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Characterization of low-spin ferric hydroperoxo complexes with *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane

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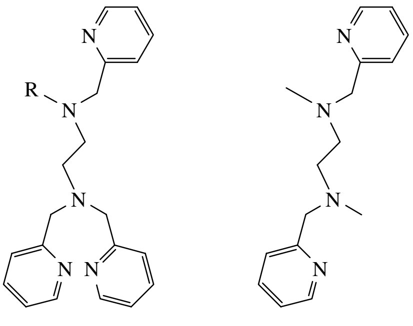
Hydroperoxo intermediates formed by the interaction of $[\mathrm{Fe^{II}(BPMEN)(MeCN)_2}](\mathrm{ClO_4})_2$ [BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane] with $\mathrm{H_2O_2}$ in a $\mathrm{CH_2Cl_2}$–MeCN mixture were characterised using EPR spectroscopy.

The catalytic system $[\mathrm{Fe^{II}(BPMEN)(MeCN)_2}](\mathrm{ClO_4})_2$ **1** + $\mathrm{H_2O_2}$ in MeCN [BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane] (Scheme 1) is a very rare example of non-heme iron catalyst/$\mathrm{H_2O_2}$ combination capable of selective olefin epoxidation, and the first example of an MMO model system that is useful for preparative oxidation chemistry.[1,2] It is assumed that the mononuclear hydroperoxo species $[\mathrm{Fe^{III}(BPMEN)(OOH)L}](\mathrm{ClO_4})_2$, where L = MeCN or $\mathrm{H_2O}$, is the active species (or their closest precursor) of this catalytic system.[3] However, there are no data on the characterization and kinetic studies of hydroperoxo intermediates in BPMEN-based systems. Recently, we have reported the stability and reactivity of low-spin ferric hydroperoxo and alkylperoxo complexes with tris(2-pyridylmethyl)amine (TPA) and concluded that $[\mathrm{Fe^{III}(TPA)(OOH)L}](\mathrm{ClO_4})_2$ mononuclear hydroperoxo intermediates can hardly play an essential role in the selective oxidations of hydrocarbons by the $[\mathrm{Fe^{II}(TPA)(MeCN)_2}](\mathrm{ClO_4})_2/\mathrm{H_2O_2}$ catalytic system. The actual reactive species (or their precursors) might be EPR silent binuclear species like $[\mathrm{(TPA)(HOO)Fe^{III}{-}O{-}Fe^{III}(TPA)(H_2O)}](\mathrm{ClO_4})_3$.[4] It is interesting to study the more effective and practically promising **1**/$\mathrm{H_2O_2}$ system. Here we report the characterization of low-spin mononuclear hydroperoxo intermediates formed in the **1**/$\mathrm{H_2O_2}$ system.



BZTPEN: R = $\mathrm{CH_2Ph}$
TPEN: R = 2-pyridylmethyl

BPMEN

Scheme 1

Initial complex **1** is stable in acetonitrile solution in air.[†] In agreement with earlier data,[1,2] the **1**/$\mathrm{H_2O_2}$ catalytic system can oxidise cyclohexene mainly to cyclohexene oxide (selectivity, ~70%; [**1**] = 0.03 mol dm^{-3}, $[\mathrm{H_2O_2}] = [\mathrm{C_6H_{10}}] = 1$ mol dm^{-3}, 20 °C, MeCN). The ^{1}H NMR spectrum of **1** in $\mathrm{CD_3CN}$ at 65 °C corresponds to a paramagnetic high-spin ferrous complex.[‡] As reported previously,[3] complex **1** reduces its electron spin with decreasing temperature and displays an ^{1}H NMR spectrum characteristic of diamagnetic low-spin ferrous species at –40 °C.

The addition of 2–3 equiv. of $\mathrm{H_2O_2}$ to a 0.03 M solution of **1** in $\mathrm{CD_3CN}$ at 20 °C gives rise to an immediate conversion of the major part of **1** into antiferromagnetically coupled μ-oxo dimeric complex **2**. The ^{1}H NMR spectrum of **2** is characteristic of $\mathrm{Fe_2^{III}}$ (μ-O) complexes, and it is very similar to that of the μ-oxo dimeric complex $[\mathrm{(OH)(BPMEN)Fe^{III}{-}O{-}Fe^{III}(BPMEN)(H_2O)}](\mathrm{ClO_4})_3$, which was independently prepared as described previously.[5] Thus, the major part of iron exists in the **1**/$\mathrm{H_2O_2}$ catalytic system in the form of μ-oxo binuclear complex **2** with the proposed structure $[\mathrm{(OH)(BPMEN)Fe^{III}{-}O{-}Fe^{III}(BPMEN)(H_2O)}](\mathrm{ClO_4})_3$.

To observe very unstable hydroperoxo intermediates, we used a 2:1 $\mathrm{CH_2Cl_2}$/MeCN mixture instead of acetonitrile as a solvent. The addition of $\mathrm{CH_2Cl_2}$ allowed us to lower the reaction temperature (down to –70 °C) without freezing and provided sharper EPR resonances in frozen solutions spectra (–196 °C). This effect can be attributed to the formation of a better glass upon freezing.

The EPR spectrum of the solution frozen immediately after the addition of 2 equiv. of $\mathrm{H_2O_2}$ to a 0.03 M solution of **1** in a 2:1 $\mathrm{CH_2Cl_2}$/MeCN mixture at –60 °C displays mainly signals from low-spin ferric species **3** and high-spin ferric species **4** [peaks near $g = 2$ and $g = 4$, respectively, Figure 1(*a*)]. Low-spin ferric complexes **3** are very unstable and rapidly disappear even at –60 °C to afford more stable low-spin species **5** [Figure 1(*b*)].

Figure 2 shows the EPR spectra of intermediates **3** obtained (*a*) 1 min and (*b*) 10 min after sample preparation at –70 °C. It is seen that two types of intermediates **3** are formed. At the early stage of reaction, an intermediate with $g_1 = 2.218$, $g_2 = 2.178$ and $g_3 = 1.967$ dominates in the reaction solution [Figure 2(*a*)], then the fraction of another intermediate with $g_1 = 2.195$, $g_2 = 2.128$ and $g_3 = 1.970$ increases [Figure 2(*b*), the accuracy of the measured *g*-values was ±0.003]. A similar spectrum was observed earlier for the $[\mathrm{Fe^{II}(TPA)(MeCN)_2}](\mathrm{ClO_4})_2/\mathrm{H_2O_2}$ catalytic system.[4] By analogy with the TPA-based

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[†] *Experimental details.* Acetonitrile, [^{2}H$_3$]acetonitrile, dichloromethane, 2-picolyl chloride hydrochloride and *N,N'*-dimethyl-1,2-ethanediamine from Aldrich were used without additional purification. 95% hydrogen peroxide was obtained by concentration of commercial 30% $\mathrm{H_2O_2}$ under reduced pressure. The concentrated $\mathrm{H_2O_2}$ diluted ten times by $\mathrm{CH_2Cl_2}$ was used for the preparation of samples. X-ray quality crystals of $[\mathrm{Fe^{II}(BPMEN)(MeCN)_2}](\mathrm{ClO_4})_2$ **1** were obtained by a modified procedure.[2]

To start the reaction, 1–2 equiv. of $\mathrm{H_2O_2}$ were added to 0.5 ml of a 0.03 M solution of **1** in a 2:1 $\mathrm{CH_2Cl_2}$/MeCN mixture at –70 °C directly in quartz EPR tubes (*d* = 5 mm). For kinetic studies, solutions containing unstable intermediates in EPR tubes were placed in a thermostat. To stop the reaction, the EPR tube was immersed in liquid nitrogen, followed by the measurement of the EPR spectrum at –196 °C. If necessary, appropriate amounts of cyclohexene were added to solutions containing **1**. The yield of the reaction products was measured using a GS-MS Varian Saturn 2000 machine.

EPR spectra (–196 °C) were recorded at 9.2–9.3 GHz on a Bruker ER-200 D spectrometer. They were simulated using an extended version of the EPR1 program.[14] The dual EPR cavity furnished with the spectrometer was used. A periclase crystal (MgO) with impurities of $\mathrm{Mn^{2+}}$ and $\mathrm{Cr^{3+}}$ served as a side reference. EPR signals near $g = 2$ were quantified by double integration with copper(II) chloride as a standard at –196 °C. The EPR signal at $g = 4$ was quantified by double integration with the reference, acidic solution of $[\mathrm{Fe(EDTA)H_2O}]^-$ prepared from an appropriate amount of $\mathrm{(NH_4)Fe(SO_4)_2{\cdot}12H_2O}$ with an excess of $\mathrm{Na_2H_2EDTA}$.

^{1}H NMR spectra were recorded on a Bruker DPX-250 NMR instrument at 250.13 MHz in 5 mm NMR tubes.

[‡] ^{1}H NMR spectrum of **1** ([^{2}H$_3$]acetonitrile, +65 °C) δ: 133.9 (2H, $\Delta\nu_{1/2}$ 160 Hz, CH*H*–CH*H*), 100.6 (2H, $\Delta\nu_{1/2}$ 110 Hz, C*H*H–C*H*H), 68.3 (6H, $\Delta\nu_{1/2}$ 155 Hz, Me), 48.9 (2H, $\Delta\nu_{1/2}$ 370 Hz, C*H*H–N), 43.9 (2H, $\Delta\nu_{1/2}$ 55 Hz, picolynic H), 40.0 (2H, $\Delta\nu_{1/2}$ 50 Hz, picolynic H), 36.5 (2H, $\Delta\nu_{1/2}$ 220 Hz, CH*H*–N), 19.1 (2H, $\Delta\nu_{1/2}$ 240 Hz, picolynic H), –3.1 (2H, $\Delta\nu_{1/2}$ 65 Hz, picolynic H).

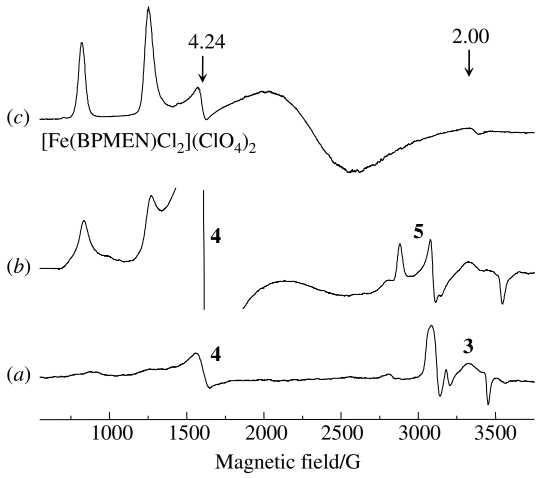

Figure 1 (*a*) X-band EPR spectrum (–196 °C) of unstable species formed just after the onset of the reaction of **1** ([**1**] = 0.03 mol dm^{-3}) with 2 equiv. of H_2O_2 at –60 °C in a 2:1 CH_2Cl_2/MeCN mixture. (*b*) Spectrum of sample in (*a*) (–196 °C) 5 min after storage at –50 °C, and (*c*) after completion of the reaction.

system, we assign the EPR spectrum ($g_1 = 2.218$, $g_2 = 2.178$ and $g_3 = 1.967$) to [Fe^{III}(BPMEN)(OOH)MeCN](ClO$_4$)$_2$ (**3**-MeCN) and EPR spectrum ($g_1 = 2.195$, $g_2 = 2.128$ and $g_3 = 1.970$) to [Fe^{III}(BPMEN)(OOH)H_2O](ClO$_4$)$_2$ (**3**-H_2O) (Table 1). The *g*-factors of **3**-MeCN and **3**-H_2O are highly characteristic of mononuclear low-spin ferric hydroperoxo intermediates and markedly differ from those for low-spin ferric hydroxo or alkoxo species.[6–8] Direct preparation of **3**-H_2O by the addition of a great excess of H_2O to the reaction mixture was complicated by rapid decomposition of **3**-H_2O and low solubility of H_2O in CH_2Cl_2/MeCN (2:1) at low temperatures. However, the addition of related O-donor base MeOH ([MeOH] = 3 mol dm^{-3}) to the reaction mixture at –70 °C results in an increase in the relative intensities of peaks at $g = 2.128$ and 2.195 belonging to **3**-MeOH, thus supporting our assignment of peaks of **3**-H_2O (Table 1).

3-MeCN decays at –60 °C with a half-life time ($\tau_{1/2}$) of 5 min. **3**-H_2O is even less stable at this temperature ($\tau_{1/2} < 2$ min). The addition of cyclohexene (1 mol dm^{-3}) to a solution containing **3** ([**3**] = 0.001 mol dm^{-3}) at –60 °C does not noticeably change the rate of self-decomposition of **3**.

The independent study of the decay of **3**-MeCN and **3**-H_2O is possible only if the time of establishing the equilibrium

$$\mathbf{3}\text{-}H_2O + MeCN \rightleftharpoons \mathbf{3}\text{-MeCN} + H_2O \qquad (1)$$

is noticeably longer than the characteristic time of decay. This condition is reasonable at –60 °C. According to our previous data, the equilibrium between the related low-spin alkylperoxo intermediates [Fe(bpy)$_2$(OOBu^t)MeCN)]$^{2+}$ and [Fe(bpy)$_2$(OOBu^t)-H_2O]$^{2+}$ is established within 5–10 min at –35 °C in MeCN.[9]

The EPR spectrum of complex **5** [$g_1 = 2.37$, $g_2 = 2.20$ and $g_3 = 1.92$, Figure 1(*b*)] is very similar to that of [Fe^{III}(BZTPEN)-(OH)]$^{2+}$ or [Fe^{III}(TPEN)(OH)]$^{2+}$ ($g_1 = 2.39$, $g_2 = 2.19$ and $g_3 = 1.91$; the structures of BZTPEN and TPEN ligands are shown in Scheme 1).[10] It is reasonable to assume that **5** is a ferric hydroxo complex. To be low-spin, it should contain a solvent molecule L at the sixth coordination site and could be represented as [Fe^{III}(BPMEN)(OH)L](ClO$_4$)$_2$, where L = MeCN or H_2O.

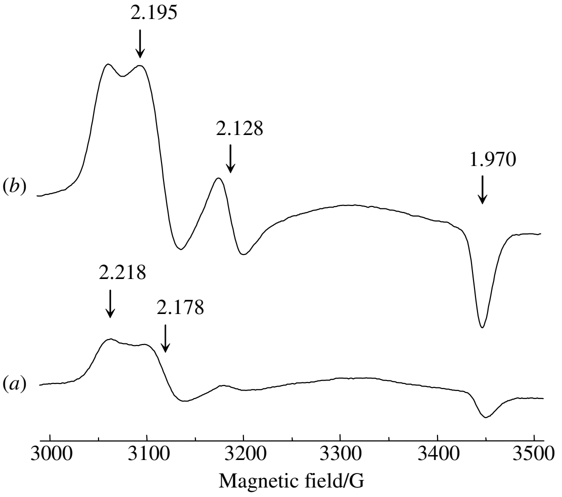

Figure 2 X-band EPR spectrum (–196 °C) of species **3** recorded (*a*) 1 and (*b*) 10 min after mixing **1** and H_2O_2 at –70 °C in a 2:1 CH_2Cl_2/MeCN mixture ([**1**] = 0.03 mol dm^{-3}, [H_2O_2] = 0.06 mol dm^{-3}).

The EPR spectra of low-spin hydroperoxo complexes **3** and hydroxo complex **5** could be reasonably assigned due to highly characteristic anisotropy of their *g*-factors, whereas the nature of complex **4** is less evident. Complex **4** could be attributed to a high-spin counterpart of low-spin complex **5** with vacant sixth coordination site [Fe^{III}(BPMEN)(OH)](ClO$_4$)$_2$.

Concentrations of complexes **3**–**5** do not exceed 1–5% of the total iron concentration. Species **3**–**5** convert with time mainly into EPR-silent species (probably, μ-oxo dimers **2**). After completion of the reaction with H_2O_2 in the sample of Figure 1(*a*), the EPR spectrum of a new complex was observed at $g = 8.24$, 5.36, 2.70 [Figure 1(*c*)]. This spectrum coincides with that of [Fe^{III}(BPMEN)Cl$_2$]$^+$ reported earlier.[11] The chlorinated solvent CH_2Cl_2 could be the source of Cl ligands. The concentration of [Fe^{III}(BPMEN)Cl$_2$]$^+$ does not exceed 5% of the total iron concentration, and the major part of iron exists in a 2:1 CH_2Cl_2/MeCN mixture in the form of binuclear EPR-silent complex **2**, as in the case of a neat MeCN solvent.

Note that no EPR-active unstable species were detected when fresh portions of H_2O_2 were added to the samples of Figure 1(*a*) at –60 °C after completion of the reaction with the first 2 equiv. of H_2O_2. Thus, unstable species **3**–**5** are formed in detectable amounts only *via* the reaction of H_2O_2 with **1** rather than **2**.

The data presented show that very unstable low-spin hydroperoxo species [Fe^{III}(BPMEN)(OOH)MeCN](ClO$_4$)$_2$ (**3**-MeCN) and [Fe^{III}(BPMEN)(OOH)H_2O](ClO$_4$)$_2$ (**3**-H_2O) could be detected in the **1**/H_2O_2 catalytic system. However, species **3** are not the active intermediates (or their precursors) of the test catalytic system. Complexes **3** could be detected only at the early stage of the reaction of **1** with H_2O_2. All our attempts to recover **3** by the addition of fresh portions of H_2O_2 to the solution containing mainly μ-oxo dimeric species **2** were unsuccessful. Hence, mononuclear hydroperoxo complexes **3** are not regenerated in a detectable amount in the catalytic cycle.

Table 1 EPR spectroscopic data (–196 °C) for ferric species formed in the **1**/H_2O_2 catalytic systems in comparison with those for related complexes.

Complex		Solvent	g_1	g_2	g_3
[Fe(BPMEN)(OOH)MeCN](ClO$_4$)$_2$ (**3**-MeCN)	LS	MeCN/CH_2Cl_2	2.218	2.178	1.967
[Fe(BPMEN)(OOH)H_2O](ClO$_4$)$_2$ (**3**-H_2O)	LS	MeCN/CH_2Cl_2	2.195	2.128	1.970
[Fe(BPMEN)(OOH)MeOH](ClO$_4$)$_2$ (**3**-MeOH)	LS	MeCN/CH_2Cl_2	2.195	2.128	1.970
[Fe(TPA)(OOH)MeCN](ClO$_4$)$_2$[a]	LS	MeCN/CH_2Cl_2	2.194	2.152	1.970
[Fe(TPA)(OOH)H_2O](ClO$_4$)$_2$[a]	LS	MeCN/CH_2Cl_2	2.19	2.12	1.97
[Fe(BPMEN)(OH)L](ClO$_4$)$_2$ **5**	LS	MeCN/CH_2Cl_2	2.37	2.20	1.92
[Fe^{III}(BZTPEN)(OH)]$^{2+}$ [b]	LS	MeCN	2.39	2.19	1.91
[Fe^{III}(TPEN)(OH)]$^{2+}$ [b]	LS	MeCN	2.39	2.19	1.91
[Fe(BPMEN)(OH)](ClO$_4$)$_2$ **4**[c]	HS	MeCN/CH_2Cl_2	4.52	4.31	4.14

[a]Ref. 4. [b]Ref. 11. [c]Complex **4** exhibits weak signals near $g = 8$ and $g = 5$ along with an intense anisotropic peak near $g = 4$.

For the Fe^{III} state, oxo-bridged binuclear species are well known to be thermodynamically favourable.[12] It is reasonable to expect that complex **1** reacts with H_2O_2 to afford mononuclear hydroperoxo complexes **3** only at the early stage of the reaction of **1** with H_2O_2. After this, only oxo-bridged dimeric species become accessible to coordination by the hydroperoxo moiety. Thus, the actual precursor of the active species of the **1**/H_2O_2 catalytic system could be EPR-silent binuclear μ-oxo ferric hydroperoxo complex $[(BPMEN)(HOO)Fe^{III}–O–Fe^{III}(BPMEN)L](ClO_4)_3$ **6** rather than mononuclear complex **3**. Unfortunately, we have no spectroscopic evidence for the formation of **6** in the **1**/H_2O_2 catalytic system.

Mekmouche *et al.*[13] used enantioselective sulfoxidation by H_2O_2 as a probe for comparison between mono- and binuclear iron catalysts. Whereas both systems formed peroxoiron intermediates as active species, the binuclear one proved to be more efficient and selective.[13] These data support our assumption that binuclear species **6** are actual precursors of active species in the **1**/H_2O_2 catalytic system.

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