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Synthesis and structure of a μ-oxo diiron(III) complex with an *N*-pyridylmethyl-*N*,*N*-bis(4-methylbenzimidazol-2-yl)amine ligand and its catalytic property for hydrocarbon oxidation

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A μ-oxo diiron(III) complex [{Fe(pbba)Cl}$_2$(μ-O)]Cl$_2$ (1, pbba = *N*-pyridylmethyl-*N*,*N*-bis(4-methylbenzimidazol-2-yl)amine) bearing multi-imidazolyl motifs was synthesized and characterized by X-ray crystallography to closely mimic the structural features of methane monooxygenase. As shown by its X-ray crystal structure, complex 1 is a centrosymmetric dimer with an Fe–O–Fe angle of 180°, and pseudo-octahedral around each iron(III) center. The catalytic ability of title compound in the oxidation of alkane and alkene is investigated by employing *tert*-butylhydroperoxide and *m*-chloroperbenzoic acid as oxidants under mild conditions. The catalytic oxidation results showed that radical intermediate dominates the oxidation process. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: non-heme iron; diiron complex; alkane oxidation; epoxidation; imidazolyl ligand

Introduction

Synthesis and biomimetic oxidation chemistry of iron complexes has attracted a great deal of interest in the light of the remarkable catalytic activity of non-heme iron enzymes in the selective oxidation of alkanes and alkenes under mild conditions.[1] In recent years much effort has been put into the synthesis of model complexes that are capable of mimicking the alkane functionalization chemistry of methane monooxygenase enzymes (MMO).[2,3] Spectroscopic and crystallographic studies on MMO have shown that the active site has a diiron μ-hydroxo core [Fe$_2$(μ-OH)], containing both terminal and μ-carboxylate anions as well as H_2O and histidine ligands.[4–7] Over the last decade, a large number of μ-oxo- and μ-hydroxo-bridged diiron complexes have been prepared as structural models of the active site in MMO, and their catalytic activities in the oxidation of hydrocarbons in the presence of oxidants have been widely investigated.[8,9] Systems of non-porphyrin iron complexes containing Fe–O–Fe units such as [Fe$_2$O(TPA)$_2$X$_2$]$^{m+}$/*t*-BuOOH (H_2O_2) (TPA = tris(2-pyridylmethyl)amine, X = Br, Cl, H_2O),[10–13] [Fe$_2$O(L)$_4$X$_n$]$^{m+}$/*t*-BuOOH [where L = bipyridine, 4,4′-(Me)$_2$-bipy, phen; X = H_2O, Cl],[14,15] [Fe$_2$O(H_2O)$_2$(tmima)$_2$]$^{4+}$/H_2O_2 {tmima = tris[(l-methylimidazol-2-yl)methyl]amine},[16] [Fe$_2$O(salen)$_2$]/2-mercaptoethanol/O_2;[17] [Fe$_2$OL$_4$(H_2O)$_2$](ClO$_4$)$_4$/H_2O_2 [L = L(−)-4,5-pinenebipyridine],[18,19] [Fe$_2$O(bbp)$_2$(MeOH)$_2$(NO$_3$)$_2$](NO$_3$)$_2$/*t*-BuOOH (H_2O_2) (bbp = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine),[20] [Fe$_2$O(mebpa)$_2$Cl$_2$](ClO$_4$)$_2$/H_2O_2 [mebpa = *N*-(2-methoxyethyl)-*N*,*N*-bis(pyrid-2-ylmethyl)amine][21] have been reported by different research groups.

We have recently engaged in the preparation of μ-oxo-bridged diiron complexes containing the benzimidazolyl ligand for structural and functional biomimic of the MMO enzyme active site. Herein we report the preparation and the crystal structure of a new μ-oxo diiron complex [{Fe(pbba)Cl}$_2$(μ-O)]Cl$_2$ [**1**, pbba = *N*-pyridylmethyl-*N*,*N*-bis(4-methylbenzimidazol-2-yl)amine], as well as the catalytic properties in the oxidation of cyclohexane, cyclohexene, styrene and adamantane with *m*-chloroperbenzoic acid (*m*CPBA) and *tert*-butylhydroperoxide (*t*-BuOOH) as oxidants.

Experimental

Materials and instruments

All chemicals were of reagent grade, and were used as received. Dipotassium *N*-(2-pyridylmethyl)iminodiacetate was prepared according to the published procedure.[22] Infrared spectra were recorded from KBr pellets on a Jasco FT/IR 430 spectrophotometer. Proton and ^{13}C NMR spectra were collected on a Varian Inova 400NMR spectrometer. Elemental analysis was performed on a Thermoquest-Flash EA 1112 elemental analyzer. GC were performed on a Hewlett–Packard instrument equipped with an FID detector and an HP-5 column (30 m × 0.32 mm) and GC/MS analyses on an HP6890GC/5973MS apparatus.

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Preparation of the ligand pbba and complex 1

The ligand *N*-pyridylmethyl-*N*,*N*-bis(4-methylbenzimidazol-2-yl)amine (pbba) was prepared according to the literature procedure for the analogous ligand bis(2-benzimidazolylmethyl)(2-pyridylmethyl)amine.[22] The dipotassium *N*-(2-pyridylmethyl)iminodiacetate (0.75 g, 2.5 mmol) and 2,3-diaminotoluene (0.61 g, 5.0 mmol) were dissolved in hydrochloric acid (50 ml, 7 M). The mixture was refluxed with stirring for 72 h. The hydrochloride salt of product precipitated from the aqueous layer upon cooling to 4 °C. The subsequent work-up followed the method described in the literature.[22] Yield: 0.31 g (31%). ^{1}H-NMR (CD_3Cl, 400 MHz) δ (ppm): 2.65 (s, 6H, CH_3), 3.86 (s, 2H, $CH_{2(Py)}$), 4.00 (s, 4H, $CH_{2(Bzim)}$), 7.03 (d, 2H, $CH_{(Bzim)}$), 7.15 (t, 2H, $CH_{(Bzim)}$), 7.26 (t, 1H, $CH_{(Py)}$), 7.36 (d, 1H, $CH_{(Py)}$), 7.45 (d, 2H, $CH_{(Bzim)}$), 7.66 (t, 1H, $CH_{(Py)}$), 8.62 (d, 1H, $CH_{(Py)}$). ^{13}C-NMR (CD_3Cl, 400 MHz) δ (ppm): 17.3 (CH_3), 51.6 ($CH_{2(bzim)}$), 55.7 ($CH_{2(Py)}$), 122.5, 122.9, 123.1, 125.1, 137.7, 148.9, 151.0, 157.6.

The ligand pbba (0.40 g, 1.0 mmol) in methanol (10 ml) was added to a stirred methanol solution (5 ml) of $FeCl_3 \cdot 6H_2O$ (0.27 g, 1.0 mmol) to form a red solution. After the solution was stirred for 1 h, the resulting solution was evaporated in vacuum to *ca* 5 ml and kept in a refrigerator at −18 °C for 3 days, giving red microcrystals of the desired complex (0.22 g, 42%), which was suitable for X-ray crystal structure study. Found: C, 53.60; H, 4.77; N, 15.47%. $C_{49}H_{52}Cl_4Fe_2N_{12}O_2$ (**1**) calcd: C, 53.77; H, 4.79; N, 15.36%. IR data (KBr): ν 790 cm^{-1} for (Fe–O–Fe_{asym}).

General oxidation procedures

In a typical run, 0.5 mmol of oxidant (*t*-BuOOH or *m*CPBA) was added to an acetonitrile solution (5 mL) containing 5 μmol of complex **1** and 5 mmol of the substrate (cyclohexane, cyclohexene, styrene or adamantane) at room temperature with the ratios of catalyst:oxidant:substrate = 1 : 100 : 1000. The mixture was stirred under N_2 atmosphere for 3 h. The organic products were quantified by GC with 1,2-dichlorobenzene as internal standard and further verified by GC/MS.

X-Ray structure determination of complex 1

The single-crystal X-ray diffraction data were collected on a Siemens SMART CCD diffractomer with agraphite-monochromated Mo-K_α radiation (λ = 0.071073 Å) at 186 K using the ω–2θ scan mode. Data processing was accomplished with the SAINT processing program.[23] Intensity data were corrected for absorption by the SADABS program.[24] All structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods using the SHELXTL 97 program package.[25] All non-hydrogen atoms were refined anisotropically. Details of crystal data, data collections and structure refinements are summarized in Table 1. Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC–641 253. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336–033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data and processing parameters for complex **1**

Chemical formula	$C_{54}H_{72}C_{l4}Fe_2N_{12}O_7$
M	1254.74
System	Monoclinic
Space group	P2(1)/*n*
a (Å)	12.122(6)
b (Å)	12.480(7)
c (Å)	20.102(1)
α (°)	90.00
β (°)	97.312(1)
γ (°)	90.00
V (Å^3)	3016.6(3)
Z	2
D (mg m^{-3})	1.381
μ (mm^{-1})	0.717
Crystal size (mm)	0.16 × 0.18 × 0.12
θ range (deg)	2.94–17.55
F(000)	1312
*R*1[a] [$I > 2\sigma(I)$]	0.0560
*wR*2[b] [$I > 2\sigma(I)$]	0.0646
GOF (on F^2)	1.010

[a] $R1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Results and Discussion

The ligand pbba was prepared by the reaction of dipotassium *N*-(2-pyridylmethyl)iminodiacetate with 2 equiv of 2,3-diaminotoluene in a moderate yield according to the procedure for preparation of the analogous ligands.[22] Reaction of the ligand pbba and $FeCl_3 \cdot 6H_2O$ in methanol under air afforded the μ-oxo diiron(III) complex **1**. The extra oxidant is not needed for formation of the μ-oxo diiron complex.[26] Recrystallization of the diiron complex from methanol gave red crystals suitable for X-ray analysis.

The molecular structure of **1** was determined by X-ray analysis at a temperature of 186 K. To the best of our knowledge, this is the first crystallographically characterized linear μ-oxo diiron complex with a tetradentate ligand containing both benzimidazole and pyridine units. The ORTEP drawing of the cation of **1** is shown in Fig. 1. Selected bond lengths and angles are listed in the figure caption. The cation $[\{Fe(pbba)Cl\}_2(\mu\text{-}O)]^{2+}$ has a standard linear μ-oxo diiron(III) core [Fe(I)–O–Fe(1A) 180.00(2)°], with the Fe–O bond length of 1.7926(5) Å, which is similar to those reported for other analogous μ-oxo diiron complexes [1.771(5)-1.901 (1) Å] [16,26–28]. The oxygen atom O(1), linking two halves of the molecule, lies on the crystallographic center of symmetry. The distance between two iron atoms is 3.585 Å. Each iron center contains a distorted octahedral coordination geometry with two benzimidazole nitrogen atoms on the vertexes, and a pyridine nitrogen, an amine nitrogen, a chlorine, and the μ-oxygen atom in the tetragonal plane. The ligand pbba coordinates to the iron atom with the pyridine nitrogen atom *trans* to the oxo bridge. The eight Fe–N bonds of $[\{Fe(pbba)Cl\}_2(\mu\text{-}O)]^{2+}$ are in the range of 2.109–2.307 Å. The molecular structure of **1** is different from those of $[Fe_2O(H_2O)_2(tmima)_2](ClO_4)_4$ and $[Fe_2O(TPA)_2Cl_2]^{2+}$, which feature the Fe–O–Fe bond angles of 162.0(3) and 174.7(5)°, respectively.[7,15] The linear Fe–O–Fe structure of complex **1** might be caused by the significant π–π stacking interaction between the two parallel aromatic rings of the two ligands in one molecule. The inter-ligand π-stacking interaction between the two halves of the molecule may also play a role in the stabilization of the singly oxo-bridged diiron complex. Similar to complex **1**, compound $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$ was also reported

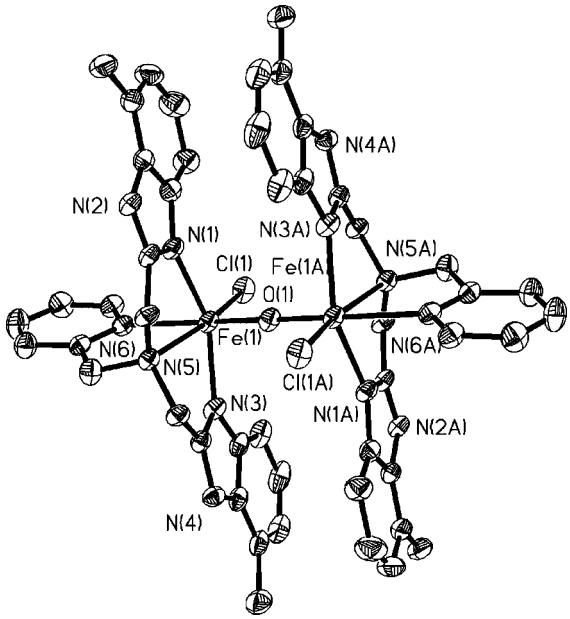

Figure 1. The cation structure of $[\{Fe(pbba)Cl\}_2(\mu\text{-}O)]Cl_2$ (**1**) with 30% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)–O(1) 1.7929(5), Fe(1)–N(1) 2.109(3), Fe(1)–N(3) 2.102(3), Fe(1)–N(5) 2.307(3), Fe(1)–N(6) 2.281(3), Fe(1)–Cl(1) 2.307(1), Fe(1)–O(1)–Fe(1A) 180.00(2).

to contain a linear Fe–O–Fe core width of 180°, in which strong interligand $\pi-\pi$ stacking between two N_3 tridentate merdional ligands was found.[20] In the tetradentate ligand of complex **1**, both benzimidazole groups and tertiary amine N atom are essentially located in a plane, providing a similar coordination environment to ligand bbp. Two labile positions occupied by exchangeable MeOH and NO_3^- in $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$ were substituted by Cl^- anion and blocking by pyridine coordination in complex **1**. Since $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$ is a good epoxidation catalyst under mild conditions, the structural influence on oxidation catalytic property was expected to be understood by comparison of the catalytic results of the two complexes.

The catalytic activity of complex **1** in the oxidation of hydrocarbon was explored under mild conditions with *m*CPBA and *t*-BuOOH as oxidants. The preliminary results are summarized in Table 2. Cyclohexane was oxidized to the corresponding alcohol and ketone in a ratio (A : K) of 1.48 with low conversion for *t*-BuOOH and 1.42 for *m*CPBA with moderate conversion (entries 1 and 4). The oxidation of adamantane catalyzed by complex **1** with *m*CPBA as terminal oxidant displayed a moderate regioselectivity with a 3°/2° ratio of 9.75 (entry 5), which is similar to the published results (9.6–11.0) performed with diiron complexes $[Fe_2O(bipy)_4(H_2O)_2(ClO_4)_4]$ and $[Fe_2O(bipy)_4(CH_3CO_2)(H_2O)_2(ClO_4)_3]$.[15,27] The selectivity for the oxidation at the tertiary position is higher than the average value of 2.7 found for Gif-type oxidations.[20]

In the presence of *t*-BuOOH the oxidation of cyclohexene afforded cyclohexenol and cyclohexenone as major products (62.0%), together with a small amount (5.2%) of the epoxide product (entry 2).When styrene was used as substrate, the aliphatic product benzaldehyde was detected by GC analysis as a major product (entry 3). The low epoxidation selectivity is in sharp contrast with the catalyst system of the iron complex $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$, which gave a high selectivity to epoxide (99.2%).[20] As shown above, the structural differences between two complexes may give clue to the low selectivity of **1** on epoxidation. Except for the labile position in $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$ being blocked by strong pyridine N coordination in the present iron complex, Cl^- as a labile ligand in complex **1** is relatively difficult to exchange with oxidant or substrate under reaction conditions, which switched a metal-based selective oxidation for $[Fe_2O(bbp)_2(MeOH)_2(NO_3)_2](NO_3)_2$ to non-selective autoxidation for **1**, decreasing the activity towards alkene's epoxidation. Unfortunately, an attempt to synthesize the corresponding complex with more flexible OTf^- or NO_3^- ligand was unsuccessful.

With *t*-BuOOH as oxidant and employing **1** as catalyst, the low A : K ratio in the oxidation of cyclohexane and low epoxidation selectivity in the oxidation of alkene clearly show that the oxidation process occurs via a radical mechanism, in which the OH radical or the alkane radical is the main species responsible for the oxidation. Although it has been reported by Feringa *et al*. and us that the different oxidant has a significant influnce on the oxidation products in the alkane's oxidation, the catalytic behavior exhibited by **1** did not show a noticeable change in alkane's oxidation product distribution.[28,29] In fact, almost the same A : K

Table 2. The results of oxidation of cyclohexane, cyclohexene, styrene and adamantane catalyzed by **1**[a]

Entry	Oxidant	Substrate	Conversion (%)	Product	Yield (%)[b]	Remark
1	*t*-BuOOH	Cyclohexane	12.4	Cyclohexanol	7.4	A:K = 1.48
				Cyclohexanone	5	
2	*t*-BuOOH	Cyclohexene	67.2	Epoxide	5.2	
				Cyclohexenol	34.6	
				Cyclohexenone	27.4	
3	*t*-BuOOH	Styrene	34.3	Benzoaldehyde	31.8	
				Epoxide	2.5	
4	*m*CPBA	Cyclohexane	26.6	Cyclohexane	15.6	A:K = 1.42
				Cyclohexanone	11	
5	*m*CPBA	Adamantane	10.2	3°-ol	7.8	3°/2° = 9.75[c]
				2°-one	1.8	
				2°-ol	0.6	

[a] The reactions were carried out in CH_3CN under N_2 atmosphere at room temperature for 3 h; [**1**] = 1.0×10^{-3} M, [oxidant] = 0.1 M, [substrate] = 1.0 M.
[b] Determined by GC analysis with internal standard based on the oxidants. [c] 3°/2° = (3°-ol)/(2°-ol + 2°-one) × 3.

ratios were observed using *m*CPBA as oxidant compared with *t*-BuOOH as oxidant. Therefore it seems to be a radical mechanism involved in both systems. This opinion is further supported by adamantane's oxidation, in which a low regioselectivity was observed ($3^\circ/2^\circ > 10$ is typical for a reaction with high valent iron-oxo species as the main oxidant).

Conclusions

In summary, the μ-oxo diiron(III) complex **1**, containing two benzoimidazole units in the ligand, was prepared as a new structural model of MMO. The catalytic property of complex **1** was investigated under mild conditions. The radical mechnism dominates both the alkane and the alkene's oxidation. The structural limit of complex **1** leading to its failure in efficient epoxidation was discussed. The preparation of non-heme iron complexes bearing more flexible labile ligands as good epoxidation catalysts is now underway in our laboratory.

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