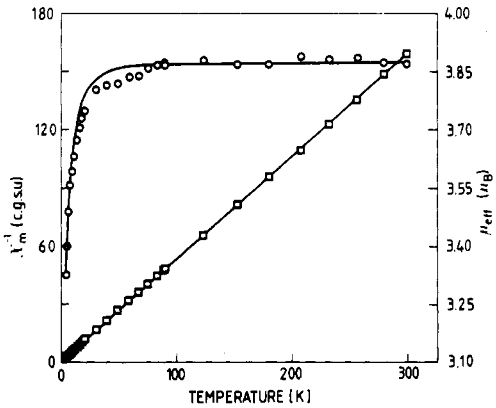

Figure 6. Variation with temperature of the magnetic moment per mole (○) and reciprocal susceptibility per mole (□) for $Cr(TPP)OH\cdot 4H_2O$.

showed the presence of virtually 1 mol of free pyridine.

Reaction of CrO(P) with Water. The chromyl compounds react with water at rates depending on the porphyrin. The reactions can be monitored by changes in the visible spectra of the complexes. CrO(TCP) and CrO(TPFP) were the most readily decomposed by water and CrO(TPP) was the least. Thus, CrO(TCP) forms a stable solution in dry toluene under a nitrogen atmosphere with λ_{max} = 431, 562, and 599 nm. On addition of a small amount of water to the solution the spectrum changes over a period of several hours to give λ_{max} = 449, 562, and 599 nm (Figure 5). A similar reaction is shown by CrO(TPP) over a much longer time span (ca. 10 h).

Observations of the times to complete changes in spectra in the presence of standard amounts of water allow the following sequence of increasing reactivity of the chromyl complexes to be determined: TPP < TMP < TTP ~ TXP ~ TFP ~ TFMP < OEP < TCP ~ TPFP.

The solid hydrolysis product obtained from CrO(TPP) reacting in aqueous toluene under nitrogen showed a broad absorption around 3600 cm^{-1}, indicating the presence of water but no bands in the regions of 1020 cm^{-1} ($\nu_{Cr=O}$) or 800–900 cm^{-1} ($\nu_{Cr-O-Cr}$). The analytical composition of the solid conformed to the formula $Cr(TPP)OH\cdot 4H_2O$, and on this empirical formula the magnetic moment of the solid was found to be 3.84 μ_B at 293 K. The presence of a μ-oxo or μ-hydroxo compound would be expected to lower the moment.

Species also formulated as hydrated Cr(TPP)OH have been reported to result from the reaction of $Cr(CO)_6$ and $(TPP)H_2$[20] (type B) and from the attack of hydroxide ions on Cr(TPP)Cl[22] (type C). Samples of these products have been prepared in the present study and their spectra (Table VI) and magnetic properties compared with those of the hydrolysis product of CrO(TPP) (type A). The visible spectra of compounds B and C agree with the published data. The spectra of A and B are very similar but differ from that of C. Compound C is insoluble in toluene whereas compounds A and B are soluble. All complexes dissolve in CH_2Cl_2 or $CHCl_3$. The infrared absorption spectra of A and B are also similar and show broad absorptions in the water region around 3600 cm^{-1} while compound C has a sharp band at 3620 cm^{-1} possibly indicative of coordinated hydroxide. The magnetic moments (μ_{eff}) calculated for the analytically determined, empirical formula of compounds A and C are each close to the spin-only value for a d^3 Cr(III) ion (Table VI). The magnetic moment of the type C compound is virtually independent of temperature over the range 75–300 K (Figure 6), quite different from the behavior found for oxo-[12] or hydroxo-[34] bridged complexes, and indicates the absence of such linkages in the compound. This confirms the formulation of the compound by Buchler[22,35] who has also pointed to the need for structural or magnetic evidence as well as infrared spectral measurements to determine whether or not oxo bridging is present.

It appears moreover that there can be two different types of hydroxochromium(III) porphyrin complexes. Although their constitutions have not been defined in the present study, the indication is that one type has a OH group coordinated directly to the metal.

One further observation is noteworthy in connection with the hydrolytic behavior of the chromyl derivatives. When dilute solutions (10^{-4} M) of the hydrolysis products of CrO(P) compounds are allowed to stand in contact with air (and moisture) for long periods (ca. 18 h or more), the visible spectra of the solutions slowly change back to those of the original CrO(P) compounds. The simple chromyls are all so susceptible to hydrolysis that reversal of the hydrolytic reaction cannot be occurring. The new species react with pyridine more rapidly than the initial CrO(P) (e.g., $t_{1/2}$ for the Cr(TFMP) product is now 46 s), but the pyridine complexes show the same spectral bands as observed for CrO(P)(py).

It is possible that the process involves some form of condensation and oxidation of the Cr(III)–OH species leading to the formation of oxo-bridged Cr(IV) derivatives, $[(P)CrO]_n$, that retain the $Cr^{IV}O$ spectral characteristics but are more resistant to hydrolytic action. A dimeric oxochromium(IV) phthalocyanine complex has

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indeed been proposed for the product formed on oxidation of (β-phthalocyaninato)chromium(II) by oxygen.[5]

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Registry No. Cr(TXP)Cl, 84151-96-2; Cr(TCP)Cl, 84151-95-1; Cr(TMP)Cl, 84151-94-0; Cr(TFP)Cl, 94904-25-3; Cr(TPFP)Cl, 94890-04-7; Cr(TFMP)Cl, 94890-05-8; Cr(TTP)Cl, 43145-39-7; Cr(OEP)Cl, 65024-11-5; Cr(TPP), 58344-06-2; CrO(TPP), 78833-34-8; CrO(TMP), 84151-99-5; CrO(TXP), 84151-98-4; CrO(TFP), 94890-06-9; CrO(TCP), 94890-07-0; CrO(TFMP), 94890-08-1; CrO(TPFP), 94890-09-2; (TPP)CrOCr(TPP), 80593-65-3; (TMP)CrOCr(TMP), 94890-10-5; (TCP)CrOCr(TCP), 94890-11-6; (TCP)CrOCr(TPP), 94904-26-4; (TMP)CrOCr(TPP), 94890-12-7; (TXP)CrOCr(TXP), 94904-27-5; (TTP)CrOCr(TTP), 94890-13-8; (TFP)CrOCr(TFP), 94904-28-6; (TPFP)CrOCr(TPFP), 94904-29-7; (OEP)CrOCr(OEP), 94928-85-5; Cr(TMP), 94890-14-9; Cr(TFMP), 94904-30-0; Cr(TXP), 94890-15-0; Cr(TCP), 94890-16-1; Cr(TPFP), 94890-17-2; Cr(TFP), 94904-31-1; Cr(OEP), 67113-83-1; Cr(TTP), 94890-18-3; Cr(TTT)Cl, 28110-70-5; $Cr(TPP)(py)_2$, 67113-84-2; CrO(TPP)(py), 94890-19-4; CrO(TMP)(py), 94890-20-7; Cr(TPP)OH, 33519-59-4; $Cr(CO)_6$, 13007-92-6; O_2, 7782-44-7.

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High-Spin ↔ Low-Spin Transition in Solid $Co(H_2fsa_2en)(H_2O)_2$ [H_4fsa_2en = *N,N′*-Ethylenebis(3-carboxysalicylaldimine)]: A Magnetic Investigation

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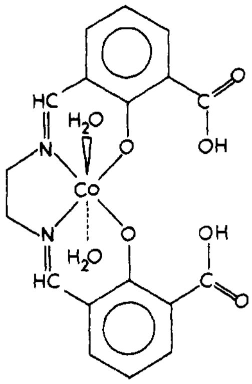
The sharp high-spin ($S = {}^3/_2$) ↔ low-spin ($S = {}^1/_2$) conversion of six-coordinate cobalt(II) in solid $Co(H_2fsa_2en)(H_2O)_2$ was investigated by variable-temperature magnetic susceptibility measurements and EPR spectroscopy (H_4fsa_2en = *N,N′*-ethylenebis(3-carboxysalicylaldimine)). Evidence was given for a small hysteresis effect of ca. 3 K, the transition being centered around 81.5 K ($T_c{\downarrow}$) and 84.6 K ($T_c{\uparrow}$) for decreasing and increasing temperatures, respectively. The temperature dependence of both $\chi_M T$ and $\mathcal{I}T$ products (χ_M = molar magnetic susceptibility, $\mathcal{I}$ = approximate intensity of EPR absorption) are in close agreement. About 9% of the molecules were found to persist in the high-spin form at low temperatures, and a substantial residue of low-spin species, estimated afterward to ca. 6%, was detected in the dominant high-spin form at high temperatures. The magnetic properties indicate a degeneracy removal of the ${}^4T_{1g}$ term and, hence, a large distortion of the $[CoN_2O_4]$ core in the high-spin phase. The g value pattern of the low-spin phase ($g_1 = 2.661$, $g_2 = 2.318$, $g_3 = 2.031$) shows that the core deformation is then constituted by an axial elongation and a rhombic distortion. The thermodynamic model of Slichter and Drickamer was applied to the magnetic data. A simple method was developed so as to enable the calculation of the interaction term ($\Gamma = 1556\ J{\cdot}mol^{-1}$) and of the enthalpy and entropy changes associated with the spin transition ($\Delta H = 1.93\ kJ{\cdot}mol^{-1}$ and $\Delta S = 23.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$). The domain size was estimated to be $n \sim 25$. These results are discussed. In particular, the relatively high value of n is related to a rather strong cooperative effect, which may explain the abruptness of the transition; the large value of ΔS, as compared with the magnetic contribution, is accounted for by the vibrational changes associated with the spin conversion.

Introduction

Investigations concerning thermally induced spin transitions in cobalt(II) (d^7) complexes are still relatively rare,[1-14] as compared with those related to iron(II) (d^6) and iron(III) (d^5) compounds. Most of the reported physical experiments were performed on solid-state samples,[1-12] and the high-spin (HS) ↔ low-spin (LS) conversions ($S = {}^3/_2 \leftrightarrow S = {}^1/_2$) were generally found to be gradual, often extending over more than 100 K.

The present work deals with the magnetic properties of $Co(H_2fsa_2en)(H_2O)_2$ (see **1**), H_4fsa_2en being the Schiff base resulting from the 2:1 condensation of 3-formylsalicylic acid with ethylenediamine. The spin crossover of this compound, previously reported by Kahn et al.,[8] takes place within a temperature range of a few degrees and is, to our knowledge, the most abrupt one ever observed in cobalt complexes. We are aware of only two other Co(II) compounds displaying rather sharp spin changes: $Co(H_2fsa_2en)(py)_2$,[11] which is closely related to the title complex, with two pyridine ligands replacing the water molecules in apical positions; Co(saloph)benzimd,[12] a five-coordinate complex that undergoes a very incomplete HS → LS conversion (saloph = dianion of the Schiff base *N,N′-o*-phenylenebis(salicylaldimine); benzimd = benzimidazole).



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The magnetic behavior of $Co(H_2fsa_2en)(H_2O)_2$ polycrystalline samples was investigated by means of variable-temperature

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