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A monocarboxylate-bridged diiron(III) μ-oxido complex that catalyzes alkane oxidation by hydrogen peroxide†

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Reaction of the ligand 2-(*N*-isopropyl-*N*-{(2-pyridyl)methyl}-aminomethyl)-6-(*N*-(carboxymethyl)-*N*-((2-pyridyl)-methyl)amino-methyl)-4-methylphenol (H_2IPCPMP) with two equivalents of $Fe(ClO_4)_2$ and two equivalents of sodium pivalate in air leads to the formation of the μ-oxido, μ-carboxylato-bridged diiron complex $[\{Fe(H\text{-}IPCPMP)\}_2(\mu\text{-}O)(Piv)]ClO_4$ (1) (Piv = pivalate). Complex 1 is capable of catalysing the oxidation of cyclohexane or 1,2-*cis*-dimethylcyclohexane by hydrogen peroxide, leading to the formation of the corresponding cyclohexanone and cyclohexanol, as well as a small amount of cyclohexyl hydroperoxide.

The selective catalytic functionalization of hydrocarbons under mild conditions is a subject of considerable current interest.[1] In this connection, bioinspired iron complexes modeling iron oxygenases, especially those capable of hydroxylating alkanes, have attracted much attention.[2] In our efforts to synthesize models for dinuclear active sites in metalloenzymes,[3] we have obtained a diiron complex that replicates the essential coordination units in the diiron cores of ribonucleotide reductase and soluble methane monooxygenase,[4] albeit that the model complex contains coordinated phenolate moieties that are not found in the immediate coordination environment of the enzyme diiron sites. However, coordinated phenolate (tyrosine) ligands are frequently encountered in metalloproteins and a posttranslationally modified tyrosine plays a key role in the catalytic cycle of galactose oxidase.[5] Furthermore, recent studies[6–8] have shown that phenolate ligands in fact are very useful for (functional) modeling of the above-mentioned diiron enzymes. Phenolate donors are capable of stabilizing the high-valent metal state of active intermediates[5,9,10] and/or may be non-innocent donors in metal complexes,[11,12] forming coordinated phenoxyl radical ligands. The key ferryl (Fe(IV)=O) oxidative intermediate of oxygenases may be very reactive when stabilized by phenolate donors,[5,7] probably because of enhanced basicity of the ferryl oxygen.[13] Despite this, bioinspired iron complexes with phenolate ligands, especially μ-oxo diiron complexes, are still rare.[5–8,14]

Here we report the synthesis and characterization of a new diiron(III) complex of a phenolate-based ligand, as well as preliminary results of alkane oxidation by H_2O_2 catalysed by this complex. In the present dinuclear iron complex, the potentially hexadentate dinucleating ligand H_2IPCPMP[15] (*vide infra*) functions as a tetradentate ligand, chelating one metal instead of two. The presence of a non-coordinated $-CH_2N(^iPr)CH_2Py$ moiety of the ligand in the biomimetic complex permits modeling of non-covalent interactions of hydrophobic or hydrophilic amino acid residues in the second coordination sphere of metallobiosites, especially those involved in H-bonding network within protein active sites.[16] Such H-bonding networks are believed to be important for tuning of the reactivity of the metal-oxo moiety in enzyme active sites.[13,17] Furthermore, each iron atom in this complex is coordinated by six different donor groups in its coordination environment, rendering each iron a stereogenic center. In principle, this type of complex may thus be useful for the preparation of catalysts for enantioselective transformations.

The μ-oxido bridged dinuclear complex $[\{Fe(H\text{-}IPCPMP)\}_2(\mu\text{-}O)(Piv)]ClO_4$ (**1**) (Piv = $^-O_2CC(CH_3)_3$) was synthesized *via* aerial oxidation of an *in situ* prepared Fe(II) precursor, made by mixing one equivalent of Na_2IPCPMP (*cf.* Fig. 1) with 2 eq. $Fe(ClO_4)_2{\cdot}xH_2O$, and two equivalents of sodium pivalate under inert conditions. The crystal structure of **1** revealed that a homovalent dinuclear Fe(III) complex, consisting of two mononuclear Fe(IPCPMP) complexes bridged by one oxido and one pivalate group, had formed (Fig. 2, selected bond distances and angles can be found in Table 1). The significant stability of mononuclear Fe(III) complexes of IPCPMP and the similar ligand ICIMP have been noted previously[3] and these mononuclear complexes, where the potentially dinucleating ligand coordinates *via* its tetradentate pocket, have been isolated and structurally characterized (*vide infra*). Similarly, the second side-arm of the IPCPMP ligand, containing a tertiary amine, a pyridyl and an isopropyl group, is free and the amines (N3 and N7) are protonated, yielding a net positive charge of the complex. There is an approximate C_2 axis going through O4 and C27 in the structure (*cf.* Fig. 2), but the two octahedral

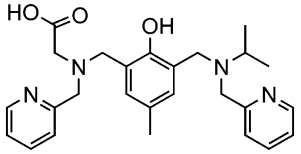

Fig. 1 The ligand H_2IPCPMP.

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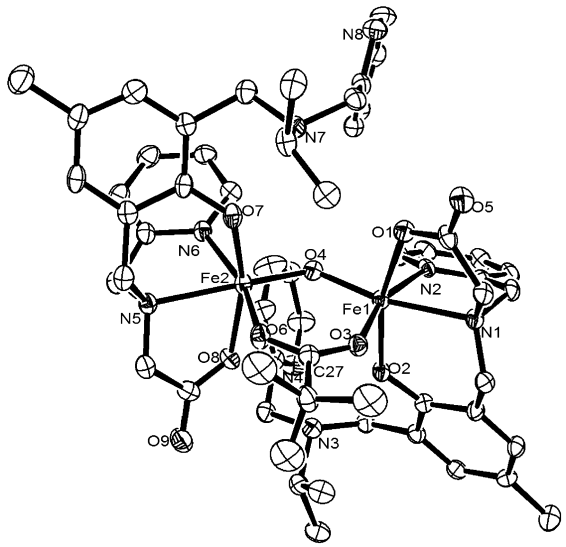

Fig. 2 ORTEP representation of the molecular structure of $[\{Fe(H\text{-}IPCPMP)\}_2(\mu\text{-}O)(Piv)]ClO_4$ (**1**). The ellipsoids are drawn at 50% probability and counterions and solvents of crystallization have been removed for clarity.

irons are slightly different, having average bond distances to coordinating atoms of 2.047 Å (Fe1) and 2.061 Å (Fe2). The largest difference between the two metal sites are the distances to the ligand-derived terminal carboxylate oxygen (Fe1–O1 2.044(3) Å *vs.* Fe2–O8 2.083(4) Å) while there is a smaller difference between the distances to the pyridyl nitrogens (Fe1–N2 2.148(4) Å, Fe2–N6 2.171(4) Å) and to the phenolate oxygens (Fe1–O2 1.973(3), Fe2–O7 2.006(4) Å). Furthermore, the oxido bridge is slightly unsymmetric (Fe1–O4 1.802(3) Å, Fe2–O4 1.786(3) Å). The Fe–Fe distance is 3.222(1) Å and the Fe–O–Fe angle is 127.8(3)°. The structure of **1** may be compared to that of the related mononuclear complex $[Fe(H_2IPCPMP)Cl_2]PF_6$ (**2**), where the metal has a similar coordination environment.[3] Complex **1** has longer phenolate–Fe(III) (**2**: Fe–Ophen 1.933(2) Å) and tertiary amine–Fe(III) distances than **2** (**1**: Fe1–N1 2.267(4), Fe2–N5 2.250(4) Å *vs.* **2**: Fe–N_{tert} 2.202(2) Å) while the pyridyl nitrogen–metal distances are similar in the two structures.

The dimeric structure of **1** is similar to what has been found for diFe(III) complexes of tripodal ligands such as *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (HDP)[18] and tris(2-pyridylmethyl)amine (TPA).[19,20] In particular ($[\{Fe(HDP)\}_2(\mu\text{-}O)(\mu\text{-}1,3\text{-}OBz)]BPh_4$) (OBz = benzoate)[18] is similar to **1** regarding the coordination of the metals with an Fe–Fe distance of 3.218(2) Å and Fe–O–Fe angle of 128.3°. The phenolate–Fe(III) bonds are shorter in the above HDP complex (Fe–Ophen 1.924(6) and 1.1.931(7) Å) than in **1** (Fe1–O2 1.973(3), Fe2–O7 2.006(4) Å), probably due to the longer distance to the pyridyl groups in the HDP complex (Fe–N_{py} 2.156(8)–2.185(9) Å) relative to the distances to the anionic carboxylate donors in **1** (Fe1–O1 2.044(3) Å *vs.* Fe2–O8 2.083(4) Å). The distances to the nitrogen functionalities are similar for all complexes compared here.

The ESI mass spectrum of **1** in positive mode indicates a complex of the formula $[\{Fe(IPCPMP)\}_2(O)(Piv)]^-$ with two positive ions (H^+, Na^+ or a combination). Only minor peaks of other species such as $[Fe_2(IPCPMP)(Piv)_2]^+$ and $[Fe_2(IPCPMP)_2(O)] + H^+$ could be observed. Electronic spectroscopy in CH_2Cl_2 solution showed characteristic absorptions for charge transfer (CT) bands from the oxido and the phenolato groups at 336 and 466 nm, respectively. The phenolate → Fe(III) LMCT band had a characteristic narrow shoulder at 487 nm.

Table 1 Selected distances (Å) and angles (°) for $[\{Fe(H\text{-}IPCPMP)\}_2(\mu\text{-}O)(Piv)]ClO_4$ (**1**)

Fe1	O1		2.044(3)
Fe1	O2		1.973(3)
Fe1	O3		2.052(4)
Fe1	O4		1.802(3)
Fe1	N1		2.267(4)
Fe1	N2		2.148(4)
Fe2	O8		2.083(4)
Fe2	O7		2.006(4)
Fe2	O6		2.037(4)
Fe2	O4		1.786(3)
Fe2	N5		2.250(4)
Fe2	N6		2.171(4)
Fe1	Fe2		3.2223(13)
Fe2	O4	Fe1	127.8(3)
O4	Fe1	O2	101.20(19)
O4	Fe1	O1	95.1(2)
O2	Fe1	O1	163.68(19)
O4	Fe1	O3	101.1(2)
O2	Fe1	O3	90.0(2)
O1	Fe1	O3	88.3(2)
O4	Fe1	N2	95.8(2)
O2	Fe1	N2	84.1(2)
O1	Fe1	N2	92.8(2)
O3	Fe1	N2	163.0(2)
O4	Fe1	N1	168.5(2)
O2	Fe1	N1	87.63(19)
O1	Fe1	N1	76.06(19)
O3	Fe1	N1	86.1(2)
N2	Fe1	N1	77.7(2)
O4	Fe2	O7	101.4(2)
O4	Fe2	O6	102.5(2)
O7	Fe2	O6	89.1(2)
O4	Fe2	O8	96.0(2)
O7	Fe2	O8	162.62(19)
O6	Fe2	O8	86.8(2)
O4	Fe2	N6	93.3(2)
O7	Fe2	N6	85.3(2)
O6	Fe2	N6	164.0(2)
O8	Fe2	N6	94.1(2)
O4	Fe2	N5	165.3(2)
O7	Fe2	N5	88.1(2)
O6	Fe2	N5	88.7(2)
O8	Fe2	N5	74.9(2)
N6	Fe2	N5	76.2(2)

Complex **1** was tested as catalyst for alkane hydroxylation using H_2O_2 as oxidant (Fig. 3). The majority of individual catalytic runs were performed at least twice at room temperature under air with [Cat] = 0.7 mM and Cat : H_2O_2 : RH = 1 : 140 : 1000. The products, alcohols (A) and ketones (K), were analyzed by GC and the small amount of cyclohexyl hydroperoxide formed was measured by the difference in total A + K content before and after reaction of the analyzed aliquots with PPh_3 (reduction of cyclohexyl hydroperoxide to cyclohexanol).[21] During a reaction time of approximately 2 h, the oxidation of cyclohexane by H_2O_2, using **1** as catalyst, produces cyclohexanol and cyclohexanone (A/K = 1.2) with a turnover number of 19 based on the combined yield of

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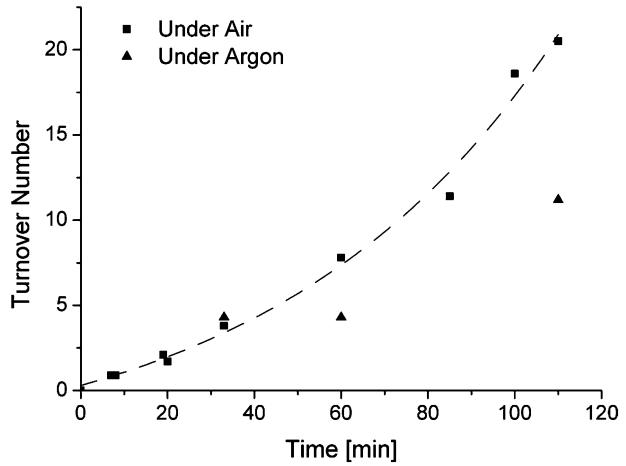

Fig. 3 Time dependence of the oxidation of cyclohexane catalyzed by **1** performed under both air (■) and argon (▲) atmosphere. The dashed line is an exponential fit to the data from the measurement under air.

products, *i.e.* a 20% yield with respect to added H_2O_2, and also produces a minor quantity of cyclohexyl hydroperoxide (0.8–1 mM in 0.5 h). The product yield is halved when the reaction is carried out under argon but the alcohol/ketone (A/K) ratio does not change. The oxidation exhibits an autocatalytic behavior, as shown in Fig. 3. A colour change of the catalytic solutions from red to orange was observed during the oxidation. Electrospray mass spectra of the catalytic solutions after reaction indicated significant decomposition of the starting complex **1**, and the reproducibility of the results decreased significantly when the reaction was carried out for longer periods than two hours. There was significant (60%) retention of configuration of the tertiary C–H bonds when *cis*-1,2-dimethylcyclohexane was used as a substrate. The related complex **2** was not found to catalyze alkane oxidation under similar conditions.

The results of alkane oxidation may be interpreted by consideration of two probable mechanisms: (i) metal based O-transfer from H_2O_2 and (ii) autooxidation with participation of O_2. The retention of configuration at the *tert*-C–H bond during oxidation of *cis*-1,2-dimethylcyclohexane is in agreement with a metal based oxidation although it has been suggested[6,22] that for such a mechanism, the alcohol/ketone (A/K) ratio should be considerably higher than observed for **1** and no alkyl hydroperoxide should be formed. However, it has recently been shown that alkyl hydroperoxides may be formed as part of a metal-based oxidation using H_2O_2 as the oxidant[23] and that very low alcohol/ketone ratios may also be observed in such systems.[24] The observed autoacceleration (Fig. 3) is compatible with a free radical autooxidation but another explanation for the autocatalysis is the formation of a more active catalyst, possibly a mononuclear complex,[25] during the oxidation reaction. A manganese complex with a similar coordination environment has been shown to exhibit good autooxidation activity.[26] It is possible, however, that both of these mechanisms may work simultaneously, as suggested earlier for a similar biomimetic system, *viz.* oxidation by H_2O_2 catalyzed by $[Fe_2O(bpy)_4](ClO_4)_4$.[27]

Experimental

General methods

All solvents were of at least 99.5% purity and used as received or dried either by distillation from CaH_2 (methanol, 2-propanol) or by keeping over 3 Å molecular sieves in a sealed bottle overnight (acetone). Reagents were of at least 99% purity and used as received. The bis-hexafluorophosphate salt of the ligand 2-(*N*-isopropyl-*N*-((2-pyridyl)methyl)aminomethyl)-6-(*N*-(carboxylmethyl)-*N*-((2-pyridyl)-methyl)amino-methyl)-4-methylphenol $(H_4IPCPMP)(PF_6)_2{\cdot}H_2O$ or **H_4L** was synthesised and converted to the analogous sodium salt as described elsewhere.[3c,d]

Physical methods

UV-vis spectroscopy was performed on a Varian 300 Bio UV/vis spectrophotometer. Infrared spectra were collected in the solid state as KBr discs on a Nicolet Avatar 360 FT-IR spectrometer. Electrospray mass spectra (ESI-MS) were collected on a Waters Micromass ZQ 4000 probe with capillary potential 3.5 kvolts, source cone 20–25 volts, source temperature 70 °C and direct infusion of 20 μl min^{-1}. Fast atom bombardment (FAB) mass spectra were collected on a JEOL SX-102 spectrometer with 2-nitrobenzyl alcohol (NBA) as matrix. All mass spectrometry data are reported as *m*/*z* with probable species and the relative intensity of the peaks in % based on the ^{56}Fe.

Synthesis of $[\{Fe(H\text{-}IPCPMP)\}_2(\mu\text{-}O)(Piv)]ClO_4$ (1)

A total of 49.1 mg (0.0997 mmol) of $Na_2IPCPMP$ was dissolved in degassed and dried acetonitrile. To this solution, 52.3 mg of $Fe(ClO_4)_2$ (0.2053 mmol) was added and the resultant solution turned first brown and then more purple (probably due to exposure to O_2 upon addition of the ferrous salt). 25.6 mg of sodium pivalate ($NaO_2CC(CH_3)_3$) was added and dissolved after stirring at room temperature for 1 h. The flask was opened to air and the colour turned dark red-purple. The solution was concentrated by evaporation and stored in a freezer overnight to yield a red violet solid which was recrystallized from dichloromethane : butylacetate by slow evaporation to afford X-ray quality crystals.

ESI-MS+ CH_3CN (rel. int., species): 1123 (12, $M^+ = [Fe_2(H\text{-}IPCPMP)_2(\mu\text{-}O)(O_2CC(CH_3)_3)]^+$; 1145 (35, $M^+ + Na^+ - H^+$); 1167 (100, $M^+ + 2Na^+ - 2H^+$); 760 (15, $[Fe_2(IPCPMP)(O_2CC(CH_3)_3)_2]^+$).

IR (KBr, cm^{-1}): 1639 (s, br, $-CO_2$ anti-sym.), 1476 (s, C–H arom.), 1441 (s, $-CO_2$ sym.), 1306 and 1269 (m, $-CO_2$ anti-sym.), 844 (vs, PF_6^-), 759 (s, PF_6^-), 558 (s).

UV-vis (CH_2Cl_2): 336 nm (sh), 466 nm (br), 487 nm (sharp).

X-Ray crystallography

The crystals of **1** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 120 K. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å). The *Denzo–Scalepack* program package[28] was used for cell refinements and data reductions. The structure was solved by direct methods using the *SHELXS-97*[29] program with the *WinGX*[30]

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graphical user interface. A semi-empirical absorption correction (*SORTAV*)[31] was applied to the data. Structural refinements were carried out using *SHELXL-97*. The *n*-butylacetate and one of the water molecules were disordered over alternative sites with occupancies 0.75 and 0.25 respectively. Another water molecule was partially lost and therefore refined with occupancy of 0.5. The methyl carbons in the *tert*-butyl group were disordered over two sites with occupancy ratio 0.72/0.28. The C28–C bond lengths and C···C distances within the *tert*-butyl group were restrained to be similar. The disordered carbons were further restrained with effective standard deviation 0.1 so that their U_{ij} components approximate to isotropic behavior. The H_2O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.2 U_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C–H = 0.95–0.99 Å, N–H = 0.93 Å and U_{iso} = 1.2–1.5 U_{eq} (parent atom).

[{Fe(H-IPCPMP)}$_2$(μ-O)(Piv)]ClO_4 (**1**) M_r = 1324.00, monoclinic, $P2_1/c$, a = 12.3777(4) Å, b = 27.7038(11) Å, c = 19.9823(7) Å, β = 100.120(2)°, V = 6745.5(4) Å^3, Z = 2, T = 120(2) K, 51 089 reflections collected, 11 854 unique reflections, R_{int} = 0.1082, R_1 = 0.0663 [$I \geq 2\sigma(I)$], wR_2 = 0.1878 (all data).†

Catalytic alkane oxidation

Investigations of catalytic alkane oxidation were carried out at 20 °C in glass vials (10 ml) closed by rubber septa. Solutions of alkane and catalyst in acetonitrile were placed in a vial and the reaction was initiated by addition of hydrogen peroxide with vigorous stirring. The volume of the catalytic solutions was 3 ml. The concentration of catalyst was 0.7 mM. The iron complex was removed by passing the solution through a silica gel column followed by elution with 3 ml of acetonitrile. An internal standard (chlorobenzene) was added at this point and oxidation products were analyzed on a Hewlett-Packard 5880A gas chromatograph with flame-ionization detector and capillary column OV-5 (60 m × 0.20 mm).

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