The Formation of Heterobinuclear μ-Oxo Cr–O–Fe Porphyrin Complexes by the Reaction of Oxochromium(IV) and Iron(II) Porphyrins

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The reaction of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinato-oxochromium(IV) [(TPP)CrO] with $\alpha,\beta,\gamma,\delta$-tetraphenyl-porphinato-iron(II)bis(piperidine) in toluene results in the formation of the mixed-metal complex (TPP)Cr^{III}–O–Fe^{III}(TPP) characterised by chemical reactions and magnetic measurements [the metal ions are antiferro-magnetically coupled Fe $(S = {}^5/_2)$–Cr $(S = {}^3/_2)$]; similar μ-oxo compounds having dissimilar porphyrin ligands on each metal have also been prepared.

Spectroscopic and chemical evidence has been presented which strongly indicates that porphyrin iron(IV) (Fe^{IV}O) species can be stabilized in the presence of nitrogenous Lewis bases at low temperatures.[1] Such molecules are considered able to react with Fe^{II} porphyrins to form the well character-ised μ-oxo–Fe^{III} species.

We now report that the analogous chromium(IV) com-pounds, (P)Cr^{IV}O[2,3,4] (P = porphyrin dianion) can react with Fe^{II} porphyrins to form mixed-metal μ-oxo complexes of general formula (P^1)Cr^{III}–O–Fe^{III}(P^2). (P^1) and (P^2) are porphyrin ligands which may be the same or different depend-ing on the initial choice of (P^1)Cr^{IV}O and (P^2)Fe^{II}. These appear to be the first mixed-metal μ-oxo complexes to have been prepared.

Thus, mixing a red solution of (TPP)Cr^{IV}O [(TPP) = dianion of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin] in toluene with an orange solution of (TPP)Fe^{II}(pip)$_2$ (pip = piperidine) results in a rapid colour change to red–green. The course of the reaction can be monitored by observing the Soret bands of each initial complex [(TPP)Cr^{IV}O, 431 nm; (TPP)Fe^{II}, 422 nm] which gradually diminish over several hours at room temperature accompanied by the rise of a new major band at *ca.* 426 nm [equation (1)]. The newly formed complex can be

$$(\text{TPP})\text{CrO} + (\text{TPP})\text{Fe(pip)}_2 \rightarrow$$
$$(\text{TPP})\text{Cr–O–Fe(TPP)} + 2\text{pip} \qquad (1)$$
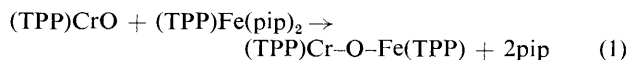
isolated from solution as a purple crystalline solid by the addition of hexane. Satisfactory elemental analyses were obtained after recrystallization from toluene–hexane (the product was heated *in vacuo* to remove traces of solvent before analysis). Its electronic absorption spectrum is shown in Figure 1: λ_{max}(toluene) (log ϵ) 403(sh), 424(5.01), 562(3.86), and 604(3.51) nm. An i.r. band at 842 cm^{-1} appears likely to be associated with the Cr–O–Fe linkage (Cr^{IV}–O absorbs at 1020 cm^{-1}).

The dinuclear identity of the complex has been confirmed by its reaction with aqueous HCl in toluene which causes
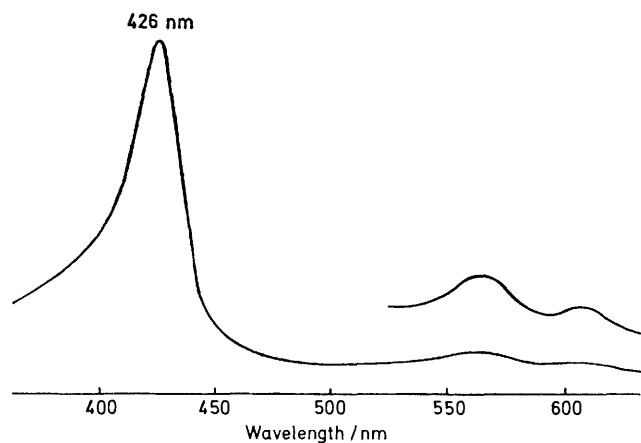
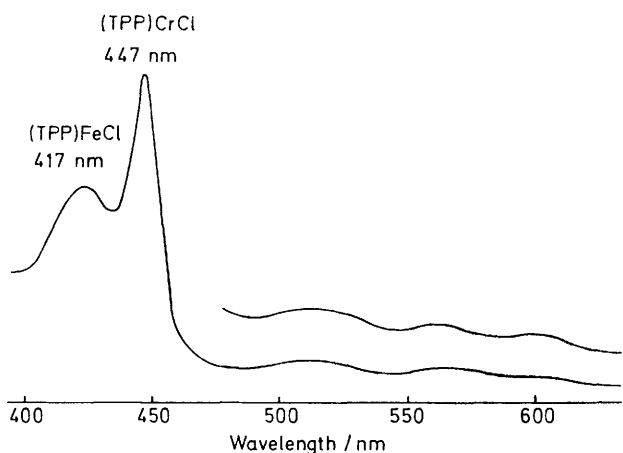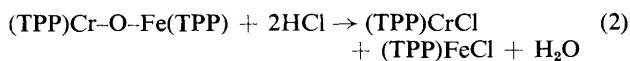Figure 1. The visible spectrum of (TPP)Cr–O–Fe(TPP) in toluene.

Figure 2. The visible spectrum of (TPP)Cr–O–Fe(TPP) following the addition of aqueous HCl to a toluene solution.

Figure 3. Variation of magnetic moment per molecule, ●, and reciprocal susceptibility per molecule, □, for (TPP)Cr–O–Fe-(TPP). Solid lines are calculated curves (i) in the region 30—300 K, using $g_{Fe} = g_{Cr} = 2.04$, $J = -153$ cm^{-1}; (ii) in the region 4.2—30 K, fitted to an intermolecular ($S' = 1$, $S' = 1$) dimer with $g = 2.14$, $J = -1.45$ cm^{-1}.

decomposition to the Cr^{III}–Cl and Fe^{III}–Cl porphyrin complexes each of which can be separately identified in the spectrum of the resulting mixture [(TPP)CrCl λ_{max}(toluene) (log ϵ) 447 (5.36), 564 (4.08), and 601 (3.97) nm; (TPP)FeCl λ_{max}(toluene) (log ϵ) 417 (5.16) and 510 (4.16) nm].

The ratio of intensities of the absorptions at 447 and 417 nm equals the ratio of extinction coefficients for the complexes at these wavelengths indicating that equivalent amounts of Cr^{III} and Fe^{III} species are formed in the reaction (Figure 2) [equation (2)].

$$\text{(TPP)Cr–O–Fe(TPP)} + 2\text{HCl} \rightarrow \text{(TPP)CrCl} \quad (2)$$
$$+ \text{(TPP)FeCl} + \text{H}_2\text{O}$$

The complex has a magnetic moment of 3.12 μ_B per dimer unit at 300 K. The temperature dependence of the reciprocal susceptibility and magnetic moment between 4.2 and 300 K is shown in Figure 3. The magnetic moment decreases from 3.12 μ_B at 300 K to 2.9 μ_B at ca. 150 K, remains approximately constant until ca. 20 K, and then decreases rapidly to 1.9 μ_B at 4.2 K. The magnetic behaviour in the range 20—300 K is that expected for a strongly antiferromagnetically coupled Fe^{III} ($S = {}^5/_2$)–Cr^{III} ($S = {}^3/_2$) pair in which the ground state $S' = 1$ is only populated below 150 K. A least-squares fit of the data in this temperature range to a simple Heisenberg model ($-2J\hat{S}_1.\hat{S}_2$) gave a good fit for the para-
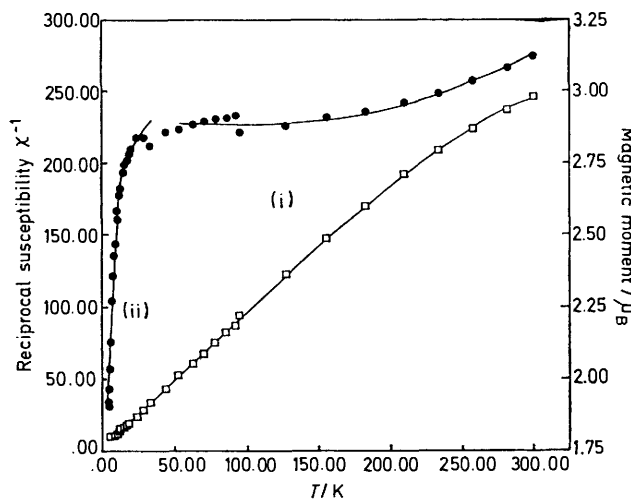
meters $g_{Fe} = g_{Cr} = 2.04$, $J = -153$ cm^{-1}. This intermolecular exchange–coupling constant lends further support to the postulated Cr–O–Fe bridge since J for the Fe^{III} ($S = {}^5/_2$)–Fe^{III} ($S = {}^5/_2$) couple[5] in [(TPP)Fe]$_2$O is -132 cm^{-1}. The analogous [(TPP)Cr]$_2$O complex has not yet been fully characterised[2,3] but other Cr–O–Cr bridged complexes[6] display J values of ca. -225 cm^{-1}. The rapid decrease in magnetic moment below 20 K could be due either to zero-field splitting of the $S' = 1$ ground state or to weak intermolecular, antiferromagnetic coupling occurring between neighbouring dinuclear molecules. We favour the latter interpretation since the reciprocal susceptibility (χ^{-1}) data show the beginning of a minimum at ca. 4 K (Figure 3) and the data from 4.2 to 30 K are well fitted by a ($S' = 1$)–($S' = 1$) coupled model for $J = -1.45$ cm^{-1} and $g = 2.14$. Similar magnetic plots to those shown in Figure 3 have recently been observed for other heterobinuclear macrocyclic complexes.[7]

Other complexes similar to the TPP derivative have been prepared by reactions between other (P)CrO compounds and (TPP)Fe^{II}(pip)$_2$, thus forming complexes with dissimilar porphyrin ligands attached to each metal. The complexes (TTP)Cr–O–Fe(TPP) and (TFP)Cr–O–Fe(TPP) have been obtained, analytically pure (TTP and TFP are the dianions of tetra-p-tolyl- and tetra-p-fluorophenyl-porphyrins, respectively). These compounds show similar reduced magnetic moments to those of the (TPP)Cr–O–Fe(TPP) complex.

The compounds appear to be indefinitely stable in the solid state but solutions in toluene show a slow decomposition to (P)Fe–O–Fe(P) and a Cr^{III} species when exposed to moist air. Similar redox reactions have not been observed between (P)CrO and (TPP)Co^{II}(N-MeIm) (N-MeIm = N-methyl-imidazole), (TPP)Mn^{II}(py) (py = pyridine), or (TPP)Mn^{II}.

(TPP)CrO was initially prepared by direct reaction of (TPP)Cr^{II} with dioxygen;[2] however in view of recent descriptions of the preparation of other (P)CrO complexes by direct oxidation of Cr^{III}–porphyrin compounds with iodosyl-benzene[3,8] or alkaline hypochlorite,[4] it is of interest to report that another synthetic route has led to the preparation of the chromium(IV) derivatives reported in this communication. Thus, solutions of (P)Cr^{III}Cl in CHCl$_3$ have been treated with aqueous HCl and the resulting mixture stirred for several days with access to air. Chromatography of the mixture on

basic Al_2O_3 allows the isolation of the appropriate chromium-(IV) derivative. The compounds (P)CrO (where P = dianions of tetra-p-chlorophenyl, tetra-3,5-xylyl, and tetra-p-methoxy porphyrins) have also been prepared by this route.

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