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Oxochromium Compounds. 1. Synthesis and Properties of μ-Oxo Chromium–Iron Porphyrin and Phthalocyanine Compounds

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The reaction between $Cr^{IV}O(P)$ and $Fe^{II}(P')$ leads to the formation of μ-oxo heterobinuclear complexes (P)CrOFe(P′) where P and P′ represent dianions of porphyrins that may be the same or different. [Abbreviations for the dianions of 5,10,15,20-tetraarylporphyrins: TPP, tetraphenylporphyrin; TTP, tetra-*p*-tolylporphyrin; TMP, tetrakis(*p*-methoxyphenyl)porphyrin; TFP, tetrakis(*p*-fluorophenyl)porphyrin; TCP, tetrakis(*p*-chlorophenyl)porphyrin; TXP, tetra-3,5-xylylporphyrin; OEP, the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; Pc, the dianion of the phthalocyanine molecule.] The complexes react with heterocyclic Lewis bases, and these coordinate to Cr only. The visible, infrared, ^1H NMR, and Mössbauer spectra are reported for the compounds. The variation of magnetic susceptibility with temperature down to 4.2 K is interpreted in terms of strong antiferromagnetic coupling between Cr(III) ($S = {}^3/_2$) and Fe(III) ($S = {}^5/_2$) centers with J values in the range -130 to -150 cm^{-1}. Zero field splitting effects are important at low temperatures. The reaction of CrO(TPP) with $Fe^{II}(Pc)$ forms an analogous μ-oxo complex having porphyrin and phthalocyanine groups attached to Cr(III) and Fe(III), respectively.

Introduction

It has been proposed[1] that the formation of μ-oxo $[Fe(P)]_2O$ compounds (where P = the dianion of a porphyrin) by reaction of oxygen with $Fe^{II}(P)$ species proceeds via the formation of a highly reactive ferryl species, $Fe^{IV}O(P)$, which gives the μ-oxo-bridged species by the redox reaction

$$Fe^{IV}O(P) + Fe^{II}(P) \rightarrow [Fe^{III}(P)]_2O$$

Such a reaction might well be expected to occur between other "metalyl" species and similar or dissimilar metal complexes in lower oxidation states provided the redox potential relationships are appropriate in whatever medium is chosen. Several such reactions have already been reported. Thus, the highly reactive $Fe^{IV}O(TPP)$, formed at low temperatures in the presence of a Lewis base,[2] has been reacted[3] with a Cu(I) cationic complex to yield a product showing considerable magnetic coupling and considered to be an Fe(III)–O–Cu(II) μ-oxo-bridged species although the product was not structurally characterized. Detection of an Fe–O–Cu heterobinuclear unit would be of considerable importance since it has been suggested to provide the active site in the oxidized resting form of cytochrome *c* oxidase.[4] Alternative attempts have been made to prepare model compounds containing this oxo-bridged structure from binucleating porphyrin ligands with two binding sites for the metal ions.[5,6]

In a further report,[7] reaction of the more stable $Cr^{IV}O(TPP)$ species[8-11] with $Fe^{II}(TPP)$ formed (TPP)CrOFe(TPP), a compound also observed to show considerable antiferromagnetic coupling.

This paper reports further details of the synthesis of these and other Cr–O–Fe derivatives and studies of their magnetic and spectroscopic properties.

Experimental Section

Materials and Techniques. Dry solvents were used in all phases of this work, benzene, toluene, methylene dichloride, and chloronaphthalene being dried by standard procedures.[12] All manipulations were carried out under nitrogen that was predried by passage through molecular seives (BDH 4A) and cleansed of oxygen to better than 0.5 ppm by passage through a heated column of BASF R311 catalyst. Schlenk apparatus, hypodermic syringes, and stainless-steel cannulae were used for filtration and solution transfers under nitrogen where oxygen and water were to be excluded. Oxygen was removed from solvents by purging with a purified nitrogen gas stream. Aluminium oxide (basic, activity II, Ajax Chemicals) and Celite (BDH) were used for chromatography. Spectra were recorded as follows: ^1H NMR, Bruker WH90; visible, Varian Super Scan 3; infrared, PE180. Microanalyses were carried out by the Australian Microanalytical Service.

Magnetic Susceptibility Measurements. Average magnetic susceptibilities were measured on an extensively modified Oxford Instruments magnetometer.[13] Samples were run as neat powders between 4.2 and 300 K with a main field of 10 kG and a gradient field of 1000 G/cm. Measurements were made manually between 4.2 and 20 K, with automatic data logging equipment used at higher temperatures. Temperatures below 30 K were measured on a carbon resistor while above this a Cu/constantan thermocouple was employed. The carbon resistor was found to be slightly field dependent below ca. 10 K. For measurements at other than the lowest attainable temperature (ca. 4.28 K) errors of up to 0.2 K can result from this effect. In general, the errors in temperature were found to be less than 0.1 K. Mössbauer measurements were carried out as described previously.[14] Isomer shifts were calibrated with respect to α-iron.

Porphyrins. $(TPP)H_2$, $(TTP)H_2$, $(TFP)H_2$, $(TMP)H_2$, $(TXP)H_2$, and $(TCP)H_2$ were prepared by the general literature method,[15] chlorin impurities being removed by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[16] Final purification was achieved by chromatography in CH_2Cl_2 solution on alumina.

Oxochromium(IV) Porphyrins. CrO(TPP), CrO(TTP), CrO(TFP), CrO(TMP), and CrO(TXP) were prepared by aerial oxidation of Cr(P)Cl in a mixture of aqueous HCl and chloroform[17] or by oxidation of Cr(P)Cl with iodosylbenzene.[9a]

Iron Porphyrin Compounds. Fe(TPP)Cl, Fe(TMP)Cl, Fe(TCP)Cl, and Fe(OEP)Cl were prepared by a modification[18] of the literature

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Table I. Analyses of μ-Oxo Chromium-Iron Complexes

	% found				% calcd			
compd	C	H	N	Cl	C	H	N	Cl
(TPP)CrOFe(TPP)[a]	78.1	4.21	8.15		78.3	4.18	8.30	
(TPP)CrOFe(TPP)·H_2O	76.6	4.45	8.41		76.3	4.37	8.10	
(TTP)CrOFe(TPP)[a]	78.4	4.64	7.75		78.6	4.60	7.97	
(TFP)CrOFe(TPP)[a]	74.7	3.84	8.00		74.4	3.70	7.89	
(TMP)CrOFe(TPP)·H_2O	74.0	4.92	7.99		74.3	4.48	7.53	
(TXP)CrOFe(TPP)·1.25$CHCl_3$[b]	72.9	4.42	7.09		72.5	4.59	6.96	
(TPP)CrOFe(TMP)[a]	75.5	4.05	7.91		75.2	4.39	7.62	
(TPP)CrOFe(TCP)·H_2O	70.0	3.55	7.65	9.5	70.2	3.62	7.95	9.4
(TPP)CrOFe(TMP)·py	75.4	4.61	8.09		75.2	4.50	8.14	
(TPP)CrOFe(Pc)·2H_2O	70.7	3.67	13.1		71.0	3.77	13.1	

[a] Solids isolated under nitrogen. Complexes containing H_2O isolated in contact with air. [b] Prepared using CrO(TXP) containing 1.5 mol of $CHCl_3$. Sample dried at 20 °C under vacuum before analysis.

method for Fe(TPP)Cl[19] involving $FeCl_2 \cdot 4H_2O$ in slight excess reacting with free porphyrin in dimethylformamide. Each product was precipitated by addition of dilute aqueous HCl (2 M) to the reaction mixture. Purification was found to require acid treatment to avoid contamination by oxo compounds and involved chromatography of a $CHCl_3$ solution on alumina followed by treatment of the eluate with concentrated HCl, washing with water to remove acid, drying over Na_2SO_4, concentration, and addition of dry hexane to precipitate the complex. The products were finally recrystallized from benzene solutions by slow addition of hexane.

$Fe^{II}(P)(pip)_2$ derivatives (P = TPP, TCP, TMP, OEP) were readily prepared by piperidine reduction[20] of the appropriate Fe(P)Cl complexes as described[21] for the preparation of $Fe(TPP)(pip)_2$. The compounds were stored under nitrogen and weighed when required for reactions, using a Vacuum Atmospheres Corp. Dri-Lab handling box.

In some preparations a blue microcrystalline form of the complexes could be obtained that was stable in air for short periods of time. In others a red solid was precipitated that was extremely air sensitive. It is uncertain what caused the variation in color of the complexes although variation in particle size of the precipitate due to the purification step may be involved. The blue forms crushed to give red powders that changed color on exposure to air more rapidly than the original blue solids. The complexes were diamagnetic. Their purity was checked before reaction by examination of their infrared spectra in Nujol mulls to ensure the absence of an Fe–O–Fe stretching frequency.

$Fe^{II}(TPP)$ was also prepared without additional coordinating ligands by reduction of Fe(TPP)Cl with chromium(II) acetylacetonate.[22] The complex formed in this manner was very air sensitive.

Synthesis of μ-Oxo Chromium-Iron Porphyrin Complexes. The following description is typical of the reactions carried out:

(μ-Oxo)[(5,10,15,20-tetraphenylporphyrinato)chromium(III)][(5,10,15,20-tetraphenylporphyrinato)iron(III)], (TPP)CrOFe(TPP). CrO(TPP) (45.8 mg, 0.0654 mmol) and $Fe(TPP)(pip)_2$ (54.8 mg, 0.0654 mmol) were dissolved in rigorously deoxygenated toluene (15 mL). The red-green solution was stirred for 2–3 h during which time a solid precipitated from the solution. Dry hexane was then added to aid further precipitation. The purple solid (yield 59.1 mg (65%)) was recrystallized from benzene by addition of hexane and the crystalline product heated under vacuum at 150 °C to remove occluded solvent before analysis. If the reaction vessel was opened to the air before addition of hexane, the final product gave analytical figures corresponding to the presence of one molecule of water without vacuum drying.

The other complexes isolated were prepared by essentially similar procedures (yield): (TTP)CrOFe(TPP), 55%; (TFP)CrOFe(TPP), 56%; (TMP)CrOFe(TPP), 73%; (TPP)CrOFe(TCP), 84%; (TPP)CrOFe(TMP), 65%; (TXP)CrOFe(TPP), 70%. Analytical data for the complexes are given in Table I. The product obtained from CrO(TPP) and $Fe(OEP)(pip)_2$ did not give acceptable analytical figures for the expected complex (TPP)CrOFe(OEP) even after repeated crystallization.

^{18}O-Labeled (TPP)FeOCr(TPP). Oxygen-18 labeled iodosylbenzene was prepared by the method of Hill et al.,[23] dimethoxyiodobenzene being treated with $H_2{}^{18}O$ (Yeda Research Laboratories; 61.30 atom % ^{18}O) in dry ether. The ^{18}O content of the iodosylbenzene was estimated to be 50% on the basis of the infrared spectrum of a sample of triphenylphosphine oxide prepared by reaction of the labeled iodosylbenzene with PPh_3. ^{18}O-labeled CrO(TPP) was obtained by using the method of Groves[10] whereby Cr(TPP)Cl reacted with [^{18}O]iodosylbenzene in dry methylene dichloride, followed by filtration and addition of *tert*-butylamine at −78 °C.

The μ-oxo complex was finally prepared by reacting ^{18}O-labeled CrO(TPP) with $Fe(TPP)(pip)_2$ in toluene and precipitating the purple complex by addition of hexane. Subsequent treatment of the product was as described above.

Reaction of CrO(TPP) and Fe(Pc). (Phthalocyaninato)iron(III) Chloride (Fe(Pc)Cl) was prepared by the reaction of phthalonitrile and iron(III) chloride in 1-chloronaphthalene.[24] Bis(pyridine)(phthalocyaninato)iron(II) was obtained[25] by extraction of Fe(Pc)Cl with pyridine in a Soxhlet apparatus and $Fe(Pc)(py)_2$ precipitated from the extract with hexane. The solid was purified by a solution in pyridine being passed through an alumina column and the complex reprecipitated by hexane. It had a residual magnetic moment of $\mu_{eff} = 0.7\ \mu_B$ at 293 K. Sublimation at 350 °C (10^{-2} torr) yielded the pyridine-free complex Fe(Pc). The solid was not particularly air sensitive. UV/visible, λ_{max}, nm: (pyridine) 333, 415, 658; (1-chloronaphthalene) 595, 630, 658.

(μ-Oxo)[(5,10,15,20-tetraphenylporphyrinato)chromium(III)][(phthalocyaninato)iron(III)], (TPP)CrOFe(Pc). CrO(TPP) (36 mg, 0.05 mmol) and Fe(Pc) (27.1 mg, 0.05 mmol) were dissolved in 1-chloronaphthalene (20 mL) under nitrogen, and the mixture was stirred at room temperature for 2–3 h. The resulting green solution was opened to the air and filtered and hexane (100 mL) slowly added to produce a blue, microcrystalline solid. The solid was filtered and dried under vacuum.

UV/visible (1-chloronaphthalene/benzene, 1:1) λ_{max}, nm (log ϵ): 431 (4.56), 565 (3.86), 631 (3.88), 699 (4.34). $\mu_{eff} = 3.12\ \mu_B$ per dimer at 297 K. Infrared (strong (s) and medium (m) peaks only, Nujol): 3002 m, 1486 m, 1523 m, 1436 s, 1166 m, 1120 s, 1002 m, 1084 s, 1075 s, 1008 s, 797 s, 772 s, 715 vs, 703 s cm^{-1}.

Results and Discussion

Synthesis of Cr–O–Fe Porphyrin Complexes. Reactions between $Cr^{IV}O(P)$ and $Fe^{II}(P')$ compounds occur readily in dry toluene under nitrogen to yield the μ-oxo derivatives $(P)Cr^{III}OFe^{III}(P')$ in relatively high (55–84%) yields. Reaction is complete in several minutes at room temperature. The porphyrin ligands attached to Cr and Fe may be the same or different. The Fe(P′) complexes used may be the readily prepared bis(piperidine) derivatives or the unsolvated Fe(P′). The course of reaction is shown by the initial wine red color of the mixture of chromyl and Fe(II) complexes converting to the red-green of the final μ-oxo complex. The products were isolated as purple microcrystalline solids. The complexes prepared are listed in Table I.

Addition of aqueous HCl to solutions of the compounds in benzene caused rapid conversion to the corresponding Cr(P)Cl and Fe(P′)Cl complexes whose Soret bands were generally sufficiently different to allow spectral analyses of the solutions under standard conditions to establish the formation of each complex in a 1:1 proportion.

The compounds appear to be indefinitely stable to air or moisture in the solid state and are reasonably thermally stable.

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Table II. UV/Visible Spectra of (TPP)CrOFe(TPP) in Benzene with Added Lewis Base

base	λ_{max}, nm				
none		422		561	603
pyridine	405 (sh)	429	526	567	608
N-methylimidazole	403 (sh)	428	526	568	610
piperidine	403 (sh)	427	526	567	608

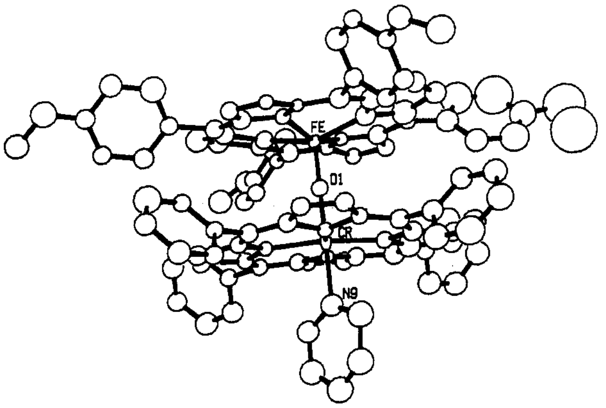

Figure 1. Molecular structure of (μ-oxo)[(pyridine)(5,10,15,20-tetraphenylporphyrinato)chromium(III)][(5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrinato)iron(III)], (py)(TPP)CrOFe(TMP).

They can be heated under vacuum to 250 °C without obvious signs of decomposition. The complexes are also stable in solution under nitrogen in benzene, toluene, or purified chloroform and appear unaffected by traces of moisture in the solvents. In the presence of oxygen, however, solutions in toluene or $CHCl_3$ rapidly formed CrO(P) and (P)FeOFe(P′) where P and P′ were the porphyrin ligands initially attached to Cr and Fe. Thus, (TMP)CrOFe(TPP) in contact with oxygen gave CrO(TMP) and $[Fe(TPP)]_2O$.

These observations suggest that the μ-oxo complexes must disproportionate to a small extent in solution.

$$(P)Cr^{III}OFe^{III}(P') \rightleftharpoons Cr^{IV}O(P) + Fe^{II}(P')$$

When oxygen is present, the Fe(P′) product can rapidly react to yield the observed $[Fe(P')]_2O$ product, displacing the above equilibrium with the resultant overall formation of CrO(P) and $[Fe(P')]_2O$.

The alternative disproportionation path is not likely to contribute to the overall reaction. Thus

$$(P)Cr^{III}OFe^{III}(P') \rightleftharpoons Cr^{II}(P) + Fe^{IV}O(P')$$

would yield the same products CrO(P) and $[Fe(P')]_2O$ in air because $Cr^{II}(P)$ would rapidly react with oxygen[9] to give $Cr^{IV}O(P)$ while FeO(P′) species are unstable[2] above −30 °C and decompose to $[Fe(P')]_2O$, which would also mean that $[Fe(P')]_2O$ should be observed to form in solutions of (P)CrOFe(P′) protected from oxygen. Experimentally however such compounds have only been observed when the solutions are in free contact with oxygen.

An interesting observation is that (P)CrOFe(P) compounds in benzene are much more slowly attacked by oxygen than in toluene. Solutions in benzene may be kept for a number of days in contact with air before the products of disproportionation are observed. This suggests a possible difference between the solvents in their abilities to solvate the μ-oxo complexes that can either stabilize or destabilize the complexes toward dissociation. Indeed, most of the heterobinuclear complexes, when recrystallized from toluene, retain some solvent in their lattices. There is also crystallographic evidence[26] that toluene can approach sufficiently close to Cr in the solvate, $Cr^{II}(TPP)(tol)_2$, to indicate some degree of intermolecular bonding.

Table III. Visible Spectra of (P)CrOFe(P′) Complexes in Benzene

complex	λ_{max}, nm (log ϵ)		
(TPP)CrOFe(TPP)	422 (5.18) 425[a]	561 (4.2) 571[a]	603 (3.81) 609[a]
(TTP)CrOFe(TPP)	426 (5.17)	564 (4.04)	605 (3.78)
(TFP)CrOFe(TPP)	422 (5.27)	562 (4.14)	603 (3.75)
(TMP)CrOFe(TPP)	427 (5.05)	565 (3.97)	608 (3.66)
(TPP)CrOFe(TMP)	424 (5.36)	566 (4.19)	610 (3.96)
(TPP)CrOFe(TCP)	423 (4.96)	562 (3.85)	602 (3.53)
(TPP)FeOFe(TPP)	407 (5.21)	560 (4.23)	610 (3.90)
(TPP)CrOFe(Pc)	431 (4.56)[b]	565 (3.86)	631 (3.88) 699 (4.34)

[a] Solid dispersed in Nujol mull. [b] Solvent 1-chloronaphthalene benzene, 1:1 mixture.

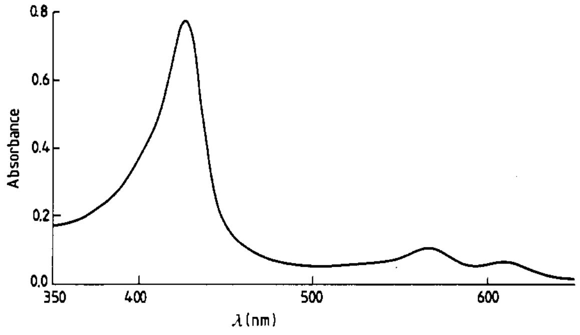

Figure 2. UV/Visible spectrum of (TPP)CrOFe(TMP) (benzene).

The Cr–O–Fe complexes can coordinate heterocyclic nitrogen bases as shown by shifts in the absorption spectrum when various bases are added to a solution of (TPP)CrOFe(TPP) under nitrogen (Table II). The solid isolated from a solution of (TPP)CrOFe(TPP) in pyridine was found to contain one molecule of pyridine by microanalytical and mass spectral analysis. A preliminary X-ray diffraction study on the complex (py)(TPP)CrOFe(TMP)[27] has defined the gross structural features of the molecule, in particular showing that pyridine is bonded to Cr in the compound (Figure 1). The Cr–O–Fe linkage is essentially linear (178 (2)°) as are the Cr–O–Cr bond systems in $[(NH_3)_5CrOCr(NH_3)_5]Cl_4$[28] and $[[Cr(NCS)(TPyEA)]_2O](BPh_4)_2$,[28] the only μ-oxo Cr complexes to have been fully defined by crystallographic studies. The μ-oxo bridges in a number of Fe–O–Fe complexes[29] depart notably from linearity although the Fe–O–Fe angle in $[(TPP)Fe]_2O$ is 174°. The two porphyrin rings are rotated by 32 (1)° with respect to one another, rather less than has been reported for $[(TPP)Fe]_2O$ (54.6°) while the plane of the pyridine ring attached to Cr bisects the N(1)–Cr–N(4) angle at 46 (3)°. The Fe atom lies somewhat above the plane of the TMP pyrrole N atoms and toward the bridging oxygen atom whereas the Cr atom lies close to the mean pyrrole N plane of the TPP molecule. The present stage of refinement of the structure has not provided sufficiently accurate individual bond distances to report in detail at this stage, but the overall Cr–Fe distance (ca. 3.6 Å) is close to the average sum of various Cr–O and Fe–O distances in other μ-oxo complexes.

The ability of μ-oxo Cr(III) derivatives to coordinate Lewis bases also appears to extend to H_2O. Thus, several of the complexes, when crystallized in contact with air, were found to show infrared spectral absorptions in the 3600-cm^{-1} region, indicating

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(27) Fallon, G. D.; Gatehouse, B. M. K.; Liston, D. J.; West, B. O., unpublished work. Considerable difficulty has been experienced in obtaining crystals of this compound suitable for diffraction studies and free from randomly arranged solvent molecules. The crystal examined was obtained from a toluene, hexane, and pyridine mixture but the refinement has converged at $R = 0.149$ owing to the presence of unresolved excess solvent molecules. Further work is in progress to obtain better crystalline samples in order to complete a full structural study.

(28) $[(NH_3)_5CrOCr(NH_3)_5]Cl_4$: Yevitz, M.; Stanko, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1512. Urushiyama, A. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2406. $[[Cr(NCS)(TPyEA)]_2O](BPh_4)_2$: Di Vaira, M.; Massi, F. *Inorg. Chem.* **1984**, *23*, 409.

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Table IV. Infrared Absorption Bands Assigned to Asymmetric Cr–O–Fe Stretching Vibrations

	ν(Cr–O–Fe), cm^{-1}		ν(Cr–O–Fe), cm^{-1}
(TPP)CrOFe(TPP)	842.5	(TMP)CrOFe(TPP)	835
	831.5 sh	(TPP)CrOFe(TMP)	842
(TTP)CrOFe(TPP)	839	(TPP)CrOFe(TCP)	845
(TFP)CrOFe(TPP)	849		

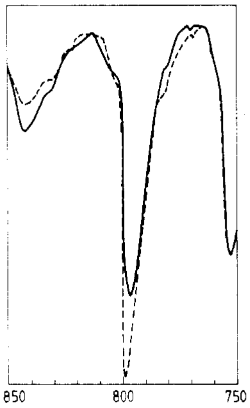

Figure 3. Infrared spectrum of (TPP)Cr–^{16}O–Fe(TPP)---(—) and the $^{16/18}$O-labeled derivative (---).

the presence of water (or OH). Microanalysis figures indicated one molecule was present, and in view of the structural evidence that pyridine can coordinate to Cr in such complexes, it is possible that a H_2O molecule is also coordinated in these hydrates. The alternative of a hydroxo-bridged system (Fe–$(OH)_2$–Cr) cannot be excluded, however.

Visible and Infrared Spectra. The UV/visible spectra of the Cr–O–Fe derivatives are each characterized by a Soret band in the 420–430-nm region and two less intense bands near 560 and 600 nm (Table III). In addition, a point of inflection occurs at ca. 400 nm in each spectrum. This pattern of spectrum is found for complexes having dissimilar porphyrin groups attached to Cr and Fe (Figure 2) as well as for (TPP)CrOFe(TPP).[7] The corresponding M(III) chloro complexes have Soret bands with maxima at quite different wavelengths (e.g.: Cr(TPP)Cl, 447 nm; Fe(TPP)Cl, 417 nm; Cr(TCP)Cl, 448 nm; Fe(TCP)Cl, 418 nm; Cr(TMP)Cl, 451 nm; Fe(TMP)Cl, 416 nm), and this might suggest that the heterobinuclear oxo derivatives would show Soret-type absorption bands arising from the separate Cr and Fe porphyrin centers. However, the Soret bands of the more comparable μ-oxo homonuclear complexes $[Fe(TPP)]_2O$ (λ_{max} = 407 nm) and $[Cr(TPP)]_2O$ (λ_{max} = 412 nm)[30] occur at relatively similar wavelengths, and it is probable therefore that the single Soret bands observed for the heterobinuclear complexes represent the superposition of the transitions associated with the Cr(P) and Fe(P′) moieties.

A common feature in the infrared spectra of the complexes is a broad, medium–strong absorption band in the region of 845 cm^{-1} that is assigned to an asymmetric Cr–O–Fe stretching vibration (Table IV). This band is at 842.5 cm^{-1} for (TPP)CrOFe(TPP), with a shoulder appearing at 831.5 cm^{-1} that is obscured for the other complexes studied. ^{18}O labeling of the complex resulted in a spectrum that showed considerable decrease in the intensities of the 842- and 831-cm^{-1} bands, but the presence of strong porphyrin absorptions in the region of 700–800 cm^{-1} prevented clear definition of any new peaks. Nevertheless, an increased intensity could be observed in the band at 795.5 cm^{-1} relative to other absorptions in the region while a shoulder appeared at ca. 784 cm^{-1} (Figure 3). Isotopic shifts to these frequencies are qualitatively in agreement with those expected.

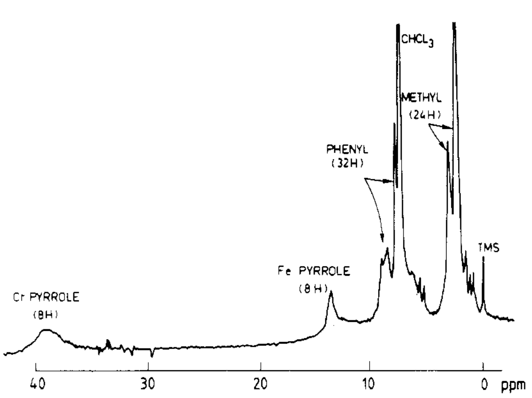

Figure 4. ^{1}H NMR spectrum of (TXP)CrOFe(TPP) ($CDCl_3$).

The bands assigned to asymmetric Fe–O–Fe stretching frequencies in (TPP)FeOFe(TPP) occur at 890.2 and 873.8 cm^{-1}, isotopic labeling studies having recently confirmed these assignments.[3] The compound considered to contain an Fe–O–Cu linkage isolated by Wilson et al.[3] had bands at the same frequencies as (TPP)FeOFe(TPP).

^{1}H NMR Spectra. The ^{1}H NMR spectrum of $[Fe(TPP)]_2O$ has resonances at −13.5 and −7.65 ppm that have been assigned to the pyrrole β and meso-phenyl protons, respectively.[31] The heterobinuclear complex (TPP)CrOFe(TPP) shows four distinguishable groups of resonances downfield from Me_4Si: viz. a broad resonance centered at ca. −38 ppm, a second broad resonance centered at ca. −13.9 ppm, a multiplet centered around −8.5 ppm, and a resonance at −7.63 pp. The features at −13.9 and −7.63 ppm are similar to those observed for $[Fe(TPP)]_2O$ although the resonance centered at −13.4 ppm in (TPP)CrOFe(TPP) is considerably broader than the corresponding peak of $[Fe(TPP)]_2O$. A sample of (TPP)CrOFe(OEP) although not obtained analytically pure showed corresponding resonances except for that in the −13 ppm region, supporting the assignment of this band to pyrrole β-hydrogen resonances.

The group of resonances centered at −8.5 ppm is comparable to those observed in the ^{1}H NMR spectra of Cr(TPP)X (X = Cl, I, N_3) in the region −7 to −8 ppm. The latter have been assigned to composites of meso-phenyl proton resonances,[32] and this assignment is suggested for the μ-oxo complex. The multiplets observed in the Cr(TPP)X compounds appear to be considerably broader than found for the CrOFe complex. The broad resonance centered at ca. −38 ppm is then associated with the pyrrole β-hydrogens of the Cr(TPP) moiety. This resonance is apparently too broad to be detected in the spectra of the Cr(TPP)X compounds.

The remaining heterobinuclear complexes examined (Table V) all show similar features. Broad resonances with a maxima in the range 37.4–38.6 ppm indicate the pyrrole β protons, and multiplets grouped around −8.5 ppm indicate meso-phenyl protons for the Cr porphyrin system together with the Fe porphyrin contributions in the region of −13.4 and −7.6 ppm. The −13.4 ppm resonance was found to be broad for several of the heterobinuclear complexes, but a sharper peak more like that given by $[Fe(TPP)]_2O$ was observed in (TXP)CrOFe(TPP) (Figure 4). Two methyl resonances are clearly observed for this complex, also suggesting that rotation is restricted about the meso C–phenyl bond.

Since the various ^{1}H resonances assigned to the Fe(P′) moieties have shifts comparable to those reported for homobinuclear $[Fe(P')]_2O$ complexes,[31] it implies that the effective electron spin at the Fe atoms is the result of similar strong magnetic coupling (as described in the magnetism section). Paramagnetic shifts for uncoupled $S = {}^5/_2$ Fe(III) porphyrin compounds such as Fe(T-

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(30) The preparation of the very air-sensitive complex $[Cr(TPP)]_2O$ by the reaction of CrO(TPP) and Cr(TPP) is described in part 2 of this series. Spectral features, λ_{max} (log ϵ) (benzene): 412 nm (4.88), 542 (3.79).

(31) (a) Nicholas, M.; Mustacich, R.; Jayne, D. *J. Am. Chem. Soc.* **1972**, *94*, 4518. (b) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63. (c) Boyd, P. D. W.; Murray, K. S. *J. Chem. Soc. A* **1971**, 2711.

(32) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6950.

Table V. ^{1}H NMR Spectral Data for Cr-O-Fe Porphyrin Complexes ($CDCl_3$, ppm)

	pyrrole		phenyl		
	Fe	Cr	Fe	Cr	methyl
(TPP)CrOFe(TPP)	−13.9	−37.8	−7.63	−8.4 to −8.9	
(TPP)FeOFe(TPP)	−13.5		−7.65		
(TTP)CrOFe(TPP)	−13.4	−37.4	−7.6	−7.9 to −8.5	−2.97
(TXP)CrOFe(TPP)	−13.4	−38.6	−7.66	−8.5 to −8.9	−2.92, −2.29
(TXP)FeOFe(TXP)	−13.8			−2.3, −2.6	
(TMP)CrOFe(TPP)	−13.4	−37.4	−7.6	ca. −8.3	−4.35
(TPP)CrOFe(TMP)	−13.7	−37.4	−7.2	−8.3 to −7.6	−4.35
(TPP)CrOFe(TCP)	−12.2	−38.6	−7.6	−8.4 to −9.1	
(TPP)CrOFe(OEP)	...	−40.0		−7 to −8	−1.6 (CH_3), −5.96, −5.03 (CH_2)

Table VI. Magnetic Moments of (P)Cr-O-Fe(P′) Compounds (μ_B/molecule)

	μ_{eff}- (300 K)	μ_{eff}- (4.2 K)		μ_{eff}- (300 K)
(TPP)CrOFe(TPP)	3.12	1.90	(TMP)CrOFe(TPP)	3.26
(TTP)CrOFe(TPP)	3.05	1.99	(TXP)CrOFe(TPP)	3.13
(TFP)CrOFe(TPP)	3.17	2.01	(TPP)CrOFe(TMP)	3.23
(TPP)CrOFe(TMP)	3.34	2.33	(TPP)CrOFe(TCP)	3.35

PP)Cl are much larger in magnitude on account of dipolar and contact contributions.

The detection of separate resonances from the Fe and Cr porphyrin moieties contrasts with the UV/visible spectra of these compounds, which do not show separate Soret bands for the Cr(P) and Fe(P′) segments.

The theory of paramagnetic shifts in complex homobinuclear systems[11,31] predicts that separate NMR resonances are likely to be observed in coupled heterobinuclear systems. Thus, for a proton H_1, which is part of the porphyrin group attached to Fe in the complex (H_1-P_1)FeOCr(P_2-H_2), the paramagnetic shift ΔH_1 will be the sum of the shifts due to interactions with both Fe and Cr; hence

$$\Delta H_1 = \frac{h}{g_n\beta_n}\left(A_{1,\mathrm{Fe}}\langle S_{1z}\rangle + A_{2,\mathrm{Cr}}\langle S_{2z}\rangle\right)$$

where $A_{1,\mathrm{Fe}}$ and $A_{2,\mathrm{Cr}}$ are the hyperfine constants for Fe and Cr. Even assuming that contact interactions with Cr are negligible, the equality for symmetrical dimers

$$\langle S_{1z}\rangle = \langle S_{2z}\rangle = \langle S_z'\rangle/2 \qquad S' = S_1 + S_2$$

does not hold true for asymmetrical dimers. This will also be true for a similar type of proton, H_2, attached to Cr(P_2). Hence, separate resonances would be expected with different values of A. The hyperfine coupling constants A for the various Fe(P) protons in the present complexes are similar to those in $[Fe(P)]_2O$ compounds.[31] Since the phenyl and methyl resonances of the Cr porphyrin segments occur at positions close to those of the free porphyrins as is the case for uncoupled Cr(P)X species,[32] the corresponding A parameters are presumably very small or zero. Assuming that the pyrrole β- resonances at ca. −38 ppm have been correctly assigned, this indicates nonzero A values for those sets of protons and/or a different orbital pathway between Cr pyrrole compared to Cr phenyl protons.

The temperature dependence of the observed shifts should, nevertheless, show the same behavior as the magnetic susceptibilities, and this remains an interesting future study. Complications could arise, however, if contributions to the observed shifts are not purely contact in origin (as implied in the above discussion) but have dipolar contributions. The latter could arise from magnetic anisotropy due to zero field splitting effects that are, in fact, clearly evident in the susceptibility data at very low temperatures.

Magnetic Susceptibilities and Mössbauer Spectra. The room-temperature magnetic moments of the μ-oxo-bridged complexes are given in Table VI. The values are in the range 3.0–3.4 μ_B per dimer unit, which is considerably less than the spin-only value of 7.07 μ_B expected for uncoupled $^5/_2$–$^3/_2$ systems.

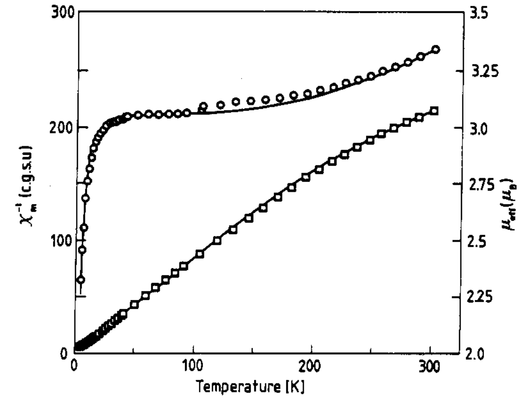

Figure 5. Magnetic moment (○) (per binuclear molecule) and reciprocal susceptibility (□) vs. temperature for (TPP)CrOFe(TMP). (Solid lines are calculated with parameters given in Table VII).

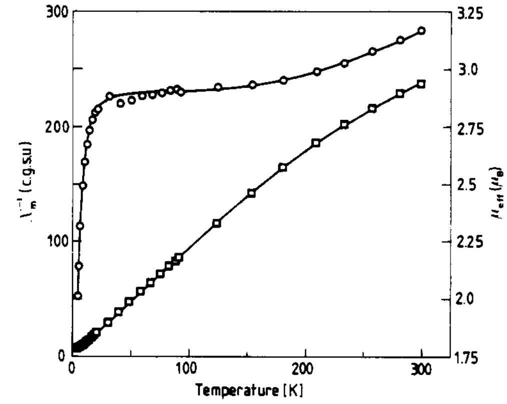

Figure 6. Magnetic moment (○) (per binuclear molecule) and reciprocal susceptibility (□) vs. temperature for (TFP)CrOFe(TPP). (Solid lines are calculated with parameters given in Table VII).

The variation in moments and susceptibility with temperature has been studied over the range 300–4.2 K for a series of four complexes. Some initial data for (TPP)CrOFe(TPP) have been previously reported.[7] The curves for the mixed-ligand heterobinuclear species (TPP)CrOFe(TMP) and (TFP)CrOFe(TPP) are shown in Figures 5 and 6. Attempts to explain the observed data in terms of a simple Heisenberg–Van Vleck isotropic coupling model[33] using eq 1 where $x = J/kT$ showed that the magnetic

$$\chi_m' = \frac{N\beta^2 g^2}{kT}\left[\frac{2\exp(-9x) + 10\exp(-7x) + 28\exp(-4x) + 60}{3\exp(-9x) + 5\exp(-7x) + 7\exp(-4x) + 9}\right] \quad (1)$$

behavior above 25 K could be satisfactorily explained by moderately strong antiferromagnetic coupling between Fe(III) ($s = {}^5/_2$) and Cr(III) ($S = {}^3/_2$) centers with a resultant $S' = 1$ ground state and J = ca. −150 cm^{-1}. The model, however, fails to predict

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[33] Wojiechowski, W. *Inorg. Chim. Acta* **1968**, *1*, 319.

Table VII. Magnetic Coupling Parameters for (P)Cr–O–Fe(P′) Compounds

	J, cm^{-1}	D_{Fe}, cm^{-1}	D_{Cr}, cm^{-1}	g_{Fe}	g_{Cr}	R,[a] %
(TPP)CrOFe(TPP)	−150	4.9	−1	2.01	1.95	1.21
(TTP)CrOFe(TPP)	−146	4.0	−1	1.98	1.98	0.65
(TFP)CrOFe(TPP)	−143	4.4	−1	2.01	2.01	0.70
(TPP)CrOFe(TMP)	−137	3.8	−1	2.05	1.90	1.05

[a] $R = [\Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}^2]^{1/2}$.

or explain the sharp decrease in μ_{eff} observed for each complex below 25 K.

Such sharp decreases in μ_{eff} at very low temperatures have been observed for a number of heterobinuclear complexes having paramagnetic ground states[34] and have been explained by postulating either weak interdimer antiferromagnetic coupling and/or zero field splitting, although few attempts have been made to fit the magnetic data obtained at such low temperatures. It may be noted that a number of high-spin Fe(III) porphyrin complexes[35,36] display quite large, axial zero field splittings, i.e. D = 5–17 cm^{-1}, while Cr(III) porphyrin derivatives, although less extensively studied,[32] display small values of D (<0.5 cm^{-1}).

Successful fits to the data have been obtained by the Hamiltonian shown in eq 2, which includes single zero field splitting terms for both metal ions (considered as Fe(III) $S = {}^5/_2$ and Cr(III) $S = {}^3/_2$) and allows for the magnetic field.

$$\mathcal{H} = -2J\hat{S}_1\hat{S}_2 + D_1(\hat{S}_{1z}^2 - {}^1\!/_3S_1^2) + D_2(\hat{S}_{2z}^2 - {}^1\!/_3S_2^2) + g_1\beta\hat{H}\hat{S}_1 + g_2\beta\hat{H}\hat{S}_2 \quad (2)$$

Preliminary fitting attempts established that J must lie in the range −100 to −200 cm^{-1} in order to reproduce the increase in μ_{eff} at temperatures above the plateau region. Varying J values within this range had little effect on the values of μ_{eff} in the "constant region" (around 100 K) or below 25 K. Further, only small positive values of D_{Fe} (ca. 4 cm^{-1}) could reproduce the rapid decrease with T below 25 K. The D_{Fe} parameter, however, had little effect above ca. 50 K. Variations in D_{Cr} in the range ±10 cm^{-1} showed negligible effects on the values of the moments or susceptibilities down to 4.0 K. A value of D_{Cr} of −1.0 cm^{-1} was therefore assumed by analogy with that measured for Cr(TPP)Cl·2CHCl$_3$ during the present study, viz. D = −1.5 ± 0.5 cm^{-1}. The insensitivity of the calculated data to variations in D_{Cr} results from the fact that for J = −150 cm^{-1} the observed zero field splitting at low temperatures will arise predominantly from splitting of the Fe(III) center. The values of g for Fe(III) and Cr(III) suitable for best fit were allowed to vary a little from the spin-only value of 2.00 in order to obtain the best fit, and values in the range 1.95–2.05 were obtained with that for Cr being just less than 2.0.

The least-squares fitting of the experimental data to the above Hamiltonian gave the parameters shown in Table VII. It is not possible to estimate the uncertainty in D_{Cr} although values outside the range (1.0 ± 1 cm^{-1}) seem unlikely. Fitting errors for the other parameters are assessed as g_{Fe} = ±0.01, g_{Cr} = ±0.02, D_{Fe} = ±0.2, and J = ±5. The rather large uncertainty in J arises in part from the small measured forces at the higher temperatures (e.g., in the 100–300 K range).

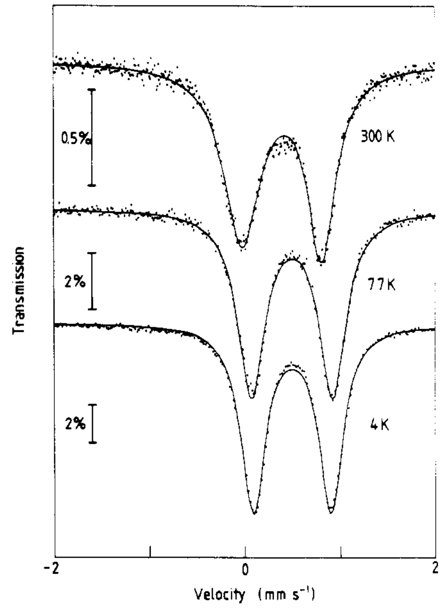

Figure 7. Mössbauer spectra of (TPP)CrOFe(TPP). (Solid lines represent fitted curves with the parameters given in Table VIII).

Table VIII. Mössbauer Spectral Parameters for μ-Oxo Chromium–Iron Porphyrin Compounds

	T, K	δ,[a] mm/s	ΔE, mm/s	Γ,[b] mm/s
(TPP)CrOFe(TPP)	4.2	0.49	0.82	0.15
	77	0.51	0.85	0.17
	295	0.39	0.84	Γ_1 0.24, Γ_2 0.19
(TTP)CrOFe(TPP)	77	0.50	1.11	0.16
(TPP)CrOFe(TMP)	77	0.50	1.11	0.17
(TPP)FeOFe(TPP)[39]	77	0.40	0.66	
	4.2	0.28	0.62	0.27[c]

[a] Relative to α-Fe at 295 K. [b] Line width Γ, half-width at half-maximum height (hwhm). [c] Fwhm.

It appears from Table VII that the calculated J values are relatively uninfluenced by changes in the porphyrin ligands and thus can be considered characteristic of the Cr–O–Fe linkage. The exchange coupling in this system can be compared to that in Fe–O–Fe and Cr–O–Cr by considering the total splittings. Thus, for (TPP)CrOFe(TPP), 18J = −2700 cm^{-1}, which is similar to that found[37] in [(NH$_3$)$_5$CrOCr(NH$_3$)$_5$]Br$_4$ for which 12J = −2700 cm^{-1} but less than that in (TPP)FeOFe(TPP)[38] for which 30J = ca. −3600 cm^{-1}.

The values for D_{Fe} appear to show a small but discernible dependence on the nature of the porphyrin group attached to Cr. The range of values observed falls outside the estimated fitting errors, but it is uncertain whether the differences are real or result from a combination of experimental and fitting errors. There is little doubt that a substantial, positive zero field splitting of the Fe^{III} ground state exists in these binuclear compounds. La Mar et al.[31] have concluded from the results of NMR studies of [Fe(TPP)]$_2$O that this molecule displayed zero field splitting although the experimental uncertainties were greater in that case.

The Fe(III)–O–Cu(II) complexes reported recently by Chang[5] and Wilson[3] show magnetic behavior that indicates moderate to weak coupling between metal centers, the strapped porphyrin complex described by Chang having a quintet–septet separation of −132 cm^{-1}.

The zero field Mössbauer spectra of three of the complexes have been obtained at 77 K and at 4.2 and 300 K for (TPP)CrOFe(TPP) (Table VIII; Figure 7). A single quadrupole-split doublet was observed for each complex at all temperatures examined. Taken together with the corresponding isomer shifts for the complexes, the data are characteristic of high-spin ($S = {}^5/_2$) Fe(III) systems. The Mössbauer spectrum of (TPP)CrOFe(TPP) at 77 K does not show magnetic broadening, unlike most high-spin Fe(III) porphyrin compounds, although some asymmetry was observed in the measurements at 300 K. In this regard it behaves

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(34) (a) Gunter, M. J.; Mander, L. N.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1981**, 799. (b) Berry, K. J.; Clark, P. E.; Gunter, M. J.; Murray, K. S. *Nouv. J. Chim.* **1980**, *4*, 581. Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J.; Jand, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585. (d) Julve, M.; Verdognier, M.; Charlot, M.-F.; Kahn, O.; Claude, R. *Inorg. Chim. Acta* **1984**, *82*, 5.

(35) Mitra, S. In "Iron Porphyrins"; Gray, H. B.; Lever, A. B. P., Eds.; Addison-Wesley: Reading, MA, 1982; Chapter 1.

(36) Gunter, M. J.; McLaughlin, G. M.; Berry, K. J.; Murray, K. S.; Irving, M.; Clark, P. E. *Inorg. Chem.* **1984**, *23*, 283.

(37) Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333.

(38) Fleischer, E. B.; Srivastava, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 2403.

like binuclear $[Fe(P)]_2O$ derivatives that have $S' = 0$ ground states.[39] Rapid spin relaxation within the $S' = 1$ state thus appears to be present in the Cr–O–Fe compounds so that only at higher temperatures, where some excited states are occupied, does any magnetic broadening occur.

An interesting feature of the Mössbauer spectra is the increase in quadrupole-splitting values observed between (TPP)CrOFe(TPP) having the same porphyrin attached to each metal and those having different porphyrins. This would imply that the Fe is sensing a small change in the ligand field symmetry caused by the (P)CrO moiety. The ΔE values observed in the (P)CrOFe(P′) compounds are higher than those generally observed for five-coordinate Fe(III) porphyrins.[39]

Synthesis of (μ-Oxo)[(tetraphenylporphyrinato)chromium(III)][(phthalocyaninato)iron(III)]. The Fe(II) phthalocyanine complex Fe(Pc) is less reactive toward oxygen than Fe(II) porphyrins, but the μ-oxo complex (Pc)FeOFe(Pc) is neverthelsss readily formed when Fe(Pc) in dimethylformamide reacts with oxygen.[40] This behavior, paralleling that of Fe(II) porphyrins, lead to an attempt to form a μ-oxo Cr–O–Fe derivative having chemically dissimilar ligands attached to each metal by reaction of CrO(TPP) with $Fe^{II}(Pc)$. Reaction was found to proceed smoothly in 1-chloronaphthalene, a solvent chosen for its ability to dissolve the phthalocyanine complex as well as the $Cr^{IV}O$ porphyrin. The μ-oxo complex (TPP)CrOFe(Pc) was obtained as a purple microcrystalline product. The compound is decomposed by aqueous HCl in 1-chloronaphthalene/benzene solution to form Cr(TPP)Cl (λ_{max} = 447 nm) and Fe(Pc)Cl (λ_{max} = 650 nm) in equimolar amounts. The complex is sparingly soluble in benzene and toluene and stable to dissociation or decomposition in the absence of oxygen, as are the porphyrin μ-oxo derivatives. It also decomposes in solution in benzene or toluene in the presence of oxygen, as do the porphyrin derivatives, yielding CrO(TPP) and $[Fe(Pc)]_2O$ as final products over a period of some hours. When a small amount of pyridine (10% by volume) was added to a toluene solution of the compound and the mixture exposed to air, the complex decomposed very rapidly, forming the products CrO(TPP)(py) (λ_{max} = 441, 561, 601 nm) and $Fe(Pc)(py)_2$, (λ_{max} = 415, 658 nm), which were detected by visible spectroscopy.

However, if the complex was first dissolved in pyridine and then the solution exposed to air, the visible absorption spectrum changed rapidly to display a mixture of absorption bands due to both $Fe(Pc)(py)_2$ and the pyridine adduct formed by $[Cr(TPP)]_2O$,[30] viz. $[Cr(TPP)(py)]_2O$ (λ_{max} = 420, 568 nm). The Soret band due to this latter species than slowly decreased over several hours as that due to the final product, CrO(TPP)(py), increased. It has been observed that $[Cr(TPP)]_2O$ reacts slowly with oxygen in pyridine whereas in toluene or other non-coordinating solvents oxidation to CrO(TPP) is rapid.[30]

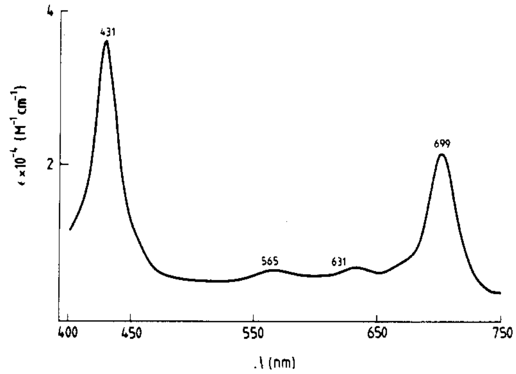

Figure 8. UV/Visible spectrum of (TPP)CrOFe(Pc) in 1-chloronaphthalene/benzene.

These observations may be rationalized in terms of the various reactions that can occur once an initial disproportionation has occurred:

$$(TPP)CrOFe(Pc) \rightarrow Cr^{IV}O(TPP) + Fe^{II}(Pc) \qquad (a)$$

$$2Fe^{II}(Pc) \xrightarrow{O_2} (Pc)FeOFe(Pc) \qquad (b)$$

In the presence of pyridine the further reactions c or d could occur,

$$Fe^{II}(Pc) + 2py \rightarrow Fe(Pc)(py)_2 \qquad (c)$$

$$(Pc)FeOFe(Pc) \xrightarrow{py} Fe(Pc)(py)_2 \qquad (d)$$

d having been reported by Ercolani et al.,[41] although the fate of the oxo group could not be determined. The initial formation of $[Cr(TPP)py]_2O$ in pure pyridine could arise from a parallel to reaction d occurring with (TPP)CrOFe(Pc) to give $Cr(TPP)(py)_2$ and $Fe(Pc)(py)_2$ followed by reaction of $Cr(TPP)(py)_2$ with oxygen to give $[Cr(TPP)(py)]_2O$ as a slowly oxidizing intermediate.[41]

The visible spectrum of the μ-oxo complex is shown in Figure 8. It displays absorption bands that can be associated with both the metalloporphyrin segment (λ_{max} = 431 nm; log ϵ = 4.56) and the metallophthalocyanine (λ_{max} = 699 nm; log ϵ = 4.34).

A band at a frequency suitable for assignment to an asymmetric Cr–O–Fe stretching frequency in the 800–850-cm^{-1} region has not been observed and may be hidden by strong ligand absorptions in the general region. Labeling experiments with ^{18}O will be required to further resolve this anomaly.

The complex has a magnetic moment of μ_{eff} = 3.12 μ_B per dimer, similar to that obtained for (TPP)CrOFe(TPP), which suggests that a strongly coupled $S = {}^5/_2$, $S = {}^3/_2$ dimer unit exists in the molecule as in the porphyrin derivatives.

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(40) (a) Ercolani, C.; Rossi, G.; Monacelli, F. *Inorg. Chim. Acta* **1980**, *44*, L215. (b) Ercolani, C.; Gardini, M.; Monacelli, F.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1983**, *22*, 2584.

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