Mono- and binuclear complexes of iron(II) and iron(III) with an N_4O ligand: synthesis, structures and catalytic properties in alkane oxidation[†]

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Three mononuclear iron complexes and one binuclear iron complex, [Fe(tpoen)Cl]·0.5(Fe₂OCl₆) (1), [Fe(tpoen)Cl]PF₆ (2), Fe(tpoen)Cl₃ (3) and [{Fe(tpoen)}₂(μ -O)](ClO₄)₄ (4) (tpoen = *N*-(2-pyridylmethoxyethyl)-*N*,*N*-bis(2-pyridylmethyl)amine), were synthesized as functional models of non-heme iron oxygenases. Crystallographic studies revealed that the Fe(II) center of 1 is in a pseudooctahedral environment with a pentadentate N₄O ligand and a chloride ion *trans* to the oxygen atom. The Fe(III) center of 3 is ligated by three nitrogen atoms of tpoen and three chloride ions in a facial configuration. Each Fe(III) center of 4 is coordinated with four nitrogen atoms and an oxygen atom of tpoen with the Fe–O–Fe angle of 172.0(3) Å. Complexes 2, 3 and 4 catalysed the oxidation of cyclohexane with H₂O₂ in the total TNs of 24–36 with A/K ratios of 1.9–2.4. Under the same conditions they also catalysed both the oxidation of ethylbenzene to benzylic alcohol and acetobenzene with good activity (30–47 TN) and low regioselectivity (3°/2° 3.0–3.2). With *m*CPBA as oxidant the catalytic activities of 2, 3 and 4 increased 1.8 to 2.3-fold for the oxidation of cyclohexane and ethylbenzene and 6.3 to 7.5-fold for the oxidation of adamantane. Drastic enhancement of the regioselectivity was observed in the oxidation of adamantane (3°/2° 18.5–30.3).

Introduction

The development of transition metal based efficient and selective catalysts for environmentally benign alkane oxidation is one of the important and challenging issues in homogeneous catalysis and synthetic chemistry. In view of the special capability of iron-containing oxygenases such as cytochrome P450, methane monooxygenase (MMO), Rieske dioxygenase and iron bleomycin (FeBLM) in the catalysis of hydrocarbon oxidation reactions, the bio-inspired iron chemistry has received intensive attention in recent decades. To mimic the structures and functions of non-heme iron enzymes, many mono- and diiron complexes with various multidentate N-based ligands were prepared and their catalytic properties were widely investigated.¹⁻³ The outcome of previous studies suggested that the metal centers of the iron complexes can incorporate hydro- or alkyl-peroxide to form Fe(III) peroxide species, which are capable of activating the C-H bonds in alkanes via a high valent iron oxo intermediate.4-9 The high performance catalysts of biomimetic non-heme mononuclear iron complexes for alkane oxidation reported so far are those with N₄tetradentate ligands, such as $[Fe(TPA)(CH_3CN)_2](ClO_4)_2$ (TPA = tris(2-pyridylmethyl)amine),6,10 $[Fe(bpmen)(CH_3CN)_2](ClO_4)_2$ (bpmen = N, N'-dimethyl-N, N'-bis(2-pyridylmethyl)ethane-1,2diamine) and their derivatives.¹¹ The monoiron complexes bearing N₅-pentadentate ligands, such as $[Fe(N4Py)(CH_3CN)](ClO_4)_2$,¹² $[Fe(PMA)(CH_3CN)](ClO_4)_2$,¹³ and $[Fe(PaPy_3)(CH_3CN)](ClO_4)_2$,¹⁴ (Fig. 1), were found to catalyse alkane and alkene oxidations with H₂O₂ or TBHP as oxidant. Many μ -oxo- and carboxylato-bridged dinuclear iron complexes have proven to be efficient catalysts for alkane hydroxylation combined with peroxide oxidants.^{15,16} Moreover, the monoiron complexes [Fe(tpmen)Cl]PF₆ and



Fig. 1 Structures of the N_4O ligand used in the present work and the analogous N_5 - and N_3O -ligands used in non-heme iron model complexes.

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[†] Dedicated to Professor Victor Riera on the occasion of his 70th birthday.

[Fe(tpmpn)Cl]PF₆ (Fig. 1) exhibit interesting properties as catalysts for the hydroxylation of aromatic compounds although they are not efficient catalysts for alkane hydroxylation and alkene epoxidation.¹⁷ The complexes [FeLCl]⁺ (L = tpmen, tphen, Fig. 1) are capable of benzylic oxidation with a peroxide oxidant and the complex [Fe(tpaen)Br]²⁺ (Fig. 1) is an efficient DNA cleaver when activated by H_2O_2 .^{18,19}

Although mono- and diiron complexes of all-N multidentate ligands were extensively studied, to the best of our knowledge, only two iron complexes with ether-containing multidentate ligands were reported active for alkane oxidation.^{20,21} It was described that the μ -oxo diiron complex [{Fe(mebpa)Cl}₂O](ClO₄)₂ (Fig. 1) exhibited high activity and good selectivity for the oxidation of cyclohexane in the presence of H_2O_2 . The N₃O-coordinate diiron complex [{Fe(tfPy) Cl}₂(μ -O)](ClO₄)₂ (Fig. 1) was also reported to be catalytically active in alkane oxidation reactions with H_2O_2 as the oxidant. The encouraging results of these reports stimulated us to explore the structures and the catalytic properties of iron complexes featuring an N₄O potentially pentadentate ligand. The O atom, a weak donor compared to the N atom, may, in the multidentate ligand, create a hemi-labile site on the iron center and thus influences the catalytic property of the iron complex. Here we describe the preparation of three monoiron and a µ-oxo diiron complexes, [Fe(tpoen)Cl]·0.5(Fe₂OCl₆) (1), [Fe(tpoen)Cl]PF₆ (2), Fe(tpoen)Cl₃ (3) and [{Fe(tpoen)}₂(μ -O)](ClO₄)₄(4) (Fig. 1), the molecular structures of complexes 1, 3 and 4, and the catalytic properties of 2, 3 and 4 in the oxidation reactions of cyclohexane, ethylbenzene and adamantane with H_2O_2 and mCPBA (mchloroperbenzoic acid) as oxidants.

Experimental

General procedures

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Solvents were distilled prior to use with routine drying agents. Other commercially available chemical reagents were used as received.

¹H NMR Spectra were collected on a Varian INOVA 400NMR apparatus. Mass spectra of iron complexes were recorded on an HP1100 MSD instrument. Elemental analyses were performed on a ThermoQuest-Flash EA 1112 elemental analyzer. Gas chromatography (GC) analyses were performed on an HP6890GC instrument equipped with a flame ionization detector and an HP-5 column (30 m \times 0.32 mm) and GC-MS analyses were carried out on an HP6890GC/5973MS apparatus. Cyclic voltammograms (CVs) were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV s⁻¹ under argon. Studies were carried out in CH₃CN solution using 0.05 M n-Bu₄NPF₆ (Fluka, electrochemical grade) as the electrolyte with 10⁻³ M of iron complexes in a three-electrode cell. The working electrode was a glass carbon disc (diameter 3 mm) successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire.

Caution: Metal perchlorates are potentially explosive and should be handled with care!

Preparation of the ligand and the iron complexes

N - (2 - Pyridylmethoxyethyl) - N,N - bis(2 - pyridylmethyl)amine (tpoen). 2-Picolyl chloride hydrochloride (2.94 g, 18 mmol) was dissolved in H₂O (6 mL) and cooled with an ice-bath. The pH value of the solution was adjusted to 7 by the addition of saturated aqueous solution of K₂CO₃ with vigorous stirring. The mixture was then extracted with THF (20 mL) to give solution A. Sodium hydride (52%, 0.92 g, 20 mmol) was gradually added to the solution of ethanolamine (0.37 g, 6 mmol) in dry THF (20 mL) under N₂ atmosphere. The mixture was stirred for 30 min to afford solution B. Solution A was added to Solution B and the resulting mixture was refluxed for 18 h. After filtration, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with NaOH aqueous solution, dried over Na₂SO₄ and concentrated in vacuo. The crude product obtained was purified by silica gel chromatography with CH2Cl2-MeOH-Et3N as eluent (20 : 1 : 0.1, v/v) to give an orange oil (1.1 g, 55%). ¹H NMR (400 MHz, CDCl₃, 293 K): δ 8.52-8.49 (m, 3H, Py), 7.81-7.73 (m, 3H, Py), 7.58 (d, 2H, Py), 7.41 (d, 1H, Py), 7.30-7.23 (m, 3H, Py), 4.54 (s, 2H, OCH₂Py), 3.86 (s, 4H, NCH₂Py), 3.67 (t, 2H, CH₂O), 2.80 (t, 2H, NCH₂).

[Fe(tpoen)Cl]·0.5(Fe₂OCl₆) (1). A 10 mL ethanol solution of the ligand tpoen (0.34 g, 1 mmol) was added to a solution of FeCl₂·H₂O (0.16 g, 1.1 mmol) in ethanol (5 mL). The yellow precipitate appeared immediately. After stirring for 30 min, the precipitate **1** (0.27 g, 82%) was collected by filtration, washed with ethanol and diethyl ether, and dried *in vacuo*. Single crystals of **1**·0.5CH₃CN were obtained by slow vapor diffusion of diethyl ether into the acetonitrile solution. Anal. Calc. (found) for C₂₀H₂₂Cl₄Fe₂N₄O_{1.5}·0.5CH₃CN: C, 40.9 (40.9); H, 3.8 (3.6); N, 10.2 (9.9)%. MS(API-ES): *m/z* 195.1 [M – 0.5(Fe₂OCl₆)–Cl]²⁺, 425.1 [M – 0.5(Fe₂OCl₆)]⁺.

[Fe(tpoen)CI]PF₆ (2). The salt FeCl₂·H₂O (0.117 g, 0.81 mmol) was dissolved in methanol (5 mL) and added to a 5 mL methanol solution of tpoen (0.277 g, 0.83 mmol). The orange solution was stirred under N₂ for 30 min and NH₄PF₆ (0.116 g, 0.71 mmol) was added. The mixture was stirred for 3 h and a yellow precipitate appeared during this time. The precipitate was collected by filtration and extracted with acetonitrile. A yellow powder **2** (0.37 g, 81%) was obtained by removing solvent *in vacuo*. Anal. Calc. (found) for C₂₀H₂₂CIF₆FeN₄OP: C, 42.1 (42.2); H, 3.9 (3.9); N, 9.8 (9.8)%. MS(API-ES): *m/z* 195.4 [M–PF₆–Cl]²⁺, 425.5 [M–PF₆]⁺.

Fe(tpoen)Cl₃ (3). The salt FeCl₃·6H₂O (0.270 g, 1 mmol) in absolute ethanol (10 mL) was added to a solution of tpoen (0.311 g, 0.93 mmol) in absolute ethanol (10 mL). A yellow precipitate **3** (0.42 g, 90%) appeared immediately, which was isolated by filtration, and washed with ethanol and diethyl ether. The crystals of **3** suitable for X-ray diffraction analysis were collected by slow vapor diffusion of diethyl ether into the acetonitrile solution of complex **3**. Anal. Calc. (found) for $C_{20}H_{22}$ Cl₃FeN₄O: C, 48.4 (48.6); H, 4.5 (4.5); N, 11.3 (11.15)%. MS (API-ES): *m/z* 130.1 [M–3Cl]³⁺, 460.0 [M–Cl]⁺.

 $\{Fe(tpoen)\}_2(\mu-O)\}(ClO_4)_4$ (4). The salt $Fe(ClO_4)_2 \cdot xH_2O$ (0.195 g, 0.75 mmol) in absolute ethanol (20 mL) was slowly

dropped into an ethanol solution (5 mL) of tpoen (0.218 g, 0.65 mmol). A yellow precipitate formed immediately. After filtration, the residue was dissolved in acetonitrile and the diffusion of diethyl ether into the solution afforded dark red crystals 4 (0.15 g, 36%). Anal. Calc. (found) for C₄₀H₄₄Cl₄Fe₂N₈O₁₉·1.25CH₃CN: C, 41.0 (40.8); H, 3.9 (3.9); N, 10.4 (10.4)%. ¹H NMR (DMSO-d₆): δ 8.49 (br s, 3H, Py), 7.76 (br s, 3H, Py), 7.56 (d, 2H, Py), 7.40 (d, 1H, Py), 7.27 (br s, 3H, Py), 4.52 (s, 2H, OCH₂Py), 3.89 (s, 4H, NCH₂Py), 3.67 (br s, 2H, CH₂O), 2.83 (br s, 2H, NCH₂).

X-Ray crystallography

Crystallographic data were measured on a Siemens SMART System CCD diffractometer using graphite monochromated MoKa radiation with a wavelength (λ) of 0.71073 Å. Data processing was accomplished with the SAINT processing program.²² Intensity data were corrected for absorption by the SADABS program.²³ The structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods using the SHELXTL 97 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed geometrically and held in the riding mode. Machine parameters, crystal data and data collection parameters are summarized in Table 1. Crystallographic data of 1, 3 and 4 have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers 247052-247054. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516697g.

Catalytic oxidation of alkanes

In a typical run, an acetonitrile solution (4 mL) of cyclohexane (5 mmol) or ethylbenzene and the catalyst (5 µmol) was precooled to 0 °C. Oxidant H₂O₂ (1 mmol, 5 M in CH₃CN) or mCPBA

(1 mmol) was added in 3 min with rapid stirring under N₂. After 1.5 h at room temperature, an internal standard (1,2-dichlorobenzene) was added to the reaction mixture. The conversions of substrates were measured by GC and the structures of the products were verified by GC-MS. In the case of the oxidation reaction of adamantane, CH₃CN-CH₂Cl₂ (3 and 2 mL, respectively) was used as the solvent due to the poor solubility of adamantane in CH₃CN.

Results and discussion

Synthesis

The new ligand tpoen, which contains three pyridine nitrogens, one tert-amine nitrogen and one ether oxygen, was conveniently prepared using cheap reagents ethanolamine and 2-picolyl chloride. Complex 1 with [Fe₂OCl₆]²⁻ as a counteranion was readily prepared by the reaction of tpoen and FeCl₂ in ethanol. To avoid the effect of the diiron counteranion in complex 1 on the oxidation experiment, complex 2 was prepared by replacement of [Fe₂OCl₆]²⁻ in complex 1 with PF_6^- . The mononuclear Fe(III) complex 3 was prepared in a similar manner to that for complex 1 by the reaction of tpoen and FeCl₃. The yellow powder directly precipitated from the reaction of $Fe(ClO_4)_2 \cdot xH_2O$ and tpoen in ethanol is paramagnetic, evidenced by broad and wide-ranged ¹H NMR signals. Recrystallization of the paramagnetic yellow powder only afforded the μ -oxo diiron complex 4, which is diamagnetic. The structure of the paramagnetic species formed initially was not determined because of its instability in solution. It is assumed to be a monoiron complex $[Fe(tpoen)(sol)](ClO_4)_2$ in the light of the similar spontaneous conversion of [Fe(SBPy₃)(DMF)](ClO₄)₃ (Fig. 1) to a diiron complex $[{Fe(SBPy_3)}_2(\mu-O)](ClO_4)_4$.²⁴ All four complexes are air stable in the solid state. They are quite soluble in acetonitrile and sparingly soluble in methanol.

Table 1 Crystallographic data and processing parameters for 1.	0.5 CH ₃ CN, 3 and 4 \cdot 2CH ₃ CN
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Complex	1.0.5CH ₃ CN	3	4-2CH ₃ CN
Formula		C H C EaN O	
M	$C_{21}\Pi_{23,50}C_{14}\Pi_{21}C_{21}\Lambda_{4,50}O_{1,50}$ 616 44	496 62	$1276\ 44$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P_2/c	P_{2}/n	P-1
a/Å	14 651(3)	12,004(4)	12,6658(5)
b/Å	8 674(3)	13.4247(10)	12 9257(5)
c/Å	20.993(4)	13,155(6)	19 7839(8)
$a/^{\circ}$	90.00	90.00	72 835(1)
B/°	90.27(2)	92 890(3)	76 497(1)
$v/^{\circ}$	90.00	90.00	65.272(1)
$V/Å^3$	2667 8(12)	2117 24(16)	2788 19(19)
Z	4	4	2
$\rho_{\rm calad}/m^{-3}$	1.535	1.558	1.520
T/K	293(2)	298(2)	273(2)
μ/mm^{-1}	1.512	1.111	0.792
F (000)	1252	1020	1312
$\theta_{\min/\max}/^{\circ}$	1.94/25.03	2.17/28.28	1.95/25.21
Reflns measured	3384	5192	9680
Refins observed $[I > 2\sigma(I)]$	2442	4794	7700
Parameters refined	300	262	712
GOF (on F^2)	1.002	1.007	1.128
$R_1 \left[I > 2\sigma(I) \right]^a$	0.0406	0.0497	0.0867
$wR_2 \left[I > 2\sigma(I)\right]^b$	0.0981	0.1202	0.1959
$R_{ m int}$	0.0295	0.0245	0.0240

 ${}^{a} R_{1} = (\Sigma | |F_{o}| - |F_{c}||) / (\Sigma | F_{o}|). {}^{b} w R_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$

The API-ES positive mode mass spectrometry and the elemental analyses of complexes **1–4** are in good agreement with the proposed compositions. Both complexes **2** and **3** display paramagnetic ¹H NMR signals in the 0–140 for **2** and 0–130 ppm range for **3**, indicative of the high spin Fe(II) (**2**) and Fe(III) (**3**) complexes.^{25,26} The ¹H NMR of complex **4** in DMSO-d₆ exhibits sharp signals in the diamagnetic field, as found for the antiferromagnetically coupled μ -oxo diiron(III,III) complexes.^{27,28}

X-Ray crystal structures

The molecular structures of 1, 3 and 4 were determined by single crystal X-ray analyses. Each crystal cell of complex 1 consists of two cations of [Fe(tpoen)Cl]⁺, an [Fe₂OCl₆]²⁻ counteranion and a solvent molecule CH₃CN. The structure of the cation of 1 is shown in Fig. 2 and the selected bond lengths and angles are summarized in Table 2. The Fe(II) center of 1 is in a six-coordinate pseudooctahedral environment. Four nitrogen atoms and an oxygen atom of the ligand constitute an N₄O donor set around the metal ion and the left coordination position is occupied by a chloride ion. Although the structure of the N₄O ligand tpoen is quite similar with the N₅-ligands tpmen, tphen, tpaen and tpmpn, the coordination configuration of tpoen around the Fe(II) ion apparently differs from that of the analogous N₅-ligands. With replacement of the nitrogen atom in the arm of the N₅-ligand



Fig. 2 Molecular structure of the cation $[Fe(tpoen)Cl]^+$ in complex 1 with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for 1.0.5CH₃CN

Fe(1) - N(1)	2.180(3)	Fe(1)-N(4)	2.156(4)
Fe(1) - N(2)	2.226(4)	Fe(1)-O(1)	2.285(3)
Fe(1)-N(3)	2.194(4)	Fe(1)-Cl(1)	2.3354(14)
N(4)-Fe(1)-N(1)	101.35(14)	N(3) - Fe(1) - O(1)	83.96(13)
N(4)-Fe(1)-N(3)	100.47(15)	N(2)-Fe(1)-O(1)	75.32(14)
N(1) - Fe(1) - N(3)	151.73(16)	N(4) - Fe(1) - Cl(1)	100.69(12)
N(4)-Fe(1)-N(2)	147.34(16)	N(1)-Fe(1)-Cl(1)	96.33(11)
N(1)-Fe(1)-N(2)	75.27(15)	N(3) - Fe(1) - Cl(1)	97.06(10)
N(3)-Fe(1)-N(2)	76.65(15)	N(2)-Fe(1)-Cl(1)	111.97(11)
N(4) - Fe(1) - O(1)	72.03(15)	O(1) - Fe(1) - Cl(1)	172.69(10)
N(1) - Fe(1) - O(1)	85.89(13)		× /

by an oxygen atom, the N_4O ligand coordinates to the Fe(II) ion in an approximate C_s symmetry (Fig. 2), while the abovementioned all π -coordinate N₅-ligands in the previously reported Fe(II) complexes all possess C_1 symmetry.^{5,7,19} The coordination geometry of tpoen in complex 1 resembles that of the N5-ligands PaPy₃ and SBPy₃ containing a carboxamide or an imine nitrogen in the arm of the ligand, in which three pyridine nitrogen atoms and one tertiary amine nitrogen atom ligate to an Fe(III) ion with π bonds and the carboxamide with a σ bond or an imine with a π bond is *trans* to the readily exchangeable ligand Cl⁻ at the sixth site. As reported for other N_5 -pentadentate Fe(II) complexes, the Fe-N_{py} bond distances of 1 (2.180(3), 2.194(4) and 2.156(4) Å) are shorter than the Fe-N_{amine} distance (2.226(4) Å). Both the Fe–N_{pv(av)} distance (2.177(1) Å) and the Fe–N_{amine} bond length are comparable to those found in the N₅-coordinate high spin Fe(II) analogues $[FeLC1]^+$ (L = tpmen, tphen, tpaen and tpmpn),^{5,7,19} but considerably longer than that noted for N_5 coordinate low spin Fe(II) complexes, [Fe(N4Py)(MeCN)]²⁺ (Fe-N_{pv(av)} 1.971(8), Fe-N_{amine} 1.961(3) Å),²⁸ [Fe(SBPy₃)(MeCN)]²⁺ (Fe-N_{py(av)} 1.970(9), Fe-N_{amine} 1.996(3) Å) and [Fe(SBPy₃)(CN)]⁺ (Fe- $N_{py(av)}$ 1.967(4), Fe– N_{amine} 1.9922(13) Å).²⁴ The chloride ion is *trans* to the oxygen atom with an O(1)-Fe-Cl(1) angle of 172.69(10)° and the amine N atom lies *cis* to the chloride ion with a N(2)-Fe-Cl(1) angle of 111.97(11)° in the cation [Fe(tpoen)Cl]⁺. While in the N₅-coordinate analogues [FeLCl]⁺ (L = tpmen, tphen, tpaen and tpmpn) the chloride ion is trans to the amine N atom attached to two pyridylmethyl groups in the ligand.5,7,19 The Fe-O distance of 2.285(3) Å and Fe-Cl bond length of 2.3354(14) Å are close to those noted for related iron complexes.^{5,19-21} All angles of N-Fe-Cl in the cis position are larger than 96° (96-112°), being considerably greater than the corresponding angles of its N₅-coordinate analogues.^{5,14,19} The crystal structure of the cation [Fe(tpoen)Cl]⁺ suggests that the coordination of the N₄Opentadentate ligand to an Fe(II) ion could provide sufficient room for lodging not only an end-on but also a side-on peroxide coordination unit.

The molecular structure of complex **3** in Fig. 3 shows the potentially pentadentate ligand tpoen is tridentate here, with an amino nitrogen and two pyridyl nitrogen atoms of the ligand in a facial configuration. The remaining facial sites are occupied by three chloride ligands. The hexacoordinated Fe(III) center possesses a pseudooctahedral geometry, which is similar to that reported for [Fe(tpmpnH⁺)Cl₃]⁺.⁷ The selected bond lengths and angles of **3** are summarized in Table 3. The Fe–N distances (2.207(3), 2.191(3) and



Fig. 3 Molecular structure of Fe(tpoen)Cl₃ (**3**) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for complex 3

Fe-N(1)	2.207(3)	Fe–Cl(1)	2.3154(9)
Fe-N(2)	2.191(3)	Fe–Cl(2)	2.2762(8)
Fe-N(3)	2.282(3)	Fe–Cl(3)	2.2946(9)
N(2)-Fe- $N(1)$	78.20(10)	Cl(2)-Fe- $Cl(3)$	97.54(3)
N(2)-Fe-Cl(2)	92.12(7)	N(3)-Fe-Cl(3)	90.70(7)
N(1)-Fe-Cl(2)	91.99(7)	N(2)-Fe-Cl(1)	89.06(7)
N(2)-Fe- $N(3)$	77.59(9)	N(1)-Fe-Cl(1)	164.22(7)
N(1)-Fe- $N(3)$	75.71(10)	Cl(2)-Fe- $Cl(1)$	97.81(3)
Cl(2)-Fe-N(3)	165.25(7)	N(3)-Fe-Cl(1)	92.62(7)
N(2)-Fe-Cl(3)	165.14(7)	Cl(3)-Fe- $Cl(1)$	100.71(4)
N(1)-Fe-Cl(3)	90.16(7)		

2.282(3) Å) of **3** close to those in [Fe(tpmpnH⁺)Cl₃]⁺ are indicative of the high spin Fe(III) ion of **3**. The Fe–Cl distances of 2.3154(9), 2.2762(8) and 2.2946(9) Å are comparable to the lengths of the Fe–Cl bonds in [Fe(tpmpnH⁺)Cl₃]⁺ and in the Fe(III) complexes with TPA or other N₃ ligands.^{7,29,30} In the coordination sphere, the angles between the chloride ion and the *trans*-positioned nitrogen atom are around 165°, and those between the chloride ion and the *cis*-positioned nitrogen atom are close to 90°. The angles between the chloride ions are larger than 97°.

The structure of the μ -oxo diiron complex 4 is shown in Fig. 4 and the selected bond lengths and angles are given in Table 4. All four nitrogen atoms and an oxygen atom in the ligand are coordinated to one of the Fe(III) centers together with a µoxo ligand, to form a distorted octahedral geometry on each Fe(III) ion. The two parts of the dimer are unsymmetric in the spatial orientation. The oxygen in the ligand is *trans* to the μ oxo group to construct a slightly zigzag O(2)-Fe(1)-O(1)-Fe(2)-O(3) linkage with the bond angles of 171.76(18) for O(2)-Fe(1)-O(1), 172.34(18) for O(3)-Fe(2)-O(1) and 172.0(3)° for Fe(1)-O(1)-Fe(2). The structure of 4 is reminiscent of that reported for $[{Fe(SBPy_3)}_2(\mu-O)](ClO_4)_4$, in which the bond angle of Fe-O-Fe is 175.4°.24 The average distance of the Fe-O_{ether} bonds in 4 (2.163(9) Å) are shorter than the Fe–O bond of complex 1 (2.283(4) Å), reflecting the weaker *trans* effect of the μ -oxo group relative to the chloride ion. The Fe-O_{u-oxo} bond lengths of 1.786(4) and 1.790(4) Å fall in with those found for other μ -

Table 4 Selected bond lengths (Å) and bond angles (°) for 4.2CH₃CN

Fe(1)-N(1) Fe(1)-N(2) Fe(1)-N(3) Fe(1)-N(4) Fe(1)-O(1) Fe(1)-O(2) N(1)-Fe(1)-N(2)	2.092(5) 2.192(5) 2.128(5) 2.142(5) 1.786(4) 2.156(4) 150.3(2)	Fe(2)-N(5) Fe(2)-N(6) Fe(2)-N(7) Fe(2)-N(8) Fe(2)-O(1) Fe(2)-O(3) N(5)-Fe(2)-N(6)	2.091(5) 2.173(5) 2.140(6) 2.140(6) 1.790(4) 2.171(4) 150.9(2)
N(1)-Fe(1)-N(3)	102.9(2)	N(5)-Fe(2)-N(7)	99.1(2)
N(1)-Fe(1)-N(4)	99.4(2)	N(5)-Fe(2)-N(8)	102.8(2)
N(1)-Fe(1)-O(1)	99.71(19)	N(5)-Fe(2)-O(1)	101.76(19)
N(1)-Fe(1)-O(2)	73.03(19)	N(5)-Fe(2)-O(3)	73.36(19)
N(2)-Fe(1)-N(3)	76.3(2)	N(6)-Fe(2)-N(7)	77.6(2)
N(2)-Fe(1)-N(4)	76.9(2)	N(6)-Fe(2)-N(8)	76.2(2)
N(2)-Fe(1)-O(1)	109.9(2)	N(6)-Fe(2)-O(1)	107.29(19)
N(2)-Fe(1)-O(2)	77.30(19)	N(6)-Fe(2)-O(3)	77.56(19)
N(3)-Fe(1)-N(4)	153.2(2)	N(7)-Fe(2)-N(8)	153.8(2)
N(3)-Fe(1)-O(1)	95.40(19)	N(7)-Fe(2)-O(1)	93.4(2)
N(3)-Fe(1)-O(2)	90.13(19)	N(7)-Fe(2)-O(3)	81.78(19)
N(4)-Fe(1)-O(1)	95.28(19)	N(8) - Fe(2) - O(1)	96.11(19)
N(4)-Fe(1)-O(2)	82.32(19)	N(8) - Fe(2) - O(3)	90.79(18)
O(2)-Fe(1)-O(1)	171.76(18)	O(3) - Fe(2) - O(1)	172.34(18)
Fe(1)-O(1)-Fe(2)	172.0(3)		



Fig. 4 Molecular structure of $[{Fe(tpoen)}_2(\mu-O)](ClO_4)_4$ (4) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

oxo diiron(III,III) complexes (1.77–1.82 Å).^{20,24,28} It is noteworthy that the Fe–N_{py(av)} bond length (2.122(7) Å) and the Fe–N_{amine(av)} (2.183 Å) of **4** are very close to the corresponding values found in the antiferromagnetically coupled complex [{Fe(N4Py)}₂(μ -O)](CIO₄)₄ (Fe–N_{py(av)} 2.125 and Fe–N_{amine(av)} 2.244 Å).^{24,28}

Electronic spectra of complexes 1-4

The UV-Vis spectra of complexes 1–4 were recorded in acetonitrile. Complex 1 exhibits two bands at 260 (17000) and 317 nm (sh, 10 500 mol⁻¹ cm⁻¹), which are assigned to the characterization of the [Fe₂OCl₆]²⁻ counteranion,³¹ and the absorption bands from the cation [Fe(tpoen)Cl]⁺ are enveloped by the two intense absorption bands of the anion [Fe₂OCl₆]²⁻. Complex 2 displays two bands at 258 (10300) and $382 \text{ nm} (1280 \text{ mol}^{-1} \text{ cm}^{-1})$ in close analogy to the UV-Vis spectrum of [Fe(tpmpn)Cl](PF₆).⁷ The first band is due to a pyridyl π - π * transition and the second band is assigned to the metal-to-ligand charge-transfer (MLCT) band, which shows a slight blue shift compared to that observed for [Fe(tpmen)Cl](PF₆) $(\lambda_{max} = 399 \text{ nm}).^{4,5}$ The intensity of the MLCT band gives a further clue to the high spin state of the Fe(II) ion in complex 2.4 The electronic spectrum of complex 3 shows three bands in the range of 200-500 nm. Like complex 2, the first band of 3 at 255 nm (19100 mol⁻¹ cm⁻¹) is due to the π - π * transition of the ligand. The two other broad bands at 290 (sh, 8400) and 384 nm (5000 mol⁻¹ cm⁻¹) are assigned to the chloro-to-Fe(III) charge transfer.⁷ These absorption bands are quite similar to those found for the other N₃-tridentate high spin Fe(III) complexes.^{7,29,30} The UV-Vis spectrum of 4 is dominated by two bands at 254 (39500) and 354 nm (10900 mol⁻¹ cm⁻¹). A red shift of ca. 40 nm is observed for the second band in the spectrum of 4 compared to the corresponding bands in the UV-Vis spectra of the N₅coordinate μ -oxo diiron complexes [{Fe(SBPy₃)}₂(μ -O)](ClO₄)₄ and [{Fe(N4Py)}_2(\mu\text{-O})](ClO_4)_4.^{24,28}

The positions and intensities of the two absorptions of 2 in the UV-Vis spectrum in CH₃CN are identical to those measured

in MeOH. The UV-Vis spectra of 4 in CH₃CN and MeOH gave similar results. The UV-Vis spectra suggest that the ether oxygen of the tpoen ligand in complexes 2 and 4 is not displaced by the molecule of acetonitrile in solution.

Redox properties of complexes 2 and 4

The redox properties of complexes 2 and 4 were studied by cyclic voltammetry. Complex 2 exhibits a reversible one-electron wave in CH₃CN with an $E_{1/2}$ value of +0.37 V vs Ag/AgNO₃ for the redox potential of Fe^{II}/Fe^{III} couple. Compared with the $E_{1/2}$ value of +0.57 and +0.64 V vs SCE for the monoiron complexes of the closely related N_5 ligands, tpmen and tpmpn,^{4,7,17} complex 2 shows a slightly higher Fe(II)/Fe(III) redox potential (+0.65 V vs SCE) if the measured potential is corrected to the values of SCE.³² It can be attributed to the higher acidity of the Fe(II) center of 2, resulting from the replacement of one of the nitrogen atoms in the N5 ligand with an oxygen atom. Cyclic voltammogram of complex 4 is shown in Fig. 5, which displays two reduction peaks typical of a µ-oxo diiron core.33 The quasi-reversible reduction peak at +0.11 V with an $E_{1/2}$ value of +0.06 V vs Ag/AgNO₃ is ascribed to the one-electron reduction process of Fe(III)Fe(III) to Fe(III)Fe(II). The irreversible reduction peak at -0.83 V is assigned to the oneelectron reduction process of Fe(III)Fe(II) to Fe(II)Fe(II).

Catalytic oxidation of alkanes

Entry

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

Ethylbenzene

Cyclohexane

The catalytic activities of complexes **2**, **3** and **4** were explored for the oxidation of alkanes, *e.g.*, cylcohexane, ethylbenzene and

Catalyst

 2^d

2^e 2 2 3^d

3.

3

3

4

4

2 2 3

3 4 4 Oxidant

 H_2O_2

 H_2O_2

 H_2O_2

 H_2O_2

 H_2O_7

 H_2O_2

 H_2O_2

 H_2O_2

 H_2O_2

 H_2O_2

mCPBA

mCPBA

mCPBA

mCPBA

mCPBA

*m*CPBA

 $\begin{array}{c}
20 \\
10 \\
-10 \\
-20 \\
1.5 \\
1.0 \\
0.5 \\
0.0 \\
0.5 \\
0.0 \\
-0.5 \\
-1.0 \\
-1.5 \\
E / V vs Ag/Ag^+
\end{array}$

Fig. 5 Cyclic voltammogram of $[{Fe(tpoen)}_2(\mu-O)](ClO_4)_4$ (4), 1.0 mM in 0.05 M *n*-Bu₄NPF₆-CH₃CN at a scan rate of 100 mV s⁻¹.

adamantine, with H_2O_2 and *m*CPBA as oxidants in acetonitrile at room temperature under a N_2 atmosphere. The results are summarized in Table 5. Complexes **2**, **3** and **4** catalysed the oxidation of cyclohexane to cyclohexanol (A) and cyclohexanone (K). As illustrated in Table 5, when H_2O_2 was employed as an oxidant, the catalysts performed with the best reactivity in a molar ratio of 1 : 200 : 1000 for catalyst : oxidant : substrate. Complex **2** bearing an N₄O-pentadentate ligand catalysed cyclohexane to 17.2 TN (turnover number) of cyclohexanol and 7.2 TN of cyclohexanone (A/K = 2.4) with 12.2% conversion based on oxidant (entry 3). Complex **3**, with an N₃ and 3Cl *fac*coordination configuration, exhibited a catalytic activity of 25 TN for cyclohexanol and 11.1 TN for cyclohexanone (A/K = 2.3)

Conversion (%)

10.3

6.1

12.2

24.9

14.7

9.3

18.1

36.2

11.9

27.1

19.2

41 9

14.9

33.5

21.3

38.1

Remarks

A/K

1.8

2.2

2.4

3.2

1.5

16

2.3

3.0

1.9

2.9

07

0.8

0.7

1.0

0.7

1.0

Table 5Oxidation of alkanes catalysed by complexes 2, 3 and 4^a

3°/2°h Adamantane^g 1-01 2-ol + 2-one 17 2 2 3 3 H_2O_2 7.9 7.7 3.2 7.4 18 **mCPBA** 91.3 14.8 53.1 18.5 19 H_2O_2 8.9 8.9 8.9 3.0 100.1 19.4 20 15.5 57.8 mCPBA 21 4 H_2O_2 8.4 8.2 8.3 3.1 4 22 **mCPBA** 95.0 9.4 52.2 30.3 ^a Reaction conditions: catalyst 5 µmol; catalyst : oxidant : substrate in a molar ratio of 1 : 200 : 1000; reaction time 90 min; reaction temperature 20 °C; solvent CH₃CN 4 mL. ^b TN = mol of product/mol of catalyst. ^c Conversions are based on oxidant. ^d The molar ratio of catalyst : oxidant : substrate is 1:100:100. "The molar ratio of catalyst: oxidant: substrate is 1:200:100 and the corresponding conversions are based on substrate." For all reactions with complex 4 as catalyst, 2.5 μ mol of catalyst was used. "The reactions were carried out in 3 mL CH₃CN and 2 mL CH₂Cl₂. "3°/2° = 1-adamantanol/(2-adamantanol + 2-adamantanone) multiplied by 3.

Product (TN)^b

Ketone

3.7

3.8

7.2

11.8

5.8

7.1

11.1

18.3

8.2

13.8

2-one

22.7

46.0

17.2

33.4

26.2

38.1

Alcohol

6.6

8.3

17.2

37.9

11.5

25.0

54.1

15.6

40.3

2-ol

15.7

37.9

12.7

33.6

16.4

38.1

8.9

with 18.1% conversion (entry 7), which is higher than complex 2. In contrast, the analogous Fe(III) complex with an N₃ and 3Cl *mer*-coordination configuration did not show catalytic activity in the oxidation of cyclohexane with H₂O₂ and t-BuOOH.³⁴ Although high turnover numbers were obtained in the oxidation reactions catalysed by 2 and 3, the conversions based on H_2O_2 were lower than those observed for non-heme mononuclear iron complexes bearing well-known N₄- and N₅-ligands, e.g., TPA, bpmen and N4Py.^{2,11,12} The conversions with 2 and 3 under similar oxidation conditions are higher than those found for other reported monoiron complexes bearing N₃-,³⁵ N₄-,³⁶ N₅- and N₃Oligands.^{2,14,20} Under our standard reaction conditions ($2 : H_2O_2$: cyclohexane = 1 : 200 : 1000), complex 2 displayed an A/K of 2.4, which is superior to those for all previously reported monoiron complexes featuring N₅-pentadentate ligands, such as N4Py, PaPy₃ and PMA.^{2,12-14} In those cases, the A/K values are in the range of 0.9-1.4. In the molar ratios of 1:100:100 and 1:200:100 for catalyst : oxidant : substrate (entries 1, 2 and 5, 6), lower activities and selectivities were detected. These results indicate with a large excess of substrate, 2 and 3 perform higher activities and the overoxidation of cyclohexanol to cyclohexanone can be depressed to a certain extent.

It has been reported recently that the chemo- and regioselectivity of the alkane oxidation can be greatly enhanced for some non-heme iron complexes when mCPBA was used as the oxidant.37,38 With a catalyst : oxidant : substrate molar ratio of 1: 200: 1000 with mCPBA as the oxidant, the oxidation of cyclohexane catalysed by complex 2 can be completed within 20 min with a total TN of 49.7 and a conversion of 24.9% based on mCPBA (entry 4), which are twice as high as those observed for H₂O₂. The A/K value was improved to 3.2. A total TN of 72.4 and a conversion of 36.2% with an A/K ratio of 3.0 (entry 8) were obtained for oxidation of cyclohexane by the 3/mCPBA system. With mCPBA as a surrogate of H_2O_2 , complexes 2 and 3 did not show great enhancement of the selectivity as reported for iron complexes containing N4Py and dpan (dpan = 3,3'-bis[N,N-bis(2-pyridylmethyl)aminomethyl]-1,1'-bi-2-naphthoxy) ligands.^{37,38} The μ -oxo dinuclear iron complex 4 displayed an activity similar to the mononuclear Fe(II) complex 2 and the chemical selectivity of 4 (A/K = 1.9 for H_2O_2 and 2.9 for mCPBA, entries 9 and 10) is somewhat lower than that shown by complex 2.

The catalytic activities of complexes **2**, **3** and **4** were further explored for the oxidation of ethylbenzene and adamantane (Table 5, entries 11–22). Catalytic oxidation of ethylbenzene with H_2O_2 by **2**, **3** and **4** gave more acetobenzene than benzylic alcohol (A/K = 0.7) in moderate H_2O_2 -based conversions (entries 11, 13 and 15) as compared to the non-heme iron complexes of N and O multidentate ligands for the benzylic oxidation.¹⁸ Replacement of H_2O_2 with *m*CPBA led to the promotion of the conversions to 41.9% for **2**, 33.5% for **3** and 38.1% for **4** with nearly equivalent benzylic alcohol and acetobenzene (entries 12, 14 and 16). Compared with other non-heme model complexes, which normally afforded benzylic alcohol as the major product with an A/K ratio of 1.1–7.9,^{18,37,38} complexes **2**, **3** and **4** manifested low selectivities towards the alcohol product.

Oxidation of adamantane with H_2O_2 catalysed by 2, 3 and 4 afforded 1-adamantanol, 2-adamantanol and 2-adamantanone with moderate efficiencies (TN = 15–18) and low regioselectivity

 $(3^{\circ}/2^{\circ} = 3.0-3.2$, entries 17, 19 and 21) compared to the iron complexes of tpa and tpa-derived ligands.11 The total TNs and the regioselectivity of 2, 3 and 4 are similar to those displayed by [Fe(N4Py)(CH₃CN)](ClO₄)₂,¹² but the H₂O₂-based conversions are only half of that performed by the iron complex of the N4Py ligand. Appealingly, complexes 2, 3 and 4 showed much higher efficiency in adamantane oxidation with mCPBA as the oxidant relative to H_2O_2 . The total TNs reached 106.2 for 2, 115.6 for 3 and 104.4 for 4 and the regioselectivity was also drastically improved to the $3^{\circ}/2^{\circ}$ ratios of 18.5 for 2, 19.4 for 3 and 30.3 for 4 (entries 18, 20 and 22). The high catalytic activities and the promising regioselectivity of complexes 2, 3 and 4 in the oxidation of adamantane with mCPBA are comparable to the previously reported most efficient non-heme iron catalysts, e.g. iron complexes of bpmen, tpa and tpa-derived ligands and the diiron complex [Fe₂((S)-dpan)(O)(OBz)]ClO₄.^{11,38} The low A/K ratios close to 1 in the oxidation of ethylbenzene with either H₂O₂ or mCPBA and the poor regioselectivity with $3^{\circ}/2^{\circ}$ ratios close to 3 in adamantane oxidation with H₂O₂ convey a hint of the presence of long lifetime alkyl radicals, which react rapidly with O₂ to initiate a radical chain autoxidation.² In contrast, significantly enhanced regioselectivity in the oxidation of adamantane with the catalyst/mCPBA system indicates the involvement of a metal-centered oxidant that acts as an active intermediate in the oxidation of the C-H bonds of adamantane.

Conclusions

In summary, mono- and dinuclear complexes 1-4 were synthesized using an N₄O multidentate ligand (tpoen). Monoiron complexes 1 and 2 each possess an Fe(II) center with an N₄O-pentadentate ligand. The Fe(III) center of 3 is coordinated by three N atoms of the N_4O ligand, in which the O and N_{Pv} atoms of the pendant arm are non-coordinate. Complex 4 has an Fe(III)Fe(III) µ-oxo core featuring an N₄O-pentadentate ligand in each moiety. Complexes 2, 3 and 4 displayed moderate activities and low to moderate selectivities in the oxidation of cyclohexane, ethylbenzene and adamantane with H_2O_2 . Although mononuclear iron complexes with the N₃-meridional tridentate ligands are poor catalysts for the oxidation of cyclohexane,^{34,35} complex 3, which has an N₃-facial tridentate ligand, exhibited good catalytic activity. Replacement of the oxidant H₂O₂ with mCPBA led to significant enhancement of the catalytic activity of 2, 3 and 4. The A/K values of cyclohexane oxidation were apparently improved and the regioselectivity of adamantane oxidation was drastically raised. According to the catalytic results, a radical-based oxidant was proposed to play the dominant role in the oxidation of alkanes by catalyst/ H_2O_2 systems, while the oxidation of adamantane by catalyst/mCPBA systems is mainly due to metal-based oxidation.

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