Isolation of two geometrical isomers of bis(μ-acetato)(μ-oxo)diiron(III) complexes with tridentate ligands and their activities for functionalization of cyclohexane in the presence of hydrogen peroxide

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Two geometrical isomers of bis(μ-acetato)(μ-oxo)diiron(III) complexes with tridentate ligands were isolated and characterized by X-ray crystallography and their activities for cyclohexane functionalization in the presence of hydrogen peroxide examined.

μ-Oxodimetal units have emerged as the demonstrated or proposed structural motifs for the active sites of a number of proteins.[1] The bis(μ-carboxylato)(μ-oxo)diiron(III) core is well established in the crystal structures of methemerythrin and its anionic complexes, and ribonucleotide reductase; in the case of methane monooxygenase, the presence of a hydroxide bridge instead of an oxo one is confirmed.[2] Bis(μ-carboxylato)(μ-oxo)diiron(III) complexes are readily synthesized by spontaneous self-assembly using tridentate ligands.[1] Armstrong and Lippard[3] were the first to demonstrate the synthesis of such complexes using hydrotris(pyrazolyl)borate, followed closely thereafter by Wieghardt et al.[4] with 1,4,7-triazacyclononane (tacn). In this article we have prepared bis(μ-acetato)(μ-oxo)-diiron(III) complexes containing tridentate ligands (substituted N,N-bis(2-pyridylmethyl)amine) and succeeded in isolating two geometrical isomers (green and red) characterized by X-ray crystallography. The activities of these compounds have been investigated for functionalization of cyclohexane in the presence of hydrogen peroxide.
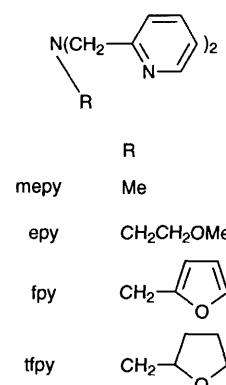
New iron(III) compounds of formula $[Fe_2O(O_2CMe)_2L_2]^{2+}$ were prepared according to general methods[5] where L are

† Red $[Fe_2O(O_2CMe)_2(tfpy)_2][ClO_4]_2$ (Found: C, 44.80; H, 4.80; N, 8.15. Calc.: C, 45.15; H, 4.80; N, 8.30%). Green $[Fe_2O(O_2CMe)_2-(tfpy)_2][ClO_4]_2·H_2O$ (Found: C, 44.15; H, 4.85; N, 8.10. Calc.: C, 44.35; H, 4.90; N, 8.15%). $[Fe_2O(O_2CMe)_2(epy)_2][ClO_4]_2·H_2O$ (Found: C, 41.45; H, 4.75; N, 8.40. Calc.: C, 41.80; H, 4.75; N, 8.60%). $[Fe_2O(O_2CMe)_2(fpy)_2][ClO_4]_2·H_2O$ (Found: C, 44.30; H, 4.15; N, 8.10. Calc.: C, 44.70; H, 4.15; N, 8.25%).

‡ Crystal data for green $[Fe_2O(O_2CMe)_2(fpy)_2][ClO_4]_2·H_2O$: $M = 1021.39$, green prism, dimensions $0.25 \times 0.15 \times 0.35$ mm, monoclinic, space group $C2/c$, $a = 25.47(2)$, $b = 20.563(3)$, $c = 19.70(1)$ Å, $\beta = 119.61(4)°$, $U = 8972(8)$ Å^3, $Z = 8$, $D_c = 1.512$ g cm^{-3}, $F(000) = 4208$; 296 K, $R = 0.070$, $R' = 0.075$ for observed 2900 reflections $[I > 3\sigma(I)]$. Crystal data for red $[Fe_2O(O_2CMe)_2(tfpy)_2][ClO_4]_2$: $M = 1011.44$, red prism, dimensions $0.15 \times 0.10 \times 0.15$ mm, monoclinic, space group $P2_1/n$, $a = 10.967(5)$, $b = 22.622(4)$, $c = 18.234(5)$ Å, $\beta = 98.85(3)°$, $U = 4476(2)$ Å^3, $Z = 4$, $D_c = 1.501$ g cm^{-3}, $F(000) = 2096$; 296 K, $R = 0.071$, $R' = 0.080$ for 1462 observed reflections $[I > 4\sigma(I)]$. All measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.710$ 69 Å) radiation and employing the ω–2θ scan technique to a maximum 2θ value of 55.0°. Lorentz-polarization absorption corrections were applied resulting in transmission factors ranging from 0.97 (0.96)–1.0 [for 1 (2)]. The structures were solved by direct methods[8] using full-matrix least-squares refinement, $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/261.

tridentate ligands derived from 2-(chloromethyl)pyridine and the corresponding amine.[6] The compounds containing fpy and epy are green, however in the case of tfpy two crystalline states, green and red forms are obtained:† at first a red form crystallized from a methanol solution containing iron(III) acetate and tfpy, and a green form crystallized from an acetonitrile–water (4:1) solution of the red form. Crystal-structure determinations on these two compounds have revealed the presence of an Fe–O (oxo) bond and that the ethereal oxygen atom of the fpy and tfpy ligands is not co-ordinated to iron(III), as exemplified by the green form of fpy shown in Fig. 1(a).‡ This complex is one of the well known binuclear iron(III) compounds with an oxo and a diacetato bridge,[1] and two aliphatic nitrogen atoms [N(1) and N(4)] are located trans to the bridging oxo-oxygen atom: structures of the green tfpy and epy complexes are assumed to be the same as that of the fpy complex. The red tfpy complex is the geometrical isomer of the corresponding green form; it should be noted that in the red form the pyridine nitrogen atoms [N(2) and N(5)] are located at the position trans to the oxo-oxygen atom [see Fig. 1(b)]. This implies that the geometrical configuration of the tfpy ligand is rather flexible in solutions containing water.

In Fig. 2 the absorption spectra of the red form of the tfpy compound is illustrated; the spectral features of the complex in MeCN are consistent with those reported previously[1] and are also identical to those of the green form (not shown). It should be noted here that the addition of water causes drastic changes in the range 800–400 nm, that is the disappearance of the bands which are characteristic of the binuclear species with a bent μ-oxo structure.[1] Lippard and co-workers[9] have reported that the spectral properties of the binuclear iron(III) complex $[Fe_2O(O_2CMe)_2(tacn)_2]^{2+}$ in water are in marked contrast to those recorded in MeCN and methanol, probably due in large part to hydrogen-bonding interactions between the solvent and the oxo-oxygen atom. In the present cases the decrease of the absorbance in the visible region is caused facilely by the addition of small amounts of water. This is not observed for the tris-(2-pyridylmethyl)amine complex, $[Fe_2O(O_2CMe)(tpa)_2]^{3+}$,[1] which contains a μ-oxo-μ-acetato bridge, suggesting that the hydrogen-bonding interaction is not a major contributor to

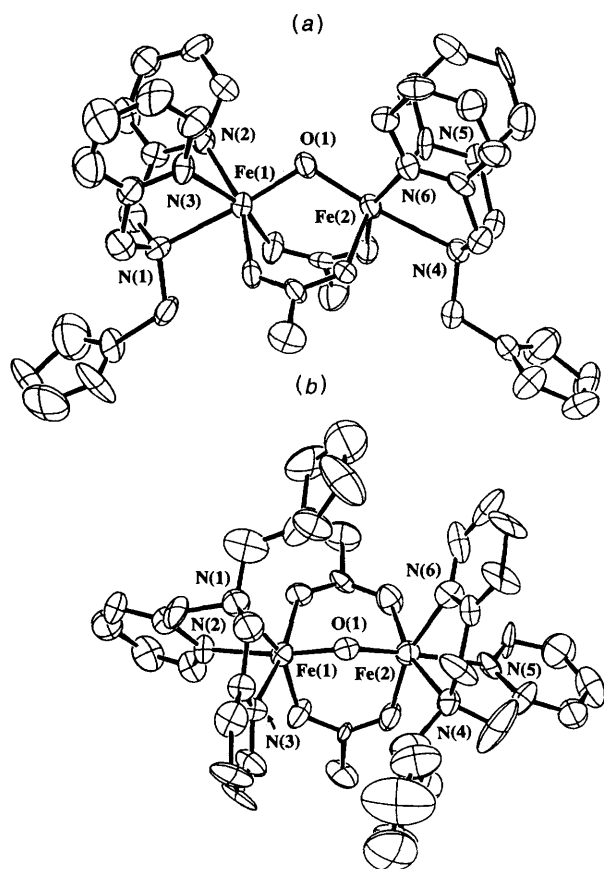|	R
mepy	Me
epy	CH₂CH₂OMe
fpy	CH₂ (furanylmethyl)
tfpy	CH₂ (tetrahydrofuranylmethyl)

Fig. 1 The ORTEP[7] views of: (a) green [Fe₂O(O₂CMe)₂(fpy)₂]²⁺, Fe(1)–O(1) 1.808(7), Fe(1)–O(2) 2.032(8), Fe(1)–O(4) 2.035(9), Fe(1)–N(1) 2.28(1), Fe(1)–N(2) 2.23(1), Fe(1)–N(3) 2.14(1), Fe(2)–O(1) 1.784(8), Fe(2)–O(3) 2.010(8), Fe(2)–N(5) 2.14(1), Fe(2)–N(6) 2.14(1) Å and Fe(1)–O(1)–Fe(2) 116.3(4)°; (b) red [Fe₂O(O₂CMe)₂(tfpy)₂]²⁺, Fe(1)–O(1) 1.78(1), Fe(1)–O(2) 2.03(1), Fe(1)–O(4) 2.00(1), Fe(1)–N(1) 2.22(2), Fe(1)–N(2) 2.19(2), Fe(1)–N(3) 2.13(2), Fe(2)–O(1) 1.79(1), Fe(2)–O(3) 1.99(1), Fe(2)–O(5) 2.07(1), Fe(2)–N(4) 2.22(2), Fe(2)–N(5) 2.12(2), Fe(2)–N(6) 2.16(2) Å and Fe(1)–O(1)–Fe(2) 119.8(6)°

the observations made in this study. The disappearance of the absorbance in the visible region may be attributed to (1) decomposition of the dimeric species into a mononuclear one, or (2) the bent structure being changed to a nearly linear one.[10] Since the absorption spectral data of the solution containing water closely resemble those of the linear μ-oxo structure, such as that found in [Fe₂OCl₂(tfpy)₂]²⁺,[11] it may be reasonable to conclude that the addition of water leads to the formation of a linear species, one of the possible structures being **A**. This consideration may be supported by the recent crystal-structure determination of [Fe₂O(tpa)₂(H₂O)(ClO₄)]³⁺,[10] and by the fact that acetate ion in the oxo-bridged binuclear complex is labile towards water;[12] this may be consistent with the fact that the green complex crystallizes from an acetonitrile–water (4:1) solution of the red form. The addition of hydrogen peroxide to an MeCN solution of the red complex leads to the same spectral change as observed above [see Fig. 2(c)] for all the complexes examined in this study; thus, we can assume that formation of an adduct **B** may occur in solution, similar to that described for species in water-containing solutions.

In Table 1, the turnover numbers of the oxygenated products are listed for the treatment of the binuclear iron(III) complexes with cyclohexane and hydrogen peroxide.* Here the yield of the

* Typically, an acetonitrile solution (20 cm³) containing iron(III) complex (0.05 mmol) and cyclohexane (840 mg) was added to an acetonitrile solution (10 cm³) containing H₂O₂ (1.13 g of 30% aqueous solution), and after 1 h the oxygenated products were determined by GC. Cyclopentanone was used as an internal standard.
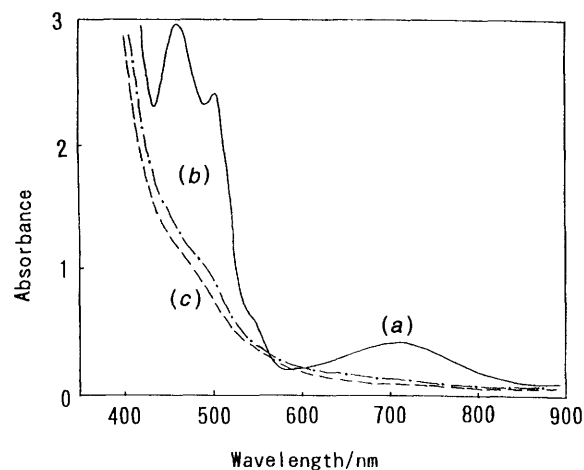

Fig. 2 Absorption spectra of red [Fe₂O(O₂CMe)₂(tfpy)₂]²⁺ in (a) MeCN (0.002 mol dm⁻³), (b) MeCN–H₂O (1:1 v/v, 0.002 mol dm⁻³), (c) MeCN containing hydrogen peroxide (concentration of hydrogen peroxide is the same as that used for the oxygenation of cyclohexane)
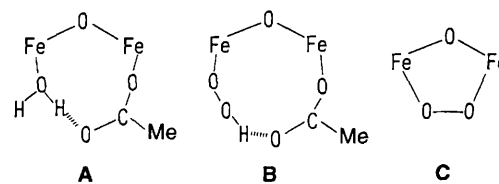

Table 1 Turnover numbers {mol of product/mol of [Fe₂O(O₂CMe)₂-L₂]²⁺ used} of the oxygenation products

L	Cyclohexanol	Cyclohexanone
fpy	3.5	1.4
tfpy (red form)*	2.7	1.3
epy	0.9	0.4
mepy	2.4	2.3
tpa	0.05	0.01

* The yields of the green form are identical.

oxygenated products is much lower for the epy and tpa complexes which show higher catalase-like functions† than any of the other compounds used in this study. Based on the above discussions and on other recent results,[13,14] the peroxide adduct **C** is found to be an active species for the decomposition of hydrogen peroxide,[13] but is not active for the oxygenation reaction of organic compounds, whereas adduct **B** is highly active for the oxygenation reaction but not for the decomposition of hydrogen peroxide.[14] It seems quite likely that both **B** and **C** are present in a solution containing the iron(III) complex and hydrogen peroxide, and that the ratio of the two adducts is highly dependent on the steric effects of R in the ligand. This may explain the diverse abilities of bis(μ-acetato)(μ-oxo)diiron(III) complexes to functionalize cyclohexane as observed in this study.

† Catalase-like function was examined by measuring the volume of dioxygen evolved from the reaction mixture.

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