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## The Formation of Heterobinuclear $\mu$ -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  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphinato-iron(II)bis(piperidine) in toluene results in the formation of the mixed-metal complex (TPP)CrIII-O-FeIII(TPP) characterised by chemical reactions and magnetic measurements [the metal ions are antiferromagnetically coupled Fe ( $S = \frac{5}{2}$ )-Cr ( $S = \frac{3}{2}$ )]; similar  $\mu$ -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<sup>IV</sup>O) species can be stabilized in the presence of nitrogenous Lewis bases at low temperatures.<sup>1</sup> Such molecules are considered able to react with Fe<sup>II</sup> porphyrins to form the well characterised  $\mu$ -oxo-Fe<sup>III</sup> species.

We now report that the analogous chromium(iv) compounds, (P)Cr<sup>IV</sup>O<sup>2,3,4</sup> (P = porphyrin dianion) can react with Fe<sup>II</sup> porphyrins to form mixed-metal  $\mu$ -oxo complexes of general formula (P<sup>1</sup>)Cr<sup>III</sup>-O-Fe<sup>III</sup>(P<sup>2</sup>). (P<sup>1</sup>) and (P<sup>2</sup>) are porphyrin ligands which may be the same or different depending on the initial choice of (P<sup>1</sup>)Cr<sup>IV</sup>O and (P<sup>2</sup>)Fe<sup>II</sup>. These appear to be the first mixed-metal  $\mu$ -oxo complexes to have been prepared.

Thus, mixing a red solution of (TPP)Cr<sup>IV</sup>O [(TPP) = dianion of  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphyrin] in toluene with an orange solution of (TPP)Fe<sup>II</sup>(pip)<sub>2</sub> (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<sup>1V</sup>O, 431 nm; (TPP)Fe<sup>11</sup>, 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

$$(TPP)CrO + (TPP)Fe(pip)_2 \rightarrow$$
  
 $(TPP)Cr-O-Fe(TPP) + 2pip$  (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:  $\lambda_{max}$ (toluene) (log  $\epsilon$ ) 403(sh), 424(5.01), 562(3.86), and 604(3.51) nm. An i.r. band at 842 cm<sup>-1</sup> appears likely to be associated with the Cr–O–Fe linkage (Cr<sup>IV</sup>–O absorbs at 1020 cm<sup>-1</sup>).

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.

decomposition to the Cr<sup>111</sup>–Cl and Fe<sup>111</sup>–Cl porphyrin complexes each of which can be separately identified in the spectrum of the resulting mixture [(TPP)CrCl  $\lambda_{max}$ (toluene) (log  $\epsilon$ ) 447 (5.36), 564 (4.08), and 601 (3.97) nm; (TPP)FeCl  $\lambda_{max}$ (toluene) (log  $\epsilon$ ) 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)].

$$(TPP)Cr-O-Fe(TPP) + 2HCl \rightarrow (TPP)CrCl (2) + (TPP)FeCl + H_2O$$

The complex has a magnetic moment of 3.12  $\mu_{\rm B}$  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  $\mu_{\rm B}$  at 300 K to 2.9  $\mu_{\rm B}$  at *ca*. 150 K, remains approximately constant until *ca*. 20 K, and then decreases rapidly to 1.9  $\mu_{\rm B}$  at 4.2 K. The magnetic behaviour in the range 20–300 K is that expected for a strongly antiferromagnetically coupled Fe<sup>III</sup> ( $S = \frac{5}{2}$ )-Cr<sup>III</sup> ( $S = \frac{3}{2}$ ) pair in which the ground state S' = 1 is only populated below 150 K. A leastsquares 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-





**Figure 3.** Variation of magnetic moment per molecule,  $\bigoplus$ , and reciprocal susceptibility per molecule,  $\square$ , for (TPP)Cr–O-Fe-(TPP). Solid lines are calculated curves (i) in the region 30-300 K, using  $g_{\text{Fe}} = g_{\text{CT}} = 2.04$ , J = -153 cm<sup>-1</sup>; (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<sup>-1</sup>.

meters  $g_{\rm Fe} = g_{\rm Cr} = 2.04$ , J = -153 cm<sup>-1</sup>. This intermolecular exchange-coupling constant lends further support to the postulated Cr-O-Fe bridge since J for the Fe<sup>111</sup> (S =  $\frac{5}{2}$ )- $Fe^{111}$  (S =  $\frac{5}{2}$ ) couple<sup>5</sup> in [(TPP)Fe]<sub>2</sub>O is -132 cm<sup>-1</sup>. The analogous [(TPP)Cr]2O complex has not yet been fully characterised<sup>2,3</sup> but other Cr-O-Cr bridged complexes<sup>6</sup> display J values of ca. -225 cm<sup>-1</sup>. The rapid decrease in magnetic moment below 20 K could be due either to zerofield 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  $(\chi^{-1})$  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<sup>-1</sup> 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<sup>II</sup>(pip)<sub>2</sub>, 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<sup>III</sup> species when exposed to moist air. Similar redox reactions have not been observed between (P)CrO and (TPP)Co<sup>II</sup>(N-MeIm) (N-MeIm = N-methylimidazole), (TPP)Mn<sup>II</sup>(py) (py = pyridine), or (TPP)Mn<sup>II</sup>.

(TPP)CrO was initially prepared by direct reaction of (TPP)Cr<sup>II</sup> with dioxygen;<sup>2</sup> however in view of recent descriptions of the preparation of other (P)CrO complexes by direct oxidation of Cr<sup>III</sup>-porphyrin compounds with iodosylbenzene<sup>3,8</sup> or alkaline hypochlorite,<sup>4</sup> 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<sup>III</sup>Cl in CHCl<sub>3</sub> 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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