# Highly selective hydroxylation of alkanes catalyzed by (μ-oxo)bis(μ-carboxylato)-bridged diiron(III) complexes: involvement of mononuclear iron(III) species in catalysis†‡

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A few diiron(III) complexes [Fe<sub>2</sub>(O)(OAc)<sub>2</sub>(L1)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 1, [Fe<sub>2</sub>(O)(OBz)<sub>2</sub>(L1)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 2,  $[Fe_2(O)(OAc)_2(L2)_2](ClO_4)_2$  3 and  $[Fe_2(O)(OBz)_2(L2)_2](ClO_4)_2$  4, where L1 = N, N-bis(pyrid-2ylmethyl)-*iso*-butylamine, L2 = N, N-bis(pyrid-2-ylmethyl)benzylamine, AcO = acetate and BzO = benzoate, have been isolated and characterized by means of elemental analysis and spectral and electrochemical methods. The molecular structures of the complexes 2 and 4 have been determined by single-crystal X-ray diffraction analysis and they possess a distorted bioctahedral geometry in which each iron atom is coordinated to the oxygen atom of the  $\mu$ -oxo bridge, two oxygen atoms of the u-benzoato bridges and three nitrogen atoms of L1 and L2 ligands capping the two ends of the diiron(III) cluster. The ESI-MS spectral data of the complexes reveal that the complexes remain intact in dichloromethane (DCM) solution. Upon adding one equivalent of Et<sub>3</sub>N to a mixture of one equivalent of the diiron(III) complexes and excess of *m*-chloroperbenzoic acid (*m*-CPBA) in DCM, an intense absorption band ( $\lambda_{max}$ , 670–700 nm) appears, which corresponds to the species [Fe<sub>2</sub>(O)(OAc)(*m*-CPBA)(L)<sub>2</sub>]<sup>2+</sup> (ESI-MS, m/z 466) suggested as the intermediate involved in the oxygenation reactions. All the present complexes show efficient alkane hydroxylation with 300-400 turn over numbers and good selectivities for cyclohexane (A/K, 10-14) and adamantane ( $3^{\circ}/2^{\circ}$ , 9-11). Interestingly, the formation of monoiron(III) species has been discerned in the alkane hydroxylation reactions beyond ~50 turnovers. The mononuclear 1 : 1 iron(III) complexes of L1 and L2 ligands generated in situ are also found to catalyze the oxygenation reactions with high selectivity and efficiency for cyclohexane (A/K, 10–14). Upon their reaction with *m*-CPBA in DCM, a characteristic absorption band ( $\lambda_{max}$ , 600 nm,  $\varepsilon_{\rm max}$ , 355 M<sup>-1</sup> cm<sup>-1</sup>) appears and decays at room temperature. This spectral feature is consistent with the mononuclear high-valent iron-oxo species suggested as an intermediate in the oxygenation reactions

# Introduction

The catalytic and selective functionalization of hydrocarbons under mild conditions is a subject of great current interest in bioinorganic and synthetic chemistry.<sup>1</sup> The iron-containing biological molecules such as soluble methane monooxygenases (sMMO), cytochrome P450 and bleomycin oxidize an aliphatic C–H bond of alkanes to give an alcohol product.<sup>2</sup> The nonheme sMMO enzyme shows remarkable catalytic activity towards the oxidation of a variety of alkanes including methane using dioxygen.<sup>3-6</sup> The selectivity, efficiency and mild reaction conditions of these reactions indicate a methodology different from traditional synthetic processes, which usually require high temperatures and pressures. Efforts have been made during the last two decades to develop synthetic analogues for sMMO and also study the mechanism of  $O_2$  activation involved in the oxygenation of alkanes.<sup>7,8</sup> The active site of reduced form of sMMO is composed of a diiron center containing four glutamate and two histidine residues, in which the iron atoms are bridged by two carboxylate ligands from glutamate residues while the oxidized form contains only one carboxylate bridge and two hydroxo bridges (sMMOox, Scheme 1) in its active site.<sup>9</sup> It is fascinating that several non-heme diiron proteins such as ribonucleotide reductases (RNR)<sup>10</sup> and methemerythrin (Hr)<sup>11</sup> also contain at least two carboxylate bridges in the active site of their reduced forms. So, the isolation and study of synthetic models containing the structural core [Fe<sub>2</sub>(O)(O<sub>2</sub>CR)<sub>2</sub>]<sup>2+</sup> have received significant interest among



Scheme 1 Active site structures of sMMO in its reduced and oxidized forms.

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the chemical and biochemical communities.<sup>12-14</sup> Synthetic models containing the structural motif  $[Fe_2(O)(O_2CR)_2(L)_2]^{2+}$ , where L is a tridentate 3N ligand, have been isolated and studied as models for metHr and sMMO.<sup>15-19</sup> Christou et al. used the triply-bridged diiron(III) complexes<sup>20,21</sup> derived from bipyridine for alkane hydroxylation using tert-butylhydroperoxide (tert-BuOOH) as the oxygen source while Kitajima et al. isolated the triply-bridged diiron(III) complexes<sup>22</sup> derived from trispyrozolylborate ligand for alkane hydroxylation using molecular oxygen (in the presence of an electron source) but lower selectivities and poor yields were observed for these reactions. Later, Kodera et al. found that the complex  $[Fe_2(O)(O_2CCH_3)_2(hexpy)](ClO_4)_2$ , where hexpy is 1,2-bis[2-(bis(pyrid-2-ylmethyl))-6-pyridyl]ethane, exhibits a high activity with notable alcohol/ketone ratio (A/K, 2.4) for the hydroxylation of cyclohexane and tertiary/secondary carbon ratio  $(3^{\circ}/2^{\circ}, 4.2)$ for monooxygenation of adamantane using *m*-chloroperbenzoic acid (m-CPBA).<sup>23-25</sup> Very recently, Itoh et al.<sup>26</sup> have isolated the triply-bridged diiron(III) complex  $[Fe_2(O)(O_2CCH_3)_2(L)](ClO_4)_2$ , where L is the dinucleating carboxylate ligand 1,2-bis(N-benzyl-2-aminomethyl-6-pyridyl)ethane-N',N'-diacetic acid, and found higher selectivities for the hydroxylation of cyclohexane (A/K, 10)and for monooxygenation of adamantane  $(3^{\circ}/2^{\circ}, 13.6)$  using hydrogen peroxide. However, the reasons for the high selectivity and the mode of action of these complexes in alkane hydroxylation remain unclear. Also, many oxo-bridged diiron(III) complexes of tetradentate ligands have been isolated<sup>27-32</sup> as synthetic models for the diiron biosites, but the catalytic efficiency and selectivity of these systems are still lower than those of the enzymes.

All the above observations prompted us to embark on the isolation of diiron(III) complexes of tri- and tetradentate ligands with various carboxylate bridging ligands and study of their use as models for the benzene/alkane hydroxylation reactions catalyzed by sMMO.33-35 In this study, we have isolated the (µ-oxo)bis(µ-carboxylato)diiron(III) complexes  $[Fe_2(O)(OAc)_2(L1)_2](ClO_4)_2$  1,  $[Fe_2(O)(OBz)_2(L1)_2](ClO_4)_2$ 2, [Fe<sub>2</sub>(O)(OAc)<sub>2</sub>(L2)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 3 and [Fe<sub>2</sub>(O)(OBz)<sub>2</sub>(L2)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 4, where L1 = N, N-bis(pyrid-2-ylmethyl)-iso-butylamine, L2 =N,N-bis(pyrid-2-ylmethyl)benzylamine (Scheme 2), AcO = acetate and BzO = benzoate, aiming at constructing more efficient synthetic analogues for sMMO and studying the intermediate species responsible for the highly selective hydroxylation. The 3N ligands chosen contain two heterocyclic pyridine nitrogen donors to mimic the imidazolyl nitrogen donors in the enzymes. The single-crystal X-ray structures of [Fe<sub>2</sub>(O)(OBz)<sub>2</sub>(L1)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 2 and  $[Fe_2(O)(OBz)_2(L2)_2](ClO_4)_2$  4 have been determined to show that in all of these diiron(III) complexes each iron atom is coordinated to one oxygen atom of the µ-oxo bridge, two oxygen atoms of the µ-benzoato bridges and three nitrogen atoms of the ligands. We have observed that all the four complexes show efficient alkane hydroxylation with approximately 300-400 turn



Scheme 2 Tridentate 3N ligands used in the study.

over numbers and excellent selectivity (A/K ratio, 10–14;  $3^{\circ}/2^{\circ}$ , 9–11). Also, in the hydroxylation reactions the diiron(III) complexes decompose to form a catalytically-active mononuclear iron(III) species after ~50 turn-overs.

# Experimental

## Materials

Pyridine-2-carboxaldehyde, *iso*-butylamine, benzylamine, AgClO<sub>4</sub>, iron(III) perchlorate hydrate, adamantane, sodium triacetoxyborohydride, *m*-chloroperbenzoic acid (Aldrich), triethylamine, benzoic acid, acetic acid glacial, dichloromethane, diethylether, tetrahydrofuran (Merck, India), cyclohexane (Ranbaxy) and ethanol (Hayman Limited, England) were used as received. Acetonitrile was distilled before use. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared in water and recrystallized twice from aqueous ethanol.

#### Synthesis of ligands

The ligand N,N-bis(pyrid-2-ylmethyl)-iso-butylamine (L1) and N,N-bis(pyrid-2-ylmethyl)benzylamine (L2) were prepared by a method reported previously.<sup>36,37</sup> To a mixture of (4.5 mmol) alkylamine and sodium triacetoxyborohydride (3.75 g, 17.7 mmol) in dichloromethane (100 mL) was added pyridine-2-carboxaldehyde (1.45 g, 13.5 mmol) and stirred for 18 h. The reaction was quenched with saturated sodium hydrogencarbonate and extracted with ethylacetate ( $3 \times 150$  mL). The organic fractions were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed under reduced pressure. The residue was redissolved in tetrahydrofuran (50 mL) and treated with NaH (0.22 g, 9.1 mmol). After the mixture was stirred for 2 h, the solvent was removed and the residue was extracted with dichloromethane. The extracts were combined and the solvent was evaporated under reduced pressure to obtain the product. N,N-Bis(pyrid-2-ylmethyl)-iso-butylamine (L1). Yield: 0.91 g (79%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 8.48–7.29 (m, 8H), 3.88 (s, 4H), 2.38 (d, 2H), 1.87 (m, 1H), 1.05 (d, 6H). EI-MS  $m/z = 255 \text{ C}_{16}\text{H}_{21}\text{N}_3^+$ . N,N-bis(pyrid-2-ylmethyl)benzylamine (L2). Yield: 1.11 g (85%). 1H NMR (200 MHz, CDCl3): δ 8.50-7.02 (m, 13H), 3.85 (s, 4H), 3.21 (s, 2H). EI-MS m/z = 289 $C_{19}H_{19}N_3^+$ .

#### Synthesis of diiron(III) complexes

An ethanol solution (8 mL) of ligand (1.0 mmol) was added to a mixture of (2 mL H<sub>2</sub>O) 354 mg of Fe(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (1.0 mmol), 1.0 mmol of carboxylic acid and 1.0 mmol of triethylamine and stirred at room temperature. The resulting dark red solution was turned reddish brown. Reddish brown microcrystals of diiron(III) complexes were formed within 24 h upon slow cooling and standing. The microcrystals were collected by suction filtration, washed by a small amount of ethanol and dried *in vacuo*. Single crystals of **2** and **4** suitable for X-ray diffraction were obtained by the slow evaporation of an acetonitrile solution of the corresponding complexes.

Downloaded by FORDHAM UNIVERSITY on 17 December 2012 ublished on 24 March 2009 on http://pubs.rsc.org | doi:10.1039/B901508F  $[Fe_2(O)(OAc)_2(L1)_2](CIO_4)_2$  (1). Yield: 0.73 g (76%) Anal. calcd for  $C_{36}H_{48}Cl_2Fe_2N_6O_{13}$ : C 45.26, H 5.06, N 8.80. Found C 45.78, H 5.32, N 8.54.

 $[Fe_2(O)(OBz)_2(L1)_2](CIO_4)_2$  (2). Yield: 0.86 g (80%) Anal. calcd for  $C_{46}H_{52}Cl_2Fe_2N_6O_{13}$ : C 51.18, H 4.86, N 7.78. Found C 51.58, H 4.89, N 7.75. ESI-MS, m/z = 880.85  $[Fe_2(O)(OBz)_2(L1)_2]^{2+}$ .

 $[Fe_2(O)(OAc)_2(L2)_2](CIO_4)_2$  (3). Yield: 0.81 g (79%) Anal. calcd for  $C_{42}H_{44}Cl_2Fe_2N_6O_{13}$ : C 49.29, H 4.33, N 8.21. Found C 49.23, H 4.26, N 8.42.

 $[Fe_2(O)(OBz)_2(L2)_2](CIO_4)_2$  (4). Yield: 0.83 g (72%) Anal. calcd for  $C_{52}H_{48}Cl_2Fe_2N_6O_{13}$ : C 54.42, H 4.22, N 7.32. Found C 54.23, H 4.18, N 7.38. ESI-MS, m/z = 971.65 $[Fe_2(O)(OBz)_2(L2)_2]^2 + Na^+$ .

**Caution!** Perchlorate salts of compounds are potentially explosive. Only small quantities of these compounds should be prepared and suitable precautions should be taken when they are handled.

#### **Reactivity studies**

In a typical reaction, a CH<sub>2</sub>Cl<sub>2</sub> solution of 179 mg of *m*-CPBA was added to a  $CH_2Cl_2$  (400 µL) solution of alkane and diiron(III) complex (100 µL in CH<sub>3</sub>CN, 1 mmol dm<sup>-3</sup>) with vigorous stirring at room temperature. The solution was stirred for another 30 min and the diiron(III) complex was removed by passing the solution through silica gel followed by elution with diethylether. An internal standard (bromobenzene) was added at this point and the solution was subjected to GC analysis. The organic products were identified by GC and GC-MS comparison with authentic compounds. All of the products were quantified using GC (FID) with the following temperature program: injector temperature 130 °C; initial temperature 60 °C, heating rate 10 °C min<sup>-1</sup> to 130 °C, then increasing at a rate of 2 °C min<sup>-1</sup> to 160 °C, and then increasing at a rate of 5 °C min<sup>-1</sup> to 260 °C; FID temperature 280 °C. GC-MS analysis was performed under conditions identical to those used for GC analysis.

#### Physical measurements

Electronic spectra were recorded on a Diode Array Spectrophotometer Agilent 8453. Low temperature spectra were obtained on a Diode Array Spectrophotometer Agilent 8453 equipped with an UNISOKU USP-203 cryostat. <sup>1</sup>H NMR spectra were recorded on a Bruker 200 MHz NMR spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed at 25  $\pm$  0.2 °C using a three-electrode cell configuration. A platinum sphere, a platinum plate and Ag(s)/AgNO<sub>3</sub> were used as working, auxiliary and reference electrodes, respectively. The platinum sphere electrode was sonicated for two minutes in dilute nitric acid, dilute hydrazine hydrate and in double distilled water to remove the impurities. The reference electrode for non-aqueous solution was Ag(s)/Ag<sup>+</sup>, which consists of a Ag wire immersed in a solution of AgNO<sub>3</sub> (0.01 M) and tetra-N-butylammonium perchlorate (0.1 M) in acetonitrile placed in a tube fitted with a vycor plug. The instruments utilized included an EG & G PAR 273 Potentiostat/Galvanostat and P-IV computer along with EG & G M270 software to carry out the experiments and to acquire the data. The temperature of the electrochemical cell was maintained by a cryo-circulator (HAAKE D8-G). The  $E_{1/2}$  observed under identical conditions for Fc/Fc<sup>+</sup> couple in acetonitrile was 0.100 V with respect to the Ag/Ag<sup>+</sup> reference electrode. The experimental solutions were deoxygenated by bubbling research grade nitrogen and an atmosphere of nitrogen was maintained over the solution during measurement. The products were analyzed by using Hewlett Packard (HP) 6890 GC series Gas Chromatograph equipped with a FID detector and a HP-5 capillary column (30 m × 0.32 mm × 2.5 µm). GC-MS analysis was performed on a Perkin-Elmer Clarus 500 GC-MS instrument using a PE-5 (HP-5 equivalent) capillary column under conditions that are identical to that used for GC analysis.

#### Crystallographic data collection and structure refinement

Suitable crystals of 2 and 4 selected from the mother liquor was immersed in paraffin oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for the crystals were collected using MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation on a Bruker SMART APEX diffractometer equipped with a CCD area detector at 293 and 100 K. The crystallographic data were collected in Table 1. The SMART<sup>38</sup> program was used for collecting frames of data, indexing the reflections, and determination of lattice parameters; SAINT<sup>38</sup> program for integration of the intensity of reflections and scaling; SADABS<sup>39</sup> program for absorption correction, and the SHELXTL<sup>40</sup> program for space group and structure determination and least-squares refinements on  $F^2$ . The structure was solved by the heavy-atom method. Other nonhydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares analysis. Hydrogen atoms attached to the ligand moiety were located from the difference Fourier map and refined isotropically.

Table 1Crystallographic data of 2 and 4

	2	4
Empirical formula	C46H52Fe2N6O13Cl2	C <sub>52</sub> H <sub>48</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>13</sub> Cl <sub>2</sub>
Formula weight/g mol <sup>-1</sup>	1079.55	1147.58
Crystal habit, colour	Needle, reddish brown	Needle, reddish brown
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\overline{1}$
a/Å	12.2855(17)	12.1543(10)
b/Å	19.283(3)	14.4925(12)
c/Å	21.682(3)	15.7642(13)
$\alpha /^{\circ}$	90	82.999(1)
$\beta/^{\circ}$	103.9(3)	87.506(1)
γ/°	90	68.929(1)
$V/Å^3$	4986.1(12)	2571.8(4)
Ζ	4	2
$\rho_{\rm calcd}/{\rm g~cm^{-3}}$	1.438	1.482
F(000)	2240	1184
T/K	293	100
No. of reflections collected	29 731	22 194
No. of unique reflections	11 534	11 641
Radiation (MoKα)/Å	0.71073	0.71073
$R_1/WR_2 [I > 2\sigma(I)]^a$	0.0667/0.1523	0.0452/0.1048
$R_1/wR_2$ (all data)	0.1241/0.1778	0.0549/0.1096
${}^{a}R_{1} = \sum_{(WF_{o}^{4})} [N_{o}  -   A_{o} ]^{1/2}$	$F_{\rm c}\parallel)/\sum  F_{\rm o} ];  wR_2 =$	$\{ [\sum (w(F_o^2 - F_c^2)^2) / $

4

# **Results and discussion**

#### Synthesis of ligands and diiron(III) complexes

The linear tridentate 3N ligands N.N-bis(pyrid-2-ylmethyl)-isobutylamine (L1) and N,N-bis(pyrid-2-ylmethyl)benzylamine (L2) were (Scheme 2) synthesized according to known procedures, which involve reductive amination.36,37 The ligands L1 and L2 were prepared by reductive amination of iso-butylamine and benzylamine, respectively, with two moles of pyridine-2-carboxaldehyde using sodium triacetoxyborohydride as reducing agent and characterized by <sup>1</sup>H NMR spectroscopy and mass spectrometry. The diiron(III) complexes 1-4 of these ligands were prepared by adding one equivalent of L1/L2 to an aqueous ethanol solution containing one equivalent each of  $Fe(ClO_4)_3 \cdot 6H_2O_2$ , acetic acid/benzoic acid and triethylamine. All of them are formulated as  $[Fe_2(O)(O_2CR)_2(L)_2](ClO_4)_2$  on the basis of elemental analysis and ESI-MS, which is supported by the X-ray crystal structures of 2 and 4. These complexes with N-alkyl substituents on the ligands are expected to mimic the active site environment of the substrate-bound protein sMMO and have been chosen to model the benzene/alkane hydroxylation reactions of the enzyme. The carboxylate bridging ligands with different electron donating abilities are expected to play an important role in determining the reactivity.

# Description of the structures of $[Fe_2(O)(OBz)_2(L1)]^{2+}$ 2 and $[Fe_2(O)(OBz)_2(L2)]^{2+}$ 4

The molecular structures of **2** and **4** have been determined by single-crystal X-ray diffraction and the structures of the complex cations together with atom numbering scheme are shown in Fig. 1 and 2, respectively, and the bond lengths and bond angles are listed in Table 2. The coordination geometry around each iron atom in the diiron(III) complex **2** is distorted octahedral constituted by the oxygen atom of  $\mu$ -oxo bridge, two oxygen atoms one each from the two  $\mu$ -benzoato bridges and three



**Fig. 1** ORTEP diagram of complex **2** showing 50% probability thermal ellipsoids and the labelling scheme for selected atoms. All hydrogen atoms are omitted for clarity.



**Fig. 2** ORTEP diagram of complex **4** showing 50% probability thermal ellipsoids and the labelling scheme for selected atoms. All hydrogen atoms are omitted for clarity.

nitrogen atoms of the ligand L1. The tridentate ligand capping the two ends of the (µ-oxo)bis(µ-carboxylato)diiron(III) cluster coordinates to iron(III) in a least strained facial rather than a meridional fashion. Also, the tertiary amine nitrogen atom of the 3N ligand is weakly coordinated (Fe–N<sub>amine</sub>, 2.286(3), 2.304(3) Å) trans to the strongly coordinated µ-oxo bridge. The Fe-Namine bonds are longer than the Fe-N<sub>py</sub> bonds (2.111-2.138 Å) located *cis* to the  $\mu$ -oxo bridge obviously due to sp<sup>3</sup> and sp<sup>2</sup> hybridizations, respectively, of the amine and pyridine nitrogen atoms. The bond lengths and bond angles in 2 are comparable to those in complexes with a similar (µ-oxo)bis(µ-carboxylato)diiron(III) core structure reported in the literature.<sup>17,41-45</sup> The Fe-O<sub>oxo</sub> distances (Fe(1)-O(1), 1.794(2); Fe(2)–O(1), 1.795(3) Å) fall within the range 1.73–1.82 Å found for oxo-bridged diiron(III) complexes reported earlier<sup>17,41-45</sup> and for  $\text{Fe}_2\text{OCl}_6^{2-}$ .<sup>46-49</sup> The Fe  $\cdots$  Fe separation (3.094 Å) and Fe-O-Fe bond angle (119.11°) are very close to those observed for the analogous complex  $[Fe_2(O)(OBz)_2(L)_2]^{2+}$ , where L is N-alkyl substituted bis(pyrid-2-ylmethyl)amine, reported earlier.<sup>18</sup> The Fe-O-Fe bond angle is well outside the range for single and double-bridged complexes (140-180°) and is closer to 120° as observed in the planar  $Fe_3O_7^+$  unit<sup>50-52</sup> and this leads to an unusually short  $Fe \cdots Fe$  separation (3.094 Å). The  $Fe \cdots Fe$ separation (3.094 Å) is shorter than those in singly- and doublybridged µ-oxodiiron(III) complexes (3.4–3.6 Å).

The molecular structure of **4** is very similar to the analogous complex cation  $[Fe_2(O)(OBz)_2(L1)_2]^{2+}$  **2** with very similar Fe–O<sub>oxo</sub> (Fe(1)–O(1), 1.7963(16); Fe(2)–O(1), 1.7904(17) Å), Fe–N<sub>py</sub> (2.121–2.141 Å) and Fe–N<sub>amine</sub> (2.270(19), 2.255(2) Å) bond distances, Fe ··· Fe separation (3.060 Å) and the Fe–O–Fe bond angle (117.13(8)°). The most notable structure difference between **2** and **4** is the Fe–N<sub>amine</sub> bond distances. The Fe ··· Fe separation (3.060 Å) and Fe–O–Fe bond angle (117.13(8)°) are very close to those observed for the analogous complex [Fe<sub>2</sub>(O)(OBz)<sub>2</sub>(L)]<sup>2+</sup>, where L is *N*-alkyl substituted bis(pyrid-2-ylmethyl)amine, reported earlier.<sup>18</sup> An analysis of the bond parameters indicates that on replacing *N*-iso-butyl group in **2** by *N*-benzyl group to obtain **4** almost all the Fe–O and Fe–N bond distances decrease while the Fe ··· Fe distance increases (0.034 Å) indicating the lower donor ability of the bulky *N*-iso-butyl group. A similar effect has been observed

	2	4		
Bond lengths/Å				
Fe(1)–O(1)	1.794(2)	1.7963(16)		
Fe(1) - O(2)	2.031(3)	2.0285(17)		
Fe(1) - O(5)	2.032(2)	2.0154(16)		
Fe(1) - N(1)	2.128(3)	2.121(2)		
Fe(1)-N(2)	2.286(3)	2.2696(19)		
Fe(1)-N(3)	2.137(3)	2.124(2)		
Fe(2) - O(1)	1.795(3)	1.7904(17)		
Fe(2) - O(3)	2.015(3)	2.0539(16)		
Fe(2) - O(4)	2.046(2)	2.0106(16)		
Fe(2) - N(4)	2.111(3)	2.1322(19)		
Fe(2) - N(5)	2.304(3)	2.255(2)		
Fe(2)–N(6)	2.138(3)	2.141(2)		
Bond angles/°				
O(1)–Fe(1)–O(2)	98.56(11)	97.07(7)		
O(1) - Fe(1) - O(5)	98.12(11)	99.54(7)		
O(1) - Fe(1) - N(1)	95.73(11)	98.43(7)		
O(1) - Fe(1) - N(2)	170.91(11)	174.70(8)		
O(1) - Fe(1) - N(3)	100.08(12)	97.46(7)		
O(2) - Fe(1) - O(5)	90.48(10)	97.53(7)		
O(2) - Fe(1) - N(1)	165.12(11)	162.11(7)		
O(2) - Fe(1) - N(2)	89.75(10)	85.90(7)		
O(2) - Fe(1) - N(3)	82.92(11)	87.40(7)		
O(5) - Fe(1) - N(1)	91.58(10)	88.68(7)		
O(5) - Fe(1) - N(2)	85.41(9)	84.37(7)		
O(5) - Fe(1) - N(3)	161.37(11)	161.55(7)		
N(1)-Fe(1)-N(2)	75.74(11)	78.00(7)		
N(1)-Fe(1)-N(3)	90.55(11)	81.78(8)		
N(2)-Fe(1)-N(3)	77.19(11)	78.24(7)		
O(1) - Fe(2) - O(3)	99.04(11)	98.96(7)		
O(1) - Fe(2) - O(4)	97.64(11)	100.39(7)		
O(1) - Fe(2) - N(4)	100.34(13)	96.05(7)		
O(1)-Fe(2)-N(5)	170.47(11)	170.27(7)		
O(1) - Fe(2) - N(6)	94.69(11)	97.43(8)		
O(3) - Fe(2) - O(4)	90.75(10)	89.84(6)		
O(3) - Fe(2) - N(4)	160.46(12)	164.26(7)		
O(3) - Fe(2) - N(5)	83.68(11)	88.84(7)		
O(3) - Fe(2) - N(6)	89.72(11)	80.94(7)		
O(4) - Fe(2) - N(4)	84.23(12)	92.08(6)		
O(4) - Fe(2) - N(5)	91.43(10)	85.35(6)		
O(4) - Fe(2) - N(6)	167.43(10)	161.02(8)		
N(4) - Fe(2) - N(5)	77.60(12)	75.76(7)		

by us in mononuclear iron(III) complexes of the type [Fe(L)Cl<sub>3</sub>], where L is *N*-alkyl substituted bis(pyrid-2-ylmethyl)amine), where the Fe–N<sub>amine</sub> bond distance increases by 0.018 Å upon changing the *N*-alkyl group from methyl to *n*-propyl.<sup>37</sup> Obviously, the lonepair orbital on the nitrogen atom of the sterically hindering *N*-alkyl group is not oriented exactly toward the iron(III) orbital, rendering the Fe–N<sub>amine</sub> bond longer. This illustrates the importance of the steric rather than the electron-releasing effect of the alkyl group in dictating the coordination environment around iron(III) center. Hence on replacing the sterically hindering *N*-iso-butyl group in **2** by the less sterically hindering *N*-benzyl group to obtain **4**, the triply-bridged diiron(III) core becomes more compact.

#### Spectral studies

The three electronic spectral bands located in the range 400– 550 nm ( $\varepsilon_{max}$ , 1150–1650 M<sup>-1</sup> cm<sup>-1</sup>, Table 3) are characteristic<sup>23,44,53</sup> of O<sup>2-</sup>  $\rightarrow$  iron(III) LMCT bands in oxo-bridged diiron(III) complexes containing two carboxylate bridges. Four weak spinforbidden d-d transitions are expected for octahedral high-spin iron(III) complexes but only one band around 700 nm is readily observed for all the complexes and the remaining bands appear to be obscured by the more intense LMCT bands. The molar absorptivity of this band is much higher than that observed for high-spin mononuclear octahedral iron(III) complexes due to the lower symmetry of the dimeric complex with the oxo-bridge and also spin-spin interactions between the iron(III) centers.44 The oxobridge of all the complexes remains intact in DCM solutions as revealed by electrospray-ionization mass-spectrum (ESI-MS) (Fig. S1, ESI).<sup>‡</sup> The reaction of the diiron(III) complexes 1-4 with the oxidants H<sub>2</sub>O<sub>2</sub>, tert-BuOOH and m-CPBA was monitored by employing electronic absorption spectroscopy as a convenient tool. The addition of H<sub>2</sub>O<sub>2</sub> and tert-BuOOH to the present diiron(III) complexes dissolved in DCM at room temperature did not show any spectral change even in the presence triethylamine. However, on adding the strong oxidant *m*-CPBA to the diiron(III) complexes in DCM at room temperature, a small shift in the visible spectral band is observed and when one equivalent of triethylamine was added to this reaction mixture a stable and intense visible band (670-700 nm) eventually develops for 1-4 (Fig. 3). The ESI-MS spectrum of the later reaction mixture shows a peak at m/z 466 (Fig. 4), the mass and isotope pattern of which corresponds to the intermediate species  $[Fe_2(O)(OAc)(m-CPBA)(L)_2]^{2+}$ . Such an intermediate species has been proposed<sup>23</sup> to be formed initially in alkane hydroxylation reactions catalysed by the complex  $[Fe_2(O)(O_2CCH_3)_2(hexpy)](ClO_4)_2$  using *m*-chloroperbenzoic acid (m-CPBA).



**Fig. 3** Reaction of complex **4** with *m*-CPBA (5 equiv.) and triethylamine (1 equiv.) followed by UV-vis at room temperature.

#### **Electrochemical properties**

The electrochemical properties of the diiron(III) complexes were investigated in dichloromethane by employing cyclic (CV) and differential pulse voltammetry (DPV) on a stationary platinum electrode. All of the complexes show a cathodic reduction current in the range -0.536 to -0.612 V but not any coupled oxidation wave in the CV (Fig. 5). The cathodic current functions (6.73–7.19 ×  $10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>) calculated (n = 1) by substituting the slope obtained from the linear  $i_{pc}$  vs.  $v^{1/2}$  plot in Randles–Sevcik's equation<sup>54</sup> are of the same order as those observed for mononuclear iron(III) complexes undergoing a one-electron reduction process<sup>55</sup> and so the reduction process in the diiron(III) corresponds to:

**Table 3** Electronic spectral data ( $\lambda_{max}$  in nm;  $\varepsilon_{max}$  in M<sup>-1</sup> cm<sup>-1</sup> in parenthesis) and electrochemical data for diiron(III) complexes in an acetonitriledichloromethane mixture

Complex	$\lambda_{\rm max}/{\rm nm}~(\epsilon_{\rm max}/{\rm M}^{-1}{\rm cm}^{-1})$	$E_{\rm p,c}~({\rm CV})^b$	$E_{1/2}{}^{b}$ (DPV)	Redox process
$[Fe_2(O)(OAc)_2(L1)]^{2+}$	460 (1650)	-0.612	-0.530	$Fe^{III}Fe^{III} \rightarrow Fe^{II}Fe^{III}$
	500 (1250)			
	$706(185)^{a}$			
$[Fe_2(O)(OBz)_2(L1)]^{2+}$	466 (1480)	-0.570	-0.525	$Fe^{III}Fe^{III} \rightarrow Fe^{II}Fe^{III}$
	506 (1205)			
	$713(190)^{a}$			
$[Fe_2(O)(OAc)_2(L2)]^{2+}$	459 (1480)	-0.602	-0.537	$Fe^{III}Fe^{III} \rightarrow Fe^{II}Fe^{III}$
	504 (1150)			
	$700(180)^a$			
$[Fe_2(O)(OBz)_2(L2)]^{2+}$	461 (1510)	-0.536	-0.469	$Fe^{III}Fe^{III} \rightarrow Fe^{II}Fe^{III}$
	505 (1165)			
	$703(190)^{a}$			

<sup>*a*</sup> d–d transition corresponds to  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$  (<sup>4</sup>G). <sup>*b*</sup> Potential measured vs. Ag/AgNO<sub>3</sub> (0.001 M, 0.1 M TBAP); add 0.544 V to convert to NHE.



Fig. 4 Electron spray ionization-mass spectra of complex 2 + 1 equiv. *m*-CPBA + 1 equiv. triethylamine.

#### Fe(III)-O-Fe(III) + $e^- \rightarrow Fe(II)$ -O-Fe(III).

The  $E_{1/2}$  values of the Fe<sup>III</sup>/Fe<sup>II</sup> redox couples (-0.469 to -0.537 V, Table 3) fall in the range observed for similar type of triply-bridged diiron(III) complexes.<sup>43,44</sup> They are highly negative mainly due to the strong coordination of the bridging carboxylate groups and follow the trend 1 < 2 > 3 < 4. On replacing the bridging acetates in 1 by the bridging benzoates to obtain 2, the Fe<sup>III</sup>/Fe<sup>II</sup> redox potential is shifted to more positive values due to the weaker coordination ( $pK_a$ , AcOH, 4.76; BzOH, 4.19) of benzoate anion to iron(III). A similar but larger shift in redox potential is observed on moving from 3 to 4. Also, on decreasing the bulkiness of the tridentate ligand backbone in 1 to obtain 3, the Fe<sup>III</sup>/Fe<sup>II</sup> redox



**Fig. 5** Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of 1 mM complex 4 in a DCM–acetonitrile mixture at 25 °C. Supporting electrolyte: 0.1 M TBAP. Scan rate: 50 mV s<sup>-1</sup> for CV and 5 mV s<sup>-1</sup> for DPV.

potential is shifted to slightly more negative values suggesting that the FeN<sub>3</sub>O<sub>3</sub> coordination sphere becomes more compact (*cf.* above) to stabilize the iron(III) oxidation state. The X-ray structural data indicate that upon replacement of the coordinated ligand L1 in **2** by L2 to obtain **4**, the diiron(III) center becomes more compact, as understood from the decrease in distances of most of the coordinate bonds, and hence the redox potential is expected to be shifted to more negative values. However, interestingly, on going from **2** to **4**, the redox potential becomes slightly more positive implying that the complex undergoes intricate structural changes upon adding an electron to the diiron(III) core in **2**.

#### Functionalization of alkanes

The experimental conditions and the results of catalytic oxidation of alkanes into alcohols for the complexes **1–4** are summarized in Table 4. The conversion of alkanes into hydroxylated products was quantified based on gas chromatographic analysis by using authentic samples and an internal standard. All the complexes display efficient alkane hydroxylation with approximately 300– 400 turn over numbers (TON) with an excellent selectivity for the hydroxylation of cyclohexane (A/K, 10–14) and adamantane (3°/2°, 9–11; Table 4). Formation of small amount of caprolactone has been observed in cyclohexane hydroxylation which

 Table 4
 Products of oxygenation<sup>a</sup> of alkanes catalysed by diiron(III) complexes

	Cyclohexane <sup>bc</sup>			Adamantane <sup>c</sup>		
Complex	-ol	-one	A/K Ratio	1-ol	2-ol	3°/2°
1	353	28	12.6	340	35	9.7
2 3	373 335	27 33	13.8 10.2	375 345	37 32	10.1 10.8
4	277	27	10.3	295	34	8.7

<sup>*a*</sup> Reaction conditions:  $[complex] = 1 \text{ mmol } dm^{-3}$ ,  $[m\text{-CPBA}] = 0.8 \text{ mol } dm^{-3}$ ,  $[alkane] = 3 \text{ mol } dm^{-3}$  for cyclohexane and  $[complex] = 1 \text{ mmol } dm^{-3}$ ,  $[m\text{-CPBA}] = 0.6 \text{ mol } dm^{-3}$ ,  $[alkane] = 1 \text{ mol } dm^{-3}$  for adamantane in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (0.9 mL) and CH<sub>3</sub>CN (0.1 mL) stirred for 30 min. <sup>*b*</sup> Formation of small amount of ester observed for all the complexes. <sup>*c*</sup> Turn over number = no. of mol of product per no. of mol of catalyst.

is produced by the reaction of formed ketone with *m*-CPBA. Obviously, a variation in the carboxylate bridges and the N-alkyl substituents on the tridentate ligands do not affect the catalytic conversion very much. In the case of complex 2 as catalyst and cyclohexane as substrate, 373 turnovers of cyclohexanol (A) and 27 turnovers of cyclohexanone (K) are obtained, corresponding to a 50% conversion of the oxidant into organic products. Also, the conversion efficiency is maintained for the subsequent addition of the oxidant into the reaction mixture demonstrating that the active species is quite robust as a catalyst for alkane hydroxylation. The complexes 1-3 display turn over numbers (360-400 for cyclohexane; 370-410 for adamantane) higher than 4 does (304 for cyclohexane; 329 for adamantane) and this may be traced to the more negative Fe<sup>III</sup>/Fe<sup>II</sup> redox potentials of the former complexes (cf. above). The stability of the high-valent iron-oxo species generated from certain mononuclear iron(II) complexes has been correlated with the number of pyridine donors present in the primary ligand and on increasing the number of pyridine donors in the ligand,<sup>56</sup> the Fe<sup>III</sup>/Fe<sup>II</sup> redox potential is shifted to more negative values suggesting that the negative charge built on iron(II) center stabilizes the high-valent iron-oxo intermediate. Such high-valent iron-oxo complexes are invoked as the key turn over intermediates,<sup>57</sup> in the C-H bond functionalization by enzymes and their synthetic analogues.<sup>8,58-60</sup> Thus, µ-oxodiiron(III) complexes with more negative iron(III)/iron(II) redox potentials (Table 3) are expected to stabilize the high-valent iron-oxo active species more so that they can activate hydrocarbon molecules with strong C-H bonds at room temperature.

Interestingly, the amount of cyclohexanol formed for 2 increases (A/K, 2.7-13.7) with that of cyclohexanone formed being constant (Fig. 6 and Table 5) beyond ~50 turnovers on increasing the concentration of m-CPBA. A similar enhancement in the yield of 1-adamantanol with the yield of 2-adamantanol being constant (Fig. S3, S5 and S7<sup>‡</sup>) is observed for adamantane. All the other three complexes show a similar trend in the selective formation of cyclohexanol (ESI, Fig. S2, S4 and S6<sup>‡</sup>) and 1-adamantanol, after ~50 turnovers illustrating that on increasing the concentration of *m*-CPBA, the A/K value and  $3^{\circ}/2^{\circ}$  ratio increase. Interestingly, the present diiron(III) complexes show higher selectivity in the hydroxylation of cyclohexane (A/K, 10–14) and adamantane  $(3^{\circ}/2^{\circ}, 9-11; \text{Table 4})$  demonstrating that at higher concentrations of m-CPBA metal-based oxidants rather than non-selective radical-based species are involved in the C-H hydroxylation. Also, no change in the product selectivity and yield is observed upon performing the hydroxylation under inert condition, which ruled out the formation of cyclohexylperoxide species. This is also strongly supported the involvement of metalbased oxidants. In contrast, Kodera et al. have reported a lower selectivity in the hydroxylation of cyclohexane (A/K, 2.4) and adamantane  $(3^{\circ}/2^{\circ}, 4.2)$  using a similar type of  $\mu$ -oxodiiron(III) complex but derived from a dinucleating ligand and m-CPBA as an oxidant.23,24

The UV-vis spectral studies of the present diiron(III) complexes show that the spectral bands characteristic of triply-bridged diiron(III) complexes disappear after 50 turnovers revealing that the diiron(III) core of mononucleating ligands degrade slowly during catalysis. This suggests that after approximately 50 turnovers a new active metal-based mononuclear intermediate  $[Fe(L)(RCO_2)(Sol)_2]^{2+}$  is formed (cf. above), which is responsible for the highly selective hydroxylation of alkanes to alcohols. To gain further insight into the nature of the active species, the complex species [Fe(L2)(CH<sub>3</sub>CN)<sub>3</sub>]<sup>3+</sup> generated in acetonitrile solution was used for catalytic studies. In a typical reaction, a DCM solution of 9.0 mg of m-CPBA was added to a DCM solution (400  $\mu$ L) of cyclohexane (324  $\mu$ L), and a 1 : 1 mixture of  $[Fe(L2)(CH_3CN)_3]^{3+}$  and benzoic acid (100 µL in CH<sub>3</sub>CN, 1 mmol dm<sup>-3</sup>) with vigorous stirring at room temperature. After 30 min the reaction mixture was analyzed by GC. The turn over number is 24.0 for the formation of cyclohexanol and 2.3 for the formation of cyclohexanone. In contrast to diiron(III) complexes, the in situ prepared mononuclear iron(III) species show a high selectivity (A/K, 10.6) at lower concentrations of

 Table 5
 Results obtained for the oxygenation<sup>a</sup> of cyclohexane employing complex 2

Exp.	Catalyst/mol dm <sup>-3</sup>	<i>m</i> -CPBA/mol dm <sup>-3</sup>	Cyclohexanol <sup>b</sup>	Cyclohexanone <sup>b</sup>	A/K ratio
1	$1 \times 10^{-3}$	$20 \times 10^{-3}$	10.2	3.2	3.2
2	$1 \times 10^{-3}$	$40 \times 10^{-3}$	18.8	7.0	2.7
3	$1 \times 10^{-3}$	$60 \times 10^{-3}$	29.0	8.7	3.3
4	$1 \times 10^{-3}$	$80 \times 10^{-3}$	38.3	10.2	3.8
5	$1 \times 10^{-3}$	$100 \times 10^{-3}$	46.0	14.8	3.1
6	$1 \times 10^{-3}$	$200 \times 10^{-3}$	78.4	20.1	3.9
7	$1 \times 10^{-3}$	$400 \times 10^{-3}$	197.4	23.4	8.4
8	$1 \times 10^{-3}$	$600 \times 10^{-3}$	293.4	26.6	11.0
9	$1 \times 10^{-3}$	$800 \times 10^{-3}$	373.2	27.2	13.7

<sup>*a*</sup> Reaction conditions: [complex] =  $1 \times 10^{-3}$  mmol dm<sup>-3</sup>, [m-CPBA] = 0.02–0.8 mol dm<sup>-3</sup>, [alkane] = 3 mol dm<sup>-3</sup> in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (0.9 mL) and CH<sub>3</sub>CN (0.1 mL). <sup>*b*</sup> Turn over number = no. of mol of product per no. of mol of catalyst.



Fig. 6 Product yields as a function of equivalents of *m*-CPBA added into an acetonitrile–dichloromethane (v/v, 1 : 9) solution of complex 2 and cyclohexane in air. (a) 0–100 equiv. of *m*-CPBA; (b) 200–800 equiv. of *m*-CPBA.

*m*-CPBA indicating the significant participation of mononuclear high-valent iron-oxo active species in catalysis. This is further supported by the formation of a stable intense band (600 nm;  $\varepsilon_{max}$ , 355 M<sup>-1</sup> cm<sup>-1</sup>, Fig. 7), which is characteristics of high-valent iron-oxo species<sup>56</sup> when five equiv. of *m*-CPBA were added to a 1 : 1 mixture of [Fe(L2)(CH<sub>3</sub>CN)<sub>3</sub>]<sup>3+</sup> and benzoic acid at -40 °C. This band disappears slowly (Fig. 8) upon increasing the temperature and the decay of the iron-oxo intermediate has been followed at 25 °C (*k*, 4.15 × 10<sup>-3</sup> s<sup>-1</sup>). Hence, the high selectivity in alkane hydroxylation observed for the present triply-bridged diiron(III) complexes of mononuclear iron(III) species (Scheme 3) during hydroxylation. It is evident that the reaction of mononuclear iron(III) species, iron(III) species with *m*-CPBA gives benzoylperoxoiron(III) species,



**Fig. 7** Electronic spectra of reaction of  $[Fe(L2)(CH_3CN)_3]^{3+}$  and benzoic acid with 5 equiv. of *m*-CPBA in a mixture of acetonitrile–dichloromethane solvent at -40 °C.



**Fig. 8** Time course of decay of high-valent iron-oxo species generated from  $[Fe(L2)(CH_3CN)_3]^{3+}$  and benzoic acid at 25 °C.

which would undergo O–O bond heterolysis to afford iron(v)-oxo intermediate and *m*-chlorobenzoic acid as byproduct or O–O bond homolysis to yield iron(IV)-oxo intermediate and chlorobenzene as byproduct. Very recently, Que *et al.* have reported that complex cation [Fe<sup>II</sup>(N4Py)(CH<sub>3</sub>CN)]<sup>2+</sup> promotes O–O bond heterolysis, while the cation [Fe<sup>III</sup>(N4Py)(CH<sub>3</sub>CN)]<sup>3+</sup> favours O–O bond homolysis and concluded that the nature of the O–O bond cleavage is dependent on the iron oxidation state.<sup>61</sup> In contrast, we have observed that the *m*-chlorobenzoic acid (byproducts of heterolytic cleavage) as the major and chlorobenzene (byproducts of homolytic cleavage) as the minor byproduct in the catalysis illustrating that most of the benzoylperoxoiron(III) species undergo O–O bond heterolysis rather the O–O bond homolysis to afford iron(v)-oxo species and *m*-chlorobenzoic acid. The strong coordination of pyridine nitrogen of the 3N ligands L1 and L2 and



Scheme 3 Proposed mechanism of alkane hydroxylation.

monoanionic carboxylate ligand would be expected to stabilize the high-valent iron(v)-oxo intermediate. This is supported by the first example<sup>62</sup> of iron(v)-oxo complex species [Fe(TAML)(O)]<sup>-</sup>, where TAML is a macrocyclic tetraamide ligand, derived from the reaction of its iron(III) precursor with *m*-CPBA in butrylonitrile solution at -60 °C and the stability of iron(v)-oxo complex is traced to the strong  $\sigma$ -coordination of the tetraanionic ligand TAML.

### Conclusions

We have isolated four new triply-bridged diiron(III) complexes derived from linear 3N ligands and studied their ability to carry out alkane functionalization using *m*-CPBA as an oxidant. Two of the complexes have been structurally characterized by singlecrystal X-ray crystallography. All the four complexes show spectral and electrochemical properties characteristic of u-oxo-bridged diiron(III) complexes also containing two carboxylate bridges. The A/K and  $3^{\circ}/2^{\circ}$  ratios for the hydrocarbon oxidation catalyzed by the present complexes are 10-14 and ~10, respectively, and are independent of the concentration of molecular oxygen. The observation of high selectivity towards alkane hydroxylation suggests the involvement of an intermediate metal-based oxidant rather than freely diffusing radicals in the oxygenation. Also, the UV-vis spectral and ESI-MS studies reveal the formation of monoiron(III) species beyond 50 turnovers, which is also responsible for the highly selective alkane hydroxylation. The corresponding mononuclear iron(III) complexes prepared independently catalyze the oxygenation reactions strongly supporting this suggestion. The involvement of iron(v)-oxo intermediate species in carrying out the challenging C-H bond hydroxylation is supported by the appearance of a band around 600 nm upon adding the oxidant to the reaction mixture.

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