Copper–Dioxygen Reactivity Involved in the Formation of μ-oxo $[(por)Fe^{III}–O–Cu^{II}L]^+$ Heterodinuclear Complexes (por = porphyrinate, L = tetradentate ligand), and Novel Synthesis of Square-Planar $Fe^{II}(por)$ Species

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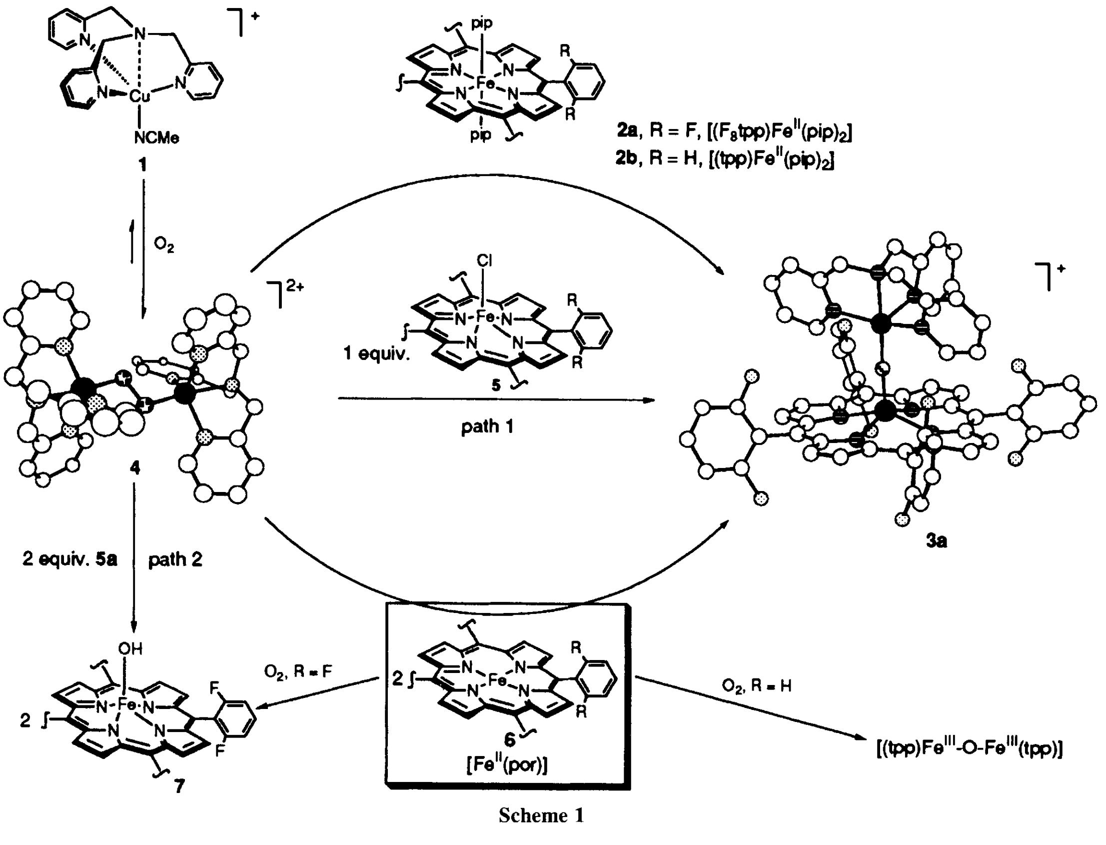
In the reaction of $Fe^{II}(por)$ species with $[LCu^{I}(MeCN)]^+$ and O_2 to give μ-oxo $[(por)Fe^{III}–O–Cu^{II}L]^+$ **3** (por = porphyrinate, L = tetradentate ligand), copper–dioxygen adducts or their decomposition products must be present, otherwise $[(por)Fe^{III}–OH]$ or $[(por)Fe^{III}–O–Fe^{III}(por)]$ products appear; a novel synthesis of square-planar $Fe^{II}(por)$ is also described.

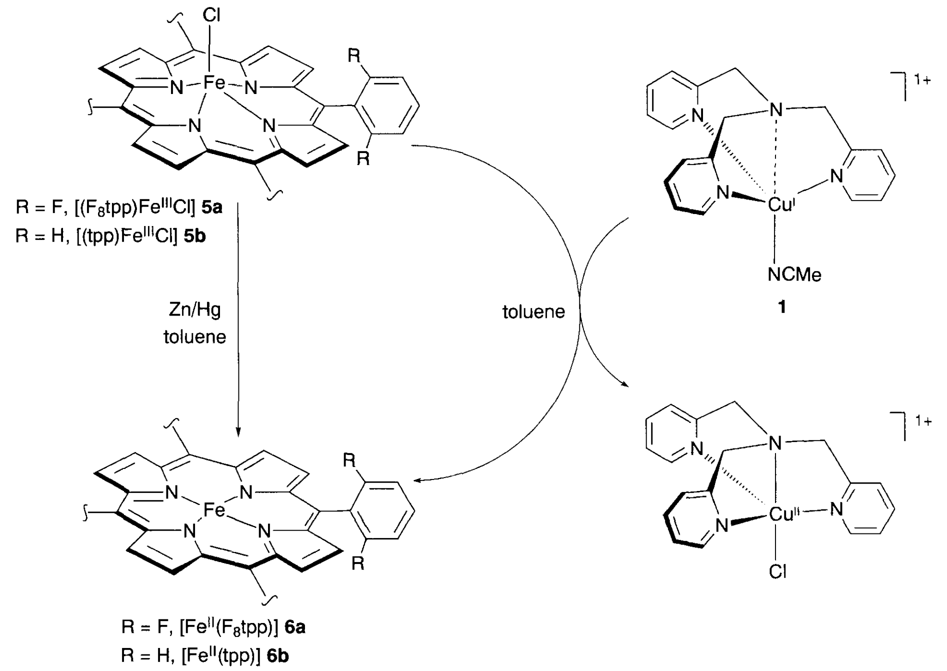
As part of our broad investigations of copper coordination chemistry relevant to dioxygen binding or activating copper proteins,[1] we have been interested in the haem–copper heterodinuclear active site implicated in the binding and reduction of dioxygen in the enzyme superfamily of cytochrome C and quinol oxidases.[2] Previously,[3] we showed that the reaction of O_2 with $[LCu^{I}(MeCN)]^+$ **1** {L = tris[(2-pyridyl)methyl]amine} (separately characterized as a reversible dioxygen-carrier)[4] and the porphyrin complexes $[(por)Fe^{II}(pip)_2]$ **2a** and **2b** (por = tetraarylporphyrinate; pip = piperidine) gave μ-oxo heterodinuclear complexes, completely characterized for $[(F_8tpp)Fe^{III}–O–Cu^{II}L]^+$ **3a**[3a] (Scheme 1). Labelling studies show that the μ-oxo oxygen atom is derived from O_2,[3] provoking questions about why **3** was generated in lieu of the typically observed $(por)Fe^{III}–O–Fe^{III}(por)$ product, the pertinent metal-O_2 chemistry and O–O cleavage reactions involved. Here, we report observations demonstrating how prior copper–dioxygen adduct formation is required in the formation of **3**. We also have discovered a novel route to the synthesis of highly reactive *S* = 1 planar porphyrinate–iron(II) species.

To probe the metal–complex O_2-reactions occurring in the transformation of $\mathbf{1} + \mathbf{2a} + O_2 \rightarrow \mathbf{3a}$ (Scheme 1), we carried out low-temperature (−80 °C) UV–VIS monitoring. We find that $[(F_8tpp)Fe^{II}(pip)_2]$ **2a** is itself unreactive towards O_2, and only the μ-1,2-peroxo dicopper(II) species $[(LCu)_2(O_2)]^{2+}$ **4** forms. This suggests the importance of prior copper–dioxygen chemistry in the formation of oxo complex $[(F_8tpp)Fe^{III}–O–Cu^{II}L]^+$ **3a**.†

We questioned whether **3** might also be generated by interception of $[(LCu)_2(O_2)]^{2+}$ **4** with porphyrinate–iron(III) complexes, or that such a reaction might possibly lead to heterodinuclear μ-peroxo $[(por)Fe^{III}–(O_2^{2-})–Cu^{II}(L)]$ intermediates.‡ We thus carried out reactions of **4** with $[(por)Fe^{III}Cl]$ **5**. Most interestingly, the nature of the product depends on the stoichiometry (Scheme 1). Reaction of **4** at −80 °C in CH_2Cl_2 with 1 equiv. of **5a** (Cu : Fe = 2 : 1; path 1), followed by warming and product isolation, gave only $[(F_8tpp)Fe^{III}–O–Cu^{II}L]^+$ **3a** in > 70% yield, as corroborated by UV–VIS and ^1H NMR spectroscopies; the fate of all the oxygen atoms involved in the reaction is not yet clear. On the other hand, when the stoichiometry of reaction involved **4** plus 2 equiv. of **5** (Cu : Fe = 2 : 2; path 2), oxidized and oxygen-atom containing complexes $[(F_8tpp)Fe^{III}–OH]$ **7**[6] or $[(tpp)Fe^{III}–O–Fe^{III}(tpp)]$ were the only products; the latter are known to be produced by oxygenation of the respective porphyrinate–iron(II) complexes. These observations can be explained, given that peroxo–dicopper(II) complex **4**, in equilibrium with 2 equiv. of $[LCu^{I}(MeCN)]^+$ **1**, can effect reduction of $[(por)Fe^{III}Cl]$ **5**. For path 1 (with Cu : Fe = 2 : 1), this reaction would yield a porphyrinate–iron(II) species, a copper(II) byproduct (*vide*



Scheme 1



Scheme 2

infra), **1** and O_2, in equimolar ratios, allowing a subsequent reaction similar to the originally observed process (Scheme 1). For path 2, complete reduction of **5** by **1** leaves copper(II) products insensitive to O_2, and porphyrinate–iron(II) species; the latter would react with dioxygen present in solution giving the iron products observed.

Supporting these conclusions are separate experiments showing that [LCu^I(MeCN)]$^+$ **1**, a strong reductant ($E_{1/2}$ = -0.61 V *vs.* Ag/Ag$^+$ in dimethylformamide),[7,8] is competent to reduce [(por)Fe^{III}Cl] **5**. Suspension of equimolar quantities of **1**[ClO$_4$] and [(F$_8$tpp)Fe^{III}Cl] **5a** (Scheme 2) in deaerated toluene under argon resulted in the immediate formation of a bright red solution and a quantitative amount of dark green solid, identified as the known complex [LCu^{II}Cl][ClO$_4$].[9] Filtration and addition of deaerated heptane yielded a new complex, the dark red microcrystalline toluene adduct [Fe^{II}(F$_8$tpp)]·C_7H_8 (**6a**·C_7H_8), which exhibits UV–VIS properties consistent with an 'in plane' iron(II)–porphyrin complex. The 'reversed' *meta*, *para* phenyl and upfield shifted pyrrole ^{1}H NMR (CD_2Cl_2) signatures§ of **6a** are consistent with the vacant $d_{x^2-y^2}$ orbital and S = 1 ground state previously demonstrated[10] for the analogous square-planar [Fe^{II}(tpp)] **6b**. By further analogy, we found that we could generate **6b** from **1** and [(tpp)FeCl] **5b**.¶ Compound **6a**·C_7H_8 could also be synthesized in high yield from the reduction of [(F$_8$tpp)Fe^{III}Cl] by Zn/Hg in toluene. In all likelihood, [Fe^{II}(por)] **6** is produced when adding [(por)-Fe^{III}Cl] **5** to [(LCu)$_2$(O$_2$)]$^{2+}$ **4** (path 1, Scheme 1) (*vide supra*); in fact, we do observe that [LCu^{II}Cl]$^+$ coprecipitates with μ-oxo product **3a**. In support of the observations cited for path 2 (Scheme 1), we find that reaction of **6a**·C_7H_8 with O_2 at room temperature gives almost exclusively [(F$_8$tpp)Fe^{III}–OH] **7**.

With highly reactive [Fe^{II}(F$_8$tpp)]·C_7H_8 (**6a**·C_7H_8) isolated, we wished to compare its behaviour with that of [(F$_8$tpp)Fe^{II}-(pip)$_2$] **2a**, in reactions with [LCu^I(MeCN)]$^+$ **1** and O_2. Surprisingly, we find that after generation of [(LCu)$_2$(O$_2$)]$^{2+}$ **4** and removal of excess O_2 *in vacuo* at -80 °C in CH_2Cl_2, UV–VIS spectroscopy reveals that **3a** is rapidly produced upon addition and dissolution of 2 equiv. of **6a**·C_7H_8; subsequent warming to 25 °C and addition of heptane allows isolation of solid **3a** ($\approx$70%) (Scheme 1). Previously, our thinking involving $\mathbf{1} + \mathbf{2} + O_2 \rightarrow \mathbf{3}$ was that the μ-peroxodicopper(II) complex **4** formed and probably decomposed homolytically (to a Cu^{II}–O· radical) during warming,[11] whereupon reaction with [(F$_8$tpp)Fe^{II}(pip)$_2$] **2a** ensued. The current observation of facile direct reaction of **4** (in the absence of excess O_2) with **6a** or **6b**, even at low temperature, suggests an alternative mode of reaction, namely Fe^{II}(por) outer-sphere reduction of **4** or reductive cleavage of the O–O bond. We cannot rule out, however, that **6a** may first react with O_2, the latter being derived from **4**.

In summary, the chemistry developed here provides new insights into the possible course of reaction and metal-dioxygen chemistry involved in the formation of μ-oxo Fe^{III}–O–Cu^{II} complex **3**, which as such, represents a crude functional model for the reductive cleavage of O_2 by haem–copper oxidases. Previous kinetic studies indicate that LCu^I combines with O_2 at rates comparable to porphyrinate–iron(II) complexes or haem proteins.[12] Here, we have shown that LCu^I, its O_2-adducts and/or their decomposition products (*e.g.* Cu–O·) must be present in order to obtain **3**, otherwise [(por)Fe^{III}–OH] or [(por)Fe^{III}–O–Fe^{III}(por)] products appear. As an aside, we have discovered a novel and very simple way to synthesize highly reactive S = 1 porphyrinate–iron(II) species **6**.‖ Most recently, we also observe that [(F$_8$tpp)Fe^{III}–O–Cu^{II}L]$^+$ **3a** is cleanly produced by the reaction of equimolar quantities of [LCu^I(MeCN)]$^+$ **1** and [Fe^{II}(F$_8$tpp)]·C_7H_8 (**6a**·C_7H_8) with dioxygen. Here, both LCu^I–O_2 and (por)Fe^{II}–O_2 reactivity are likely to be involved; future investigations will be directed towards a detailed understanding of such chemistry.

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Footnotes

† In contrast, [(tpp)Fe^{II}(pip)$_2$] **2b** is known to form a stable O_2-adduct at -80 °C (C. J. Weschler, D. L. Anderson and F. Basolo, *J. Am. Chem. Soc.*, 1975, **97**, 6707.

‡ A recent report describes such a species.[5]

§ *Data for* **6a**·C_7H_8: Analysis: Calc. for $C_{51}H_{28}F_8FeN_4$: C, 67.66; H, 3.09; N, 6.19. Found: C; 67.44; H, 3.52; 5.50. NMR ^{1}H (CD_2Cl_2): δ 3.8 (pyrrole), 11.3 (*m*-phenyl), 12.1 (*p*-phenyl), 7.2, 2.1 (toluene). UV–VIS (C_7H_8): Soret, 418, 440 (sh); 528, 558 nm.

¶ Identified by ^1H NMR (ref. 9); $[Fe^{II}(tpp)]$ ($[^2H_8]$toluene); δ 4.9 (pyrrole), 12.4 (*m*- and *p*-phenyl), 20.5 (*o*-phenyl).

‖ The analogous reaction with $[(oep)Fe^{III}Cl]$ (oep = octaethylporphyrinate) also occurs readily; $[Fe^{II}(oep)]$ ($[^2H_8]$toluene); δ 77.5 (*meso*-H), 38.6 (α-CH_2), 13.1 (β-CH_3). $[(F_8tpp)Mn^{III}Cl]$ (Soret band at 470 nm) is also reduced to a porphyrinate–manganese(II) complex (Soret band at 440 nm) with the addition of 1 equiv. of **1** in the presence or absence of dioxygen in dichloromethane at −70 °C.

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