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Stabilisation of μ -peroxido-bridged Fe(III) intermediates with non-symmetric bidentate N-donor ligands†

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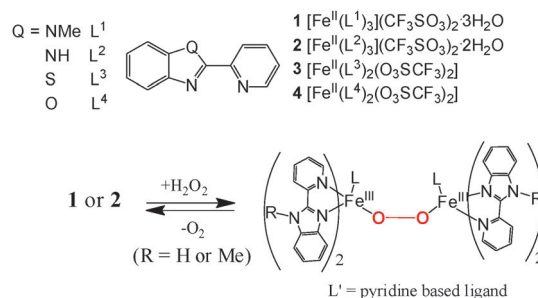
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The spectroscopic characterisation of the (μ -1,2-peroxido)diiron(III) species formed transiently upon reaction of [Fe(II)(NN)₃]²⁺ complexes with H₂O₂ by UV/vis absorption and resonance Raman spectroscopy is reported. The intermediacy of such species in the disproportionation of H₂O₂ is demonstrated.

Prominent examples of non-haem diiron enzymes that activate dioxygen in their metabolism¹ include soluble methane mono-oxygenase (SMMO), which hydroxylates methane,² the R2 subunit of ribonucleotide reductase (RNR R2), which generates a tyrosyl radical and fatty acid desaturases (Δ 9D).³ In these systems dioxygen activation involves peroxodiiiron(III) intermediates with characteristic ligand to metal charge transfer absorptions between 600 and 750 nm (SMMO,⁴ RNR R2⁵ and Δ 9D⁶) and stretching mode of the (μ -1,2-peroxido)diiron(III) core in their resonance Raman spectra (rR).^{5c,7} These intermediates typically convert into more reactive species before engaging in oxidation reactions. Hence, the factors that affect the stability, and intermediates formed from them, are of central importance both in understanding biological systems and in the development of biomimetic oxidation catalysts. The availability of semi-stable synthetic model compounds bearing the (μ -1,2-peroxido)diiron(III) core is therefore highly advantageous in obtaining spectroscopic data for comparison with enzymes and in understanding their reactivity. Typically, use is made of polydentate ligands with N-heterocyclic or mixed N-heterocyclic and aliphatic donor sets to form a range of oxygen activated complexes, e.g., Fe(III)-OOH, Fe(IV)=O, etc.^{8,9}

Bidentate ligands, such as 2,2'-bipyridyl, offer the possibility of forming binuclear (μ -1,2-peroxido) bridged Fe(III) complexes; however, generally such systems suffer from the formation of thermodynamically stable tris-ligated Fe(II) complexes (e.g., [Fe(bipy)₃]²⁺), which are essentially unreactive towards active oxygen species, except under forcing conditions. For example, the bidentate ligand bis(1-methylimidazol-2-yl)ketone (bik) can form the binuclear complex [Fe^{III}₂(bik)₄(μ -OH)₂]⁴⁺ but forms the blue [Fe^{II}(bik)₃]²⁺ species in methanol, spontaneously.¹⁰ Despite this, catalytic activity in the stereo-selective epoxidation of olefins with H₂O₂ has been demonstrated.¹⁰ Similarly, the homoleptic complex [Fe(L²)₃]²⁺, based on ligand L² (Scheme 1, *vide infra*),¹¹ has shown catalytic activity in the oxygenation of olefins by H₂O₂.¹² Similarly, an α -pinene modified bipyridine ligand was employed by Fontecave and Menage, which formed thermodynamically stable [Fe(NN)₂(CH₃CN)₂]²⁺ complexes and for which two distinct peroxy species were observed at low temperature upon addition of H₂O₂.¹³ These complexes were found to be active in (enantioselective) sulfoxidation reactions.¹⁴ Thus a complex that is predominantly in the [Fe(NN)₃]²⁺ form remains potentially capable of functioning as a model for non-haem oxygenases, albeit with, to the best of our knowledge, the detection of possible intermediates with oxidising agents, e.g., H₂O₂, ^tBuO₂H etc., has not been reported to date.

Here we show that a series of Fe(II) complexes based on the bidentate ligands L¹–L⁴ (Scheme 1)¹⁵ react with H₂O₂ to form



Scheme 1 Ligands L¹–L⁴ and schematic representation of the (μ -1,2-peroxido)-bridged intermediate formed.

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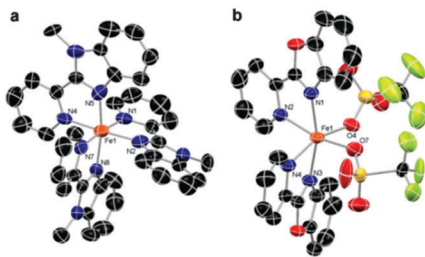


Fig. 1 X-ray structure of (a) **1** (CCDC 955599) and (b) **4** (CCDC 955600). Thermal ellipsoids are at 30% probability with H atoms omitted for clarity (see ESI† Fig. S1 and S2 for details).

intermediate (μ -1,2-peroxido)diiron(III) based complexes, which decompose to form oxygen and regenerate the Fe(II) complexes. In the case of **1** and **2**, the intermediate are sufficiently long lived at 298 K to allow for characterisation using UV/vis absorption and rR spectroscopy. The stability of the (μ -1,2-peroxido)-bridged species shows considerable dependence on both the heteroatom in the ligand and on the presence of pyridines and excess ligand.

The four hetero-bidentate ligands (Scheme 1) react spontaneously with Fe(II) salts to form thermodynamically stable red $[\text{Fe}^{\text{II}}(\text{NN})_3](\text{OTf})_2$ complexes, in the case of L^1 and L^2 , and neutral orange $[(\text{NN})_2\text{Fe}^{\text{II}}(\text{OTf})_2]$ complexes, in the case of L^3 and L^4 , even in a 3 : 1 ratio (see ESI† for details).¹⁶

Single crystals of complexes **1** and **4** suitable for structure determination were obtained from acetonitrile confirming their structure in the solid state (Fig. 1, see also Table S1, Fig. S1 and S2, ESI†). Complex **1** has Fe–N bond distances close to 2.0 Å, which are typical of low-spin Fe(II) complexes.¹⁷ The configuration is OC-6-21 (*mer*), which results in tetragonal distortion in the ligand field thus promoting a $|xy\rangle$ ground state (Fig. S1, ESI†).¹⁸ In **4** the Fe–N(O) bond distances are longer than 2.1 Å and are typical of high-spin Fe(II) complexes.¹⁹ Redox data for complexes **1** to **4** are listed in Table S4 (ESI†). Complexes **1** and **2** exhibit a quasi-reversible redox couple at *ca.* +0.85 and +0.90 V *vs.* Ag/AgCl, respectively (Table S4 and Fig. S17, ESI†). The irreversible reductions at potentials more negative than –1.0 V are assigned to ligand-centred one electron reductions (Fig. S17, ESI†). The Fe(III)/Fe(II) redox couples of **3** and **4** (Fig. S21 and S22, ESI†) are both irreversible and are at considerably higher potentials than for **1** and **2**, consistent with the electron withdrawing nature of O and S compared with NH and N–CH₃. The redox chemistry is essentially unaffected by addition of excess ligand; however water results in a complete loss in reversibility in the case of complexes **1** and **2**, which is consistent with the preference of the Fe(III) redox state for aqua over acetonitrile ligands (Fig. S18, ESI†).²⁰

For the $[\text{Fe}(\text{NN})_3]^{2+}$ complexes, **1** and **2**, an intense MLCT band is observed in the electronic absorption spectrum at ~500 nm that is typical of low-spin Fe(II) complexes.¹¹ The non-resonant Raman spectra of **1** and **2** in the solid state (Fig. S7, ESI†) and in solution (Fig. S8, ESI†) are essentially the same and show no significant effect of dilution, suggesting that the $[\text{FeL}_3]^{2+}$ structure is retained in solution. Surprisingly, the ¹H NMR spectra of both complexes in acetonitrile (Fig. S3, ESI†) are typical of high spin Fe(II) complexes, which is indicative of rapid ligand exchange with trace water present.

The effect of water on the cyclic voltammetry of the complexes, *i.e.* the irreversibility of the Fe(III)/Fe(II) redox couple (Fig. S18 and S19, ESI†), is in agreement with this assignment. Moreover, the addition of various substituted pyridines result in an increase in oxidation potential which correlates with the Hammett LFER (Fig. S6, ESI†). In contrast, **3** and **4** do not show absorption in the visible region, consistent with a high-spin electronic configuration.

Addition of H₂O₂ at room temperature to acetonitrile solutions of the complexes results in rapid changes in colour for all four complexes. In solution, **1** (Fig. 1) and **2** (Fig. S4, ESI†) change from red to green (λ_{max} = 685 nm (ϵ 1400 M^{–1} cm^{–1}) and 720 nm (ϵ 1360 M^{–1} cm^{–1}), respectively) upon addition of H₂O₂ with maintenance of isosbestic points throughout the reaction. The partial order in H₂O₂ (1st) and the complexes (also 1st) was determined (Tables S2 and S3, ESI†) with ΔH^\ddagger = 4.7 ± 0.3 kJ mol^{–1} and ΔS^\ddagger = –68 ± 9 J mol^{–1} K^{–1} for **1**, and ΔH^\ddagger = 5.1 ± 0.2 kJ mol^{–1} and ΔS^\ddagger = –57 ± 7 J mol^{–1} K^{–1} for **2**. Addition of excess ligand resulted in a slight red shift in the NIR absorption and the appearance of an additional absorption at 540 nm (Fig. S4, ESI†) albeit with relatively little effect on the reaction rate (Fig. S5, ESI†).

The species formed are stable for several minutes at room temperature and were characterised spectroscopically (*vide infra*), with the NIR absorption formed by **2** with H₂O₂ decreasing more rapidly than for **1**. The EPR spectra obtained by flash freezing solutions of **1** (Fig. S15, ESI†) and **2** (Fig. S16, ESI†) with H₂O₂, both after the NIR absorption has reached a maximum and after the absorption band disappeared, show trace levels of mononuclear high and low spin iron complexes, respectively. These data indicate that the species formed is an antiferromagnetically coupled binuclear Fe(III) complex and that once the H₂O₂ has been decomposed the complex returns to the Fe(II) redox state (Fig. 2).

Repeated addition of 3–10 eq. of H₂O₂ resulted in the reappearance of the NIR absorption bands for **1** and **2** (*e.g.* to 90% in the case of **2**). Addition of *p*-R-pyridine (R = CH₃, H, COC₆H₅, CN) to **2** resulted in a much faster decrease in the NIR absorption and a shift in λ_{max} to 680, 690, 728 and 720 nm with R = CH₃, H, COC₆H₅, CN, respectively. The initial rate of decrease of the NIR band showed a linear correlation with the change in oxidation potential (Fig. S21, ESI†) and the Hammett substituent parameters (σ = –1.98, Fig. S6, ESI†). These data indicate that the pyridines coordinate to the intermediate species with electron withdrawing groups stabilising the peroxide bridged species.

In contrast to **1** and **2**, complexes **3** and **4** did not yield detectable intermediates upon addition of H₂O₂. However, when H₂O₂ was added to the mixture of **3** and three equivalents of ligand L^3 at room temperature an absorption band was observed at 705 nm. The intensity of this band suggests ~20% conversion to an equivalent peroxido adduct, but its decomposition is rapid. Even with the added ligand, complex **4** yields only a minor transient increase in absorption in the NIR even with a gross excess of H₂O₂. These data highlight the sensitivity of the species formed with H₂O₂ to the heteroatom in the ligand (Q, Scheme 1).

rR spectroscopy at λ_{exc} 785 nm shows enhancement of bands at 876 and 473 cm^{–1} that are typical of a Fe(III)–O–O–Fe(III) core upon addition of H₂O₂ to solutions of **1** and **2**. The correspondence of the observed and calculated shifts in the bands at 876 cm^{–1} (to 826 cm^{–1})

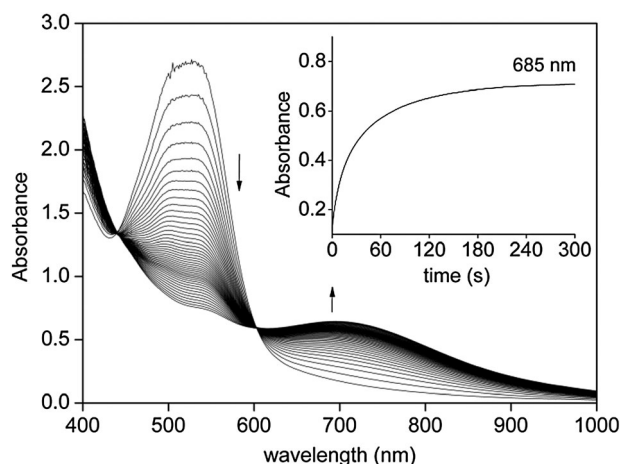


Fig. 2 Changes in the absorption spectrum of **1** (0.5 mM in CH₃CN) upon addition of H₂O₂ (10 eq.) at 20 °C.

and 473 cm⁻¹ (to 445 cm⁻¹) where H₂¹⁸O₂ (0.2% v/v in H₂¹⁶O) was employed, supports assignment of bands as the O–O and Fe–O stretching modes, respectively.^{13,21} The band position indicates an Fe–Fe bond length of 4 Å by comparison with earlier studies by Cranswick *et al.*⁹ and that the Fe(III) centres are connected solely by a μ -1,2-peroxido bridge (and not by an additional μ -oxido bridge). These bands appear and disappear concomitantly with the NIR absorption bands and the recovery of the Fe(II) species between additions of H₂O₂ can be seen in the bands at ca. 1600 cm⁻¹ (Fig. 3) and by the recovery of the redox wave at ca. 0.9 V (Fig. S22, ESI†). Furthermore, the UV/VIS spectrum of **2** (0.5 mM in CH₃CN) recovers to ~95% of its original absorbance after addition of 2 eq. H₂O₂ and decay of peroxide adduct. In Fig. 3 (Fig. S12, ESI†), the sequential addition of H₂¹⁸O₂ and,

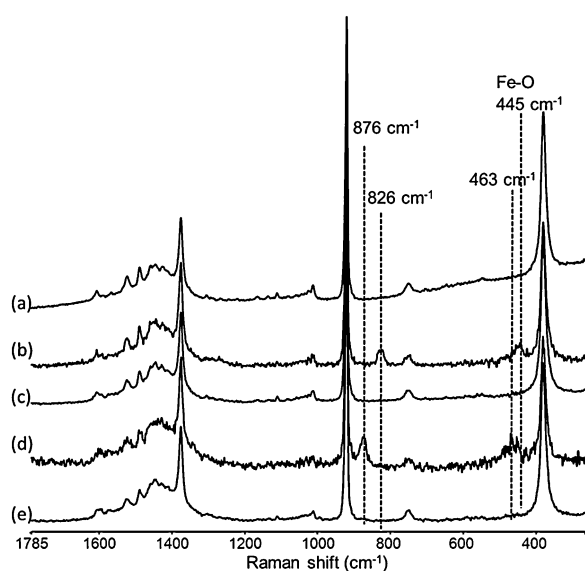


Fig. 3 Raman spectra of (a) **1** (6.5 mM) in CH₃CN, (b) 210 s and (c) 420 s after two eq. of H₂¹⁸O₂ was added, followed by (d) 180 s and (e) 390 s after addition of a 2nd two eq. of H₂¹⁶O₂. The expected shift for ν (O–O) is 50 cm⁻¹; observed 50 cm⁻¹, for ν (Fe–O) is 20 cm⁻¹; observed 18 cm⁻¹. Spectra are normalised to the solvent band at 919 cm⁻¹ (see ESI† Fig. S10 and S11 for expansion of low and high wavenumber regions).

following recovery of the Fe(II) state, H₂¹⁶O₂ shows that the complex can undergo multiple cycles and hence, exhibits catalase behaviour. The absence of additional ¹⁸O sensitive bands in the spectrum, although not conclusive, suggests that an Fe–O–Fe motif is not present in the H₂O₂ activated complex, consistent with monodentate coordination of pyridine ligands.

Although tris homoleptic iron(II) complexes are largely limited in their capacity to react with H₂O₂ directly, here we show that by tuning of the ligands σ -donor/ π -acceptor strength, the dissociation of one of the ligands is sufficiently facile to allow for reaction at a high rate in the disproportionation of H₂O₂. Although the [Fe(NN)₃]²⁺ are thermodynamically most stable an intermediate, assigned as having a Fe(III)– μ (O–O)–Fe(III) core based on the absence of EPR signals at 77 K and characteristic bands in their rR spectra, is observed. The stability of the intermediate formed in each case shows a strong dependence both on the non-coordinating heteroatom in ligands L¹–L⁴ and on the presence of coordinating substituted pyridines. Given the relative ease of synthesis and diversity of bidentate ligands available of these types it is expected that both the stability and the reactivity of H₂O₂ activated complexes such as these can be tuned widely.

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