Journal of Molecular Catalysis A: Chemical 396 (2015) 40–46

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Catalytic oxidation of dibenzothiophene and thioanisole by a diiron(III) complex and hydrogen peroxide

Alexandre Trehoux, Yoann Roux, Régis Guillot, Jean-Pierre Mahy*, Frédéric Avenier

Laboratoire de Chimie Bioorganiqe et Bioinorganique, Institut de Chimie Moléculaire et des Matériaux d'Orsay (UMR CNRS 8182), Université Paris Sud, Orsay 91405 Cedex, France

ARTICLE INFO

Article history:
Received 7 June 2014
Received in revised form
19 September 2014
Accepted 20 September 2014
Available online 30 September 2014

Keywords:
Diiron complex
Catalytic oxidation
Bio-inspired catalysis

ABSTRACT

One diiron(III) complex of the dinucleating ligand HPTP (*N,N,N′,N′*-tetrakis(2-pyridylmethyl)-2-hydroxy-1,3-diaminopropane) and one mononuclear iron(III) complex of the BPMEN ligand (N,N′-dimethyl-N,N′-bis-2-pyridinylmethyl)-1,2-ethanediamine) have been synthesized and characterized by X-ray diffraction analysis, high resolution mass spectrometry, and electronic absorption spectroscopy. The diiron(III) complex reacts with hydrogen peroxide to generate a short lived blue intermediate comparable to the previously described μ-peroxo-diiron(III) intermediate, obtained from the interaction of the corresponding HPTP diiron(II) complex with dioxygen. Both mononuclear and dinuclear iron complexes were tested for the catalytic oxidation of sulphides with H_2O_2, and the diiron complex showed good activity for the oxidation of dibenzothiophene (DBT), a fuel contaminant naturally present in crude oil. It catalyzed the total conversion of DBT into the corresponding sulfone *via* the formation of the sulfoxide, in acetonitrile at room temperature.

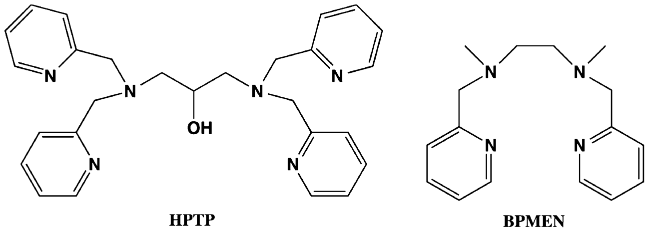
1. Introduction

Sulfur compounds are fuel contaminants naturally present in crude oil. They cause several disagreements during the process of oil refinement, such as corrosion of surfaces and poisoning of the catalysts. Upon combustion, they also generate sulfur oxidation compounds responsible for the generation of acid rain. Those major industrial and environmental issues have prompted the oil industry to develop efficient desulfurization processes [1] in order to meet new legislation standards about production of ultra-low-sulfur diesels (ULSD). Hydrodesulfurization (HDS) is the conventional process for the removal of sulfur compounds in fuels, but this process requires hydrogen under high pressure and high temperature conditions, which are energy demanding and expensive. Although HDS is efficient for the transformation of thiols, sulfides and disulfides, some sulfur containing compounds such as dibenzothiophene (DBT) and its derivatives are refractory to this process [2,3]. The alternative to HDS is the oxidative desulfurization (ODS) which works in two steps: (1) oxidation of sulfur into sulfoxide and sulfone, and (2) extraction of the oxidized compounds by polar solvents. Some catalytic systems such as H_2O_2/organic acids [4], H_2O_2/polyoxometalates [5,6], H_2O_2/ionic liquids [7,8] and H_2O_2/porphyrins [9,10] have demonstrated a good catalytic activity for this reaction. However, the development of new environmentally friendly and cheap processes is still needed, and bio-inspired iron complexes of readily accessible ligands combined to H_2O_2, are good candidates for ODS since iron presents low toxicity and since hydrogen peroxide is a benign oxidant. Bio-inspired concepts have indeed already been successful in many areas of science such as the development of artificial hydrogenases for he production of hydrogen [11] or the creation of nanodevices *via* the incorporation of enzymes in materials for various applications [12]. For instance, mononuclear iron(IV)-oxo complexes, obtained from the reaction of the corresponding iron(II) complexes and iodosylbenzene [13], have been demonstrated to oxidize DBT in stoichiometric amounts.[14] This shed light on the potential of non-heme iron catalysts inspired from iron mono-oxygenases for DBT oxidation. Amongst the members of the large family of iron mono-oxygenases, one of the most powerful catalyst described so far is the dinuclear iron enzyme, methane mono-oxygenase (MMO) [15]. Although this enzyme exhibits impressive catalytic activity, dinuclear iron complexes inspired from this system [16] have always been described as sluggish oxidants compared to heme catalysts and even to mononuclear non-heme iron complexes [17]. Only recently, highly active diiron complexes have been reported for hydrogen abstraction and oxygen atom transfer [18,19]. Interestingly, a μ-oxo dinuclear iron complex has been demonstrated to be a better catalyst for sulfide oxidation than the corresponding

---

* Corresponding author. Tel.: +33 1 69 15 74 21; fax: +33 1 69 15 72 81.
E-mail address: jean-pierre.mahy@u-psud.fr (J.-P. Mahy).

http://dx.doi.org/10.1016/j.molcata.2014.09.030



Scheme 1. Dinucleating ligand (HPTP) and monucleating ligand (BPMEN) used in this study.

mononuclear iron complex [20], suggesting a better intrinsic capability of dinuclear centres for sulfide oxidation compared to mononuclear complexes. Dinuclear systems synthesized from the dinucleating ligand HPTP (*N,N,N′,N′*-tetrakis(2-pyridylmethyl)-2-hydroxy-1,3-diamino-propane) [21] (Scheme 1) have been widely used to study dioxygen activation at diiron(II) centres [22–25]. However, very little is known about the catalytic properties of its readily available diiron(III) counterparts with hydrogen peroxide [26,27].

Here, we report the synthesis and characterization a new HPTP diiron(III) complex bearing four coordination positions occupied by exchangeable solvent molecules, in order to allow simultaneous interaction of hydrogen peroxide and substrate at the iron centres. The activity of this simple diiron(III) complex was then tested for the catalytic oxidation of sulfides and a good activity for DBT oxidation was observed. For comparison with a mononuclear iron(III) complex, we have also tested the catalytic activity of [BPMENFe(III)]Cl_2 and [BPMENFe(III)]$(ClO_4)_2$ complexes and both showed very poor activity for DBT oxidation. This is in sharp contrast with the activity of the [BPMENFe(II)]$(CH_3CN)_2$ counterpart which is known to be very active in catalytic oxidations, but for which the synthesis is much more restricting and time consuming, since it has to be prepared under inert atmosphere with multiple purification steps [28].

2. Results and discussion

2.1. X-ray diffraction analysis

The one step synthesis of the HPTP dinucleating ligand was adapted from the original synthesis developed by Suzuki et al. [21], and the corresponding diiron(III) complex was obtained by the addition of 2 equiv. of iron(III) perchlorate hexahydrate in methanol. Slow evaporation of this solution yielded crystals of sufficient quality for X-ray diffraction analysis and an ORTEP plot of compound **[1]** is shown in Fig. 1 (top). In this rather symmetrical structure, both iron have similar octahedral coordination geometries with exactly the same average distances of 2.053 Å with the various ligands, and a Fe–Fe distance of 3.734 Å. The diiron(III) centre is bridged by the alkoxo group of the ligand and both Fe(1) and Fe(2) coordinate two pyridyl moities in a *trans* geometry. The coordination sphere is completed by two methanol molecules for Fe(1), and one methanolate and one methanol for Fe(2). It is worth noting that one methanol ligand of Fe(1) forms an hydrogen bond with the methanolate ligand of Fe(2).

Synthesis of the BPMEN mononucleating ligand was realized according to Ref. [29], and the corresponding mononuclear iron complex was obtained by adding one equivalent of iron chloride, followed by precipitation with sodium hexafluorophosphate. Crystallization of this compound upon ether diffusion into an acetonitrile solution yielded crystals of sufficient quality for X-ray diffraction analysis. The ORTEP representation of this compound **[2]** is shown in Fig. 1 (bottom). This structure is comparable to structures previously described for other BPMEN mononuclear iron(III) complexes but bears different exogeneous ligands or different counter ions [30,31]. Two pyridyl moieties coordinate to the iron in a *trans* geometry, while two amine groups and two chloride ligands coordinate in a *cis* geometry with an average coodination distance of 2.220 Å for the six ligands. A similar BPMEN iron(III) complex was also synthesized by the addition of 1 equiv. of iron perchlorate hexahydrate. Unfortunately no crystal of the corresponding complex could be obtained.

2.2. Reactivity with hydrogen peroxide

In terms of reactivity, when the orange acetonitrile solution of **[1]** is submitted to the addition of hydrogen peroxide (10 equiv.), it instantly turns into a deep blue stable solution for about one minute at room temperature, with a maximum absorbance at 610 nm ($\varepsilon = 1660\ M^{-1}\ cm^{-1}$) (Fig. 2). This is similar to what was described previously for the interaction of the corresponding diiron(II) complex with dioxygen, and for which the blue intermediate was

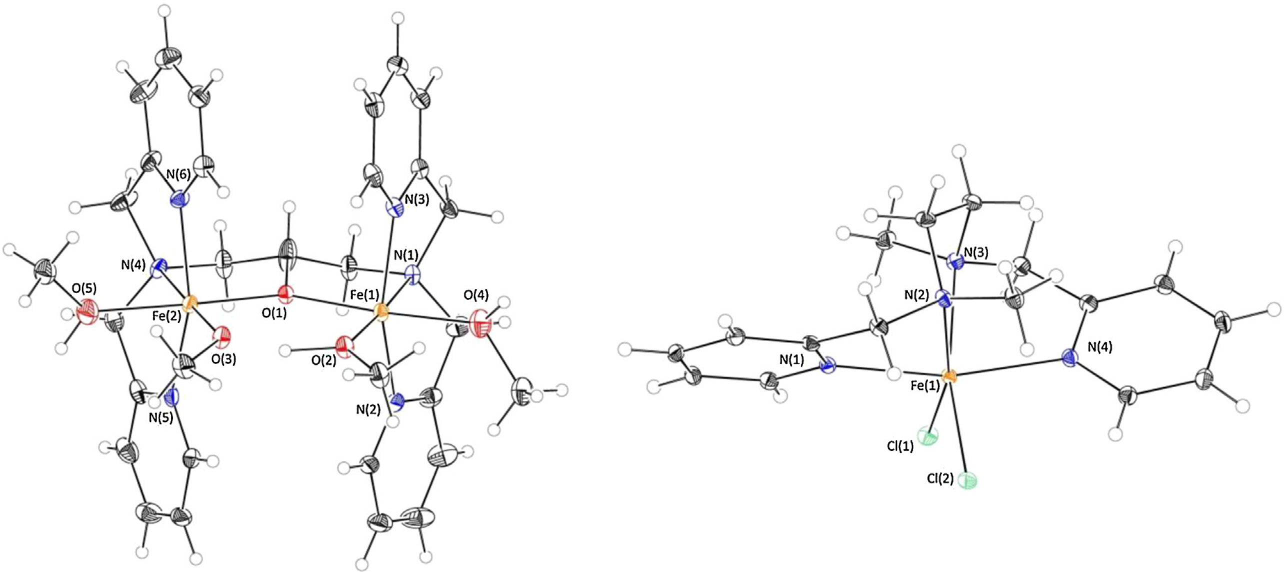


Fig. 1. ORTEP drawing (50% probability level) of $[Fe^{III}_2(HPNP)(CH_3OH)_3(CH_3O)](ClO_4)_4$ **[1]** (left), and $[Fe^{III}(BPMEN)(Cl)_2](PF_6)$ **[2]** (right). Uncoordinated anions and solvent molecules are excluded for clarity.

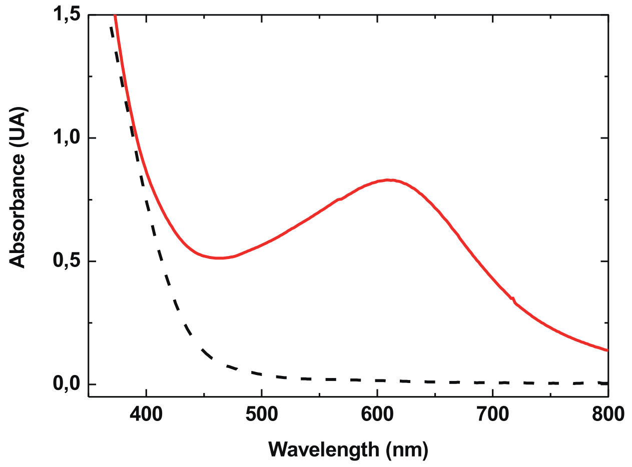


Fig. 2. UV–vis absorption spectra of complex **[1]** (dashed black line) and of the blue intermediate obtained 5 s after mixing compound **[1]** with 50 equiv. of H_2O_2 (solid red line). *Conditions:* 0.5 mM in MeCN at 20 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

assigned to a μ-peroxo-diiron(III) species by vibrational Raman spectroscopy experiments [24]. Unfortunately, the high fluorescence of our complex did not allow the characterization of the intermediate, neither by conventional vibrational Raman spectroscopy, nor by using a system equipped with a rotating cell.

In order to compare the catalytic capabilities of diiron(III) complexes with mononuclear iron(III) complexes, we have also tested the reactivity of the mononuclear complex **[2]** under the same conditions, and no UV–vis spectroscopic modifications could be observed in the first 5 s of reaction. Taking in consideration that chloride ions strongly coordinate to iron(III), and that this may affect the accessibility to the iron centre, we have also tested its reactivity for higher H_2O_2 concentration and for longer reaction time (Fig. 3). In this case, only changes are observed in the region between 300 nm and 400 nm, where amine- and pyridine-to iron(III) charge transfers are expected, suggesting that chloride ions are actually exchanged in solution. However, no absorption band in the UV–vis region, that may be associated to the formation of an iron(III)-hydroperoxo species, as previously described for similar mononuclear iron(II) complexes [32], could be observed. This is in line with the huge instability of such a species with the tetradentate BPMEN ligand, for which only traces could be detected at temperatures below −60 °C [33].

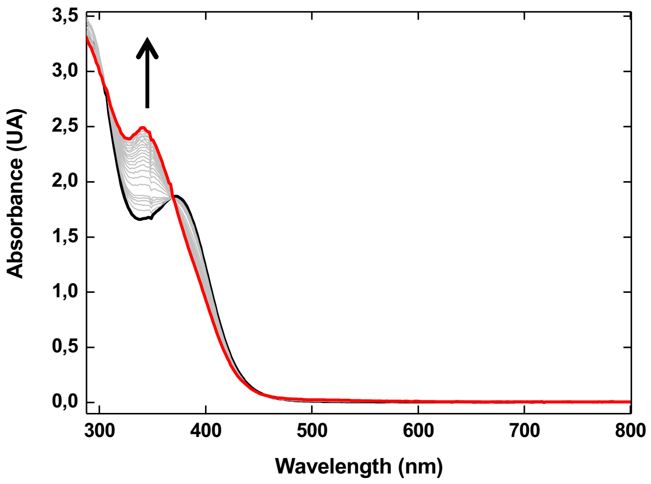
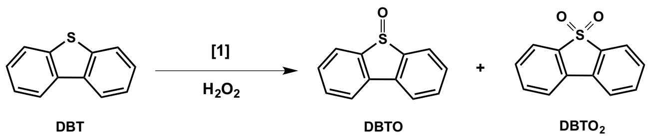


Fig. 3. UV–vis absorption spectra of complex **[2]** after addition of 100 equiv. of H_2O_2 (from 0 to 60 min). *Conditions:* 0.5 mM in MeCN at 20 °C.



Scheme 2. Oxidation of dibenzothiophene (DBT) into the corresponding sulfoxide (DBTO) and sulfone ($DBTO_2$).

2.3. *Catalysis experiments*

The catalytic activity of complex **[1]** was then studied for the oxidation of DBT in acetonitrile under aerobic conditions. When H_2O_2 was added to a solution of **[1]** in the presence of DBT, the blue intermediate disappeared immediately after its formation at room temperature, suggesting that DBT reacted either directly with the peroxo intermediate, or with a product of its degradation such as an iron(IV)-oxo species previously observed for mononuclear complexes [14]. The reaction was then followed by HPLC, looking at the degradation of DBT and the formation of the corresponding sulfoxide and sulfone upon sequential additions of H_2O_2 (Scheme 2).

The results are summarized in Fig. 4, and one can observe that DBT is rapidly consumed to form exclusively the corresponding sulfoxide (DBTO) in the early stage of the reaction. The sulfone ($DBTO_2$) only appears after the addition of eight equivalents of H_2O_2, suggesting that its formation arises only from the oxidation of DBTO and not directly from the oxidation of DBT. This stepwise oxidation of DBT into DBTO and $DBTO_2$ was confirmed by ESI-MS analysis, showing the formation of both DBTO and $DBTO_2$ for 20 equiv. of H_2O_2 and exclusively $DBTO_2$ above the addition of 44 equiv. of H_2O_2 with respect to the catalyst. The complete conversion of DBT (10 equiv./catalyst) was reached for 36 equiv. of H_2O_2, and the complete oxidation into $DBTO_2$ was reached after addition of 44 equiv. of oxidant.

The interesting catalytic activity of complex **[1]** raised the question of which active species was involved in the mechanism. The observation of a blue intermediate, upon addition of hydrogen peroxide to the complex strongly suggests the formation a μ-peroxo-diiron(III) as previously described for the reaction of similar diiron(II) complex with dioxygen. The rapid consumption of this intermediate in the presence of DBT suggests either its direct implication as an active species, or the formation of an active Fe(IV)-oxo species resulting from its homolytic cleavage. In order to clarify this mechanism, catalysis was carried out in the presence 1000 equiv. of $H_2{}^{18}O$. In that case, ESI-MS analysis shows 38% incorporation

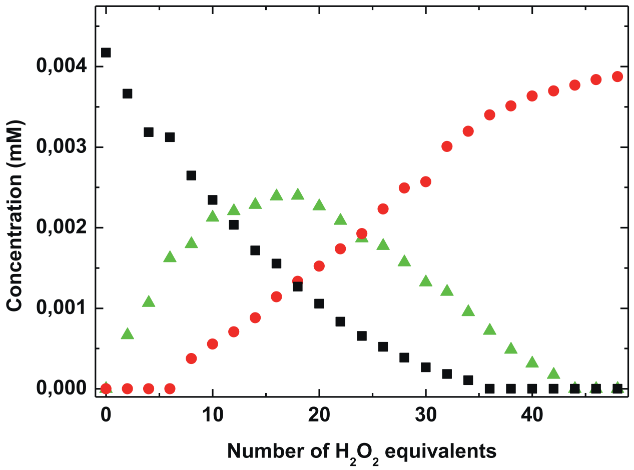


Fig. 4. Catalytic degradation of DBT (■), and formation of DBTO (▲) and $DBTO_2$ (●) in MeCN at 20 °C followed by HPLC. *Conditions:* **[1]**/H_2O_2/DBT (1/x/10) with x = 0–60.

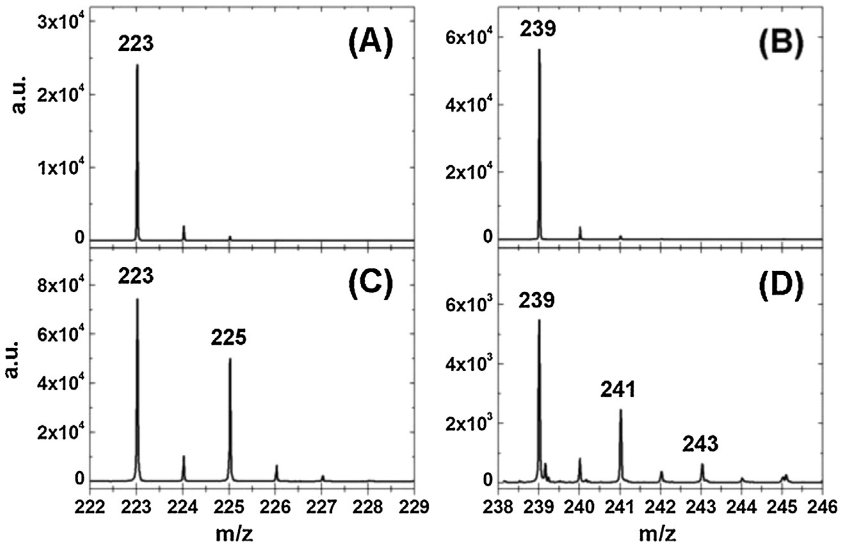


Fig. 5. ESI-MS spectra of DBTO (*m*/*z* 223) and $DBTO_2$ (*m*/*z* 239) after catalytic oxidation of DBT with complex **[1]** and H_2O_2 in the absence (A and B) and in the presence of $H_2{}^{18}O$ (C and D).

of labelled oxygen for DBTO (Fig. 5C) and about 31% incorporation for the first oxygen of $DBTO_2$ (Fig. 5D). As one would expect, the labelling of the second oxygen is less important, but can still be observed on the spectrum. This implies that both sulfoxide and sulfone products are formed *via* a similar metal centred iron-oxo intermediate capable of oxo/hydroxo tautomerism as previously described for porphyrin [34], mononuclear [35] and dinuclear iron complexes [36] (Scheme 3). These isotope labelling experiments also exclude the direct implication of a peroxo intermediate as the active species.

When catalysis is performed with the mononuclear complex **[2]**, DBT is not consumed upon the sequential addition H_2O_2 and no traces of oxidized products, neither DBTO nor $DBTO_2$, can be detected (Fig. 6). Control experiment, using solely H_2O_2, shows no DBT conversion at all (Fig. 6), while control experiments with H_2O_2 and $Fe(ClO_4)_3$ salts only show very little conversion into DBTO (Fig. S1, supporting information). Recent reports have shown that Fe(III)OOH intermediates supported by tetradentate ligands, formed upon addition of hydrogen peroxide to iron(II) complexes, can generate Fe(V)O species provided there is a labile ligand in *cis* with respect to the hydroperoxo ligand. These Fe(O) species, formed upon reaction of iron(II) complexes with H_2O_2 are active for aromatic hydroxylation [37] or epoxidation reactions [38,39].

In the case of complex **[2]**, it is likely that both chloro ligands could not be substituted at the same time, preventing the evolution of the putative $[(BPMEN)Fe^{III}Cl(OOH)]^+$ into a high valent Fe(V)O. In order to avoid the coordination of chloride ions to the iron centre, we also prepared the corresponding BPMEN mononuclear iron(III) complex directly in solution by mixing the ligand with iron(III) perchlorate, and tested its activity under the same conditions. In this case, one can observe a small improvement in the catalytic activity, but nothing significantly better than the control realized with $Fe(ClO_4)_3$ in solution (Fig. 6). The inertness of complex **[2]** and of its iron(III) perchlorate analogue could also be explained by the formation of oxo-bridged diiron(III) complexes which are known

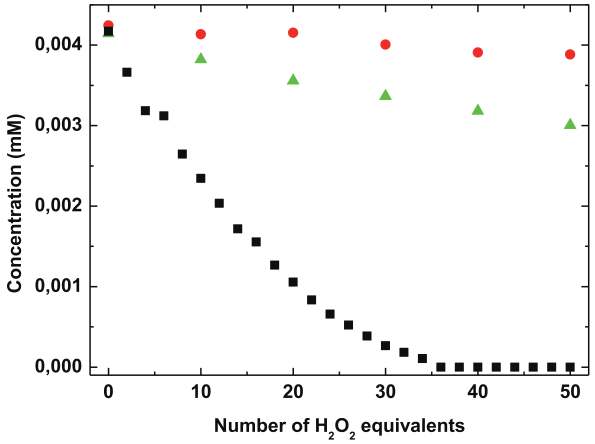
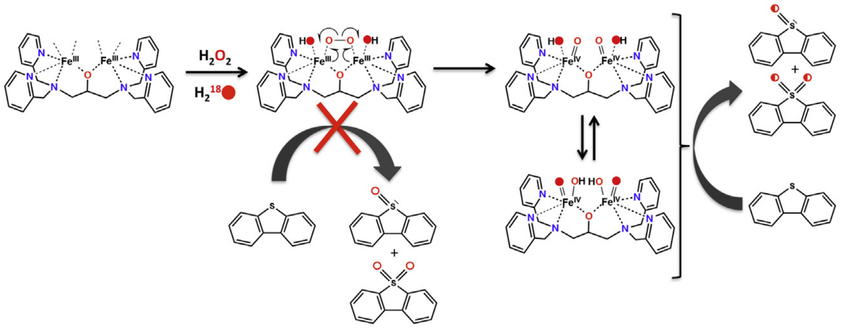


Fig. 6. Catalytic degradation of DBT using complex **[1]** (■), complex **[2]** (●) and [BPMENFe(III)]$(ClO_4)_3$ prepared *in situ* (▲) in MeCN at 20 °C followed by HPLC. *Conditions:* **[1]** or **[2]**/H_2O_2/DBT (1/*x*/10) with *x* = 0 to 60.



Scheme 3. Mechanism proposed for the catalytic oxidation of DBT by complex **[1]** and H_2O_2.

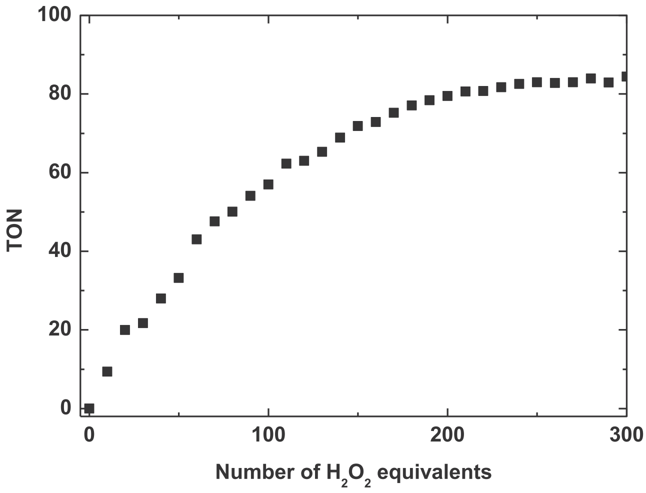


Fig. 7. Turn over numbers observed for the conversion of DBT with complex **[1]** and H_2O_2. *Conditions:* **[1]**/H_2O_2/DBT (1/*x*/100) with *x* = 0–300 equiv., in MeCN at 20 °C.

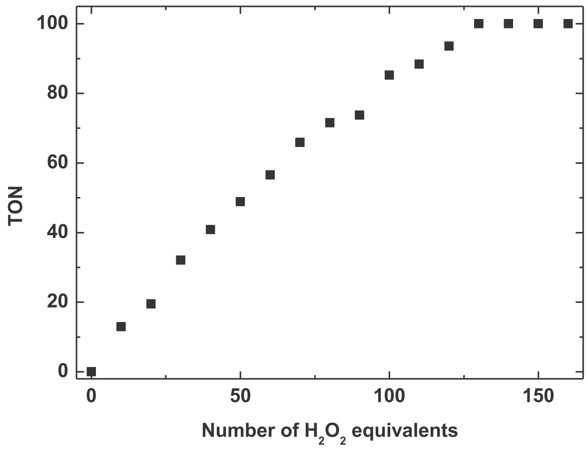


Fig. 8. Turn over numbers observed for the conversion of thioanisole with complex **[1]** and H_2O_2. *Conditions:* **[1]**/H_2O_2/thioanisole (1/*x*/100) with *x* = 0–160 equiv., in MeCN at 20 °C.

to be poorly active in substrate oxidation with hydrogen peroxide. The inertness of these mononuclear iron(III) complexes towards hydrogen peroxide stands out from the good catalytic activity of the corresponding iron(II) systems which are highly performing in oxidation catalysis (see Fig. S2, supporting information) but rather difficult to obtain in terms of conditions of preparation (inert atmosphere) and in terms of purification.

Complex **[1]** was then tested when increasing the proportions of substrate up to 100 equiv. in order to evaluate its long-term stability. Fig. 7 shows that for the first 20 equiv. of oxidant, DBT conversion is quantitative (20 turnovers observed), and above this value the activity slows down to reach a maximum of 85 turnovers. To the best of our knowledge, this is the first example of efficient catalytic oxidation of DBT by a dinuclear iron complex with hydrogen peroxide. It is also another example showing a better activity of dinuclear iron complexes for sulfide oxidation compared to mononuclear iron(III) complexes which can easily be prepared from stable iron(III) salts without any further precautions. Iron(II) complexes are better candidates for catalytic oxidations, but their preparation requires specific conditions and multiple purifications steps which are not convenient for the development of useful catalysts potentially used for fuel desulfurization. Conversely, complex **[1]** can easily be synthetized on the bench by mixing the dinucleating ligand with two equivalents of stable iron(III) salts. The overall activity of complex **[1]** is comparable to other catalytic systems recently described and working under mild conditions [5,6,40–42], with a total conversion of DBT for about three equivalents of hydrogen peroxide, and a maximum of 85 turnovers. It is worth noting that this capability of dinuclear iron complexes for the oxidation of thiophene derivatives into the corresponding sulfone could also be of high interest for the oxidation of thiophene-based oligomers, which are important active components for potential electronic applications [43].

Complex **[1]** was also tested for catalytic oxidation of thioanisole with hydrogen peroxide under the same conditions as DBT, and Fig. 8 shows that complex **[1]** easily achieves the complete conversion of 100 equiv. of thioanisole into the corresponding sulfoxide and sulfone with a slight excess of H_2O_2. The linear conversion up to 70 equiv. of H_2O_2 with respect to the catalyst also demonstrates the good robustness of the catalyst for this reaction.

Complete conversion of thioanisole is reached for 1.3 equiv. of H_2O_2 with respect to the substrate. ESI-MS analysis show the formation of both sulfoxide and sulfone compounds during the reaction, as we have previously observed for the much more difficult oxidation of DBT. Control experiment with iron(III) perchlorate hydrate showed no significant conversion compared to the blank reaction using H_2O_2 only (see Fig. S3, supporting information). The oxidation of thioanisole using dioxygen with a similar diiron(II) HPTP complex bearing a carboxylate bridge, was previously described by Costas et al. [23] In this case, the authors describe the formation of a blue peroxo intermediate which catalyzes the sub-stoichiometric sulfoxidation of thioanisole with a 59% yield (no over oxidation into the corresponding sulfone was observed). Interestingly, the same diiron(II) complex, bearing two carboxylate bridges, generates a similar and even more stable peroxo intermediate which is completely inactive for sulfide oxidation. This confirms the importance of the four exchangeable coordination sites present on our diiron(III) complexes, in order to perform efficient catalytic oxidation of sulfides.

3. Conclusions

Through this work, we have synthesized and characterized a new HPTP diiron(III) complex bearing four coordination positions occupied by exchangeable solvent molecules. Its capacity to oxidize sulfides was then tested with hydrogen peroxide, and this complex appeared to be a very good catalyst for thioanisole oxidation but also for the difficult oxidation of dibenzothiophene, a natural contaminant of crude oil. HPLC and ESI-MS analysis revealed the formation of the sulfoxide product in the early stage of the reaction and total conversion into the corresponding sulfone after addition of about 3.5 equiv. of oxidant with respect to the substrate. Experiments in the presence of $H_2{}^{18}O$ coupled to ESI-MS analysis also demonstrate the involvement of a metal centred iron-oxo species, most probably a short lived $Fe^{IV}(O)$ species formed upon the homolytic cleavage of the μ-peroxo-diiron(III) intermediate. Interestingly, catalysis performed with the BPMEN mononuclear iron(III) complex as catalyst shows very poor activity for this reaction. This points out the intrinsic capabilities of readily available dinuclear iron(III) complexes for the difficult desulfurization of dibenzothiophene and opens new routes for the facile oxidation of refractory thiophene-based oligomers, which are interesting component for potential electronic applications.

4. Experimental

Synthesis: The mononucleating ligand BPMEN was synthesized according to Ref. [29] and the dinucleating ligand HPTP was synthesized *via* the following method, adapted from the original synthesis developed by Suzuki et al. [21].

***N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,3-diaminopropan-2-ol (HPTP)**: (2-Chloromethyl)pyridine hydrochloride was dehydrochlorinated by dissolution in an aqueous solution saturated with sodium carbonate and then extracted with dichloromethane. To a 7 mL solution of 1,3-diamino-2-propanol (144 mg) in acetonitrile was added dropwise a 5 mL solution of (2-chloromethyl)pyridine (815 mg) in acetonitrile. Then, triethylamine (1.75 mL) was added dropwise to the reaction mixture that was then allowed to stir at room temperature for 5 days. After removing the solvent under vacuum, the mixture was dissolved in dichloromethane and washed three times with water. Purification by silica gel column chromatography ($CHCl_3/CH_3OH$) yielded 351 mg (48%) of the expected product as a pale yellow oil. ^1H NMR analysis ($CDCl_3$, 360 MHz): δ (ppm): 8.529 (4H, d, J_{HH} = 4.7 Hz), 7.616 (4H, td, J_{HH} = 7.7 Hz, J_{HH} = 1.8 Hz), 7.402 (4H, d, J_{HH} = 7.9 Hz), 7.152 (4H, td, J_{HH} = 4.7 Hz, J_{HH} = 1.4 Hz), 3.935–4.101 (9H, m), 2.72 (4H, m). HR ESI-MS analysis: *m*/*z* 455.2551, calculated *m*/*z* 455.2554.

$[Fe^{III}{}_2(HPTP)(CH_3O)(CH_3OH)_3](ClO_4)_4$ [1], was prepared by adding dropwise a 5 mL solution of iron(III) perchlorate hexahydrate ($Fe(ClO_4)_3$, $6H_2O$) (527 mg) to a 20 mL solution of *N,N,N′N′*-tetrakis(2-pyridylmethyl)-1,3-diaminopropan-2-ol (HPTP) (259 mg) in methanol under stirring at room temperature. Slow evaporation of the orange solution yielded orange crystals of the desired complex. HR ESI-MS analysis $[Fe^{III}{}_2(HPTP)(CH_3O)_2(ClO_4)_2]^+$: *m*/*z* 825.0426; Calculated: m/z 825.0500 and $[Fe^{III}{}_2(HPTP)(CH_3O)_3(ClO_4)]^+$: *m*/*z* 757.1119; Calculated: *m*/*z* 757.1200. Elemental Analysis: calculated for $C_{31}H_{44}Cl_4Fe_2N_6O_{21}$, C 34.15%, H 4.07%, N 7.71%, Fe 10.24%. Found, C 34.09%, H 4.28%, N 7.62%, Fe 9.84%

Warning: Perchlorate salts are explosive compounds when led to dryness and have to be handled carefully and in small quantities.

$[Fe^{III}(BPMEN)(Cl)_2](PF_6)$ [2], was prepared by adding dropwise a 10 mL solution of iron(III) chloride ($FeCl_3$) (288 mg) to a 10 mL solution of N,N′-dimethyl-N,N′-bis-2-pyridinylmethyl)-1,2-ethanediamine (BPMEN) (480 mg) in methanol under stirring at room temperature. The complex precipitated as a yellow solid upon addition of a 5 mL solution of potassium hexafluorophosphate (1 g) in methanol. Recrystallization by ether diffusion in acetonitrile yielded yellow crystals of the desired complex. HR ESI-MS analysis for $[Fe^{III}(BPMEN)(Cl)_2]^+$: *m*/*z* 396.0579; calculated: *m*/*z* 396.0566. Elemental analysis: calculated for $C_{16}H_{24}Cl_2F_{12}FeN_4P_2$, C 27,89%, H 3.51%, N 8.13%. Found, C 27.83%, H 3.25%, N 8.25%.

X-ray crystallography procedures: X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97 [44] and refined against F2 by full-matrix least-squares techniques using SHELXL-97 [45] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed using the Crystal Structure crystallographic software package WINGX [46]. The crystal data collection and refinement parameters are given in Table S1. CCDC 964616-964617 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/Community/Requestastructure. In the case of compound **[1]** crystals were very small and diffraction intensity was extremely low. In these conditions, it was not possible to get a model with an *R* factor less than 10.06%.

Electronic absorption spectroscopy: UV–vis experiments were all carried out in a Varian carry300Bio spectrophotometer.

Catalytic oxidation of DBT: A 5 mL acetonitrile solution of $[Fe^{III}{}_2(TPDP)(CH_3O)(CH_3OH)_3](ClO_4)_4$ (0.5 mM) and dibenzothiophene (5 mM) was subjected to 25 successive injections of 10 μL of a 0.5 M hydrogen peroxide solution in acetonitrile every two minutes (60 equiv. with respect to the catalyst). For HPLC measurements, 10 μL of the reaction mixture and 50 μL of a 10 mM solution of anisole were filtered off on silica (1 cm in Pasteur pipette) and eluted with 1.5 mL of acetonitrile. Finally, 12.5 μL of this filtered solution were injected in a C18 grafted silica column (Agilent eclipse plus C18, 3.5 μm, 4.6 × 10 mm) and eluted with a mixture of $MeCN/H_2O$ (70/30) at a rate of 1 mL min^{-1}. Elution times (min.): DBTO (1.24); $DBTO_2$ (1.50); anisole (1.80); DBT (4.54). All catalytic experiments were carried out under aerobic conditions.

Catalytic oxidation of thioanisole: A 5 mL acetonitrile solution of $[Fe^{III}{}_2(TPDP)(CH_3O)(CH_3OH)_3](ClO_4)_4$ (0.05 mM) and thioanisole (5 mM) was subjected to 20 successive injections of 10 μL of a 0.25 M hydrogen peroxide solution every two minutes (200 equiv. with respect to the catalyst). For HPLC measurements, a 10 μL sample of the reaction mixture, to which were added 50 μL of anisole as internal standard (10 mM), was filtered off on silica (1 cm in Pasteur pipette) and eluted with 1.5 mL of acetonitrile. Finally, 12.5 μL of this filtered solution were injected on a C18 grafted silica column (Agilent eclipse plus C18, 3.5 μm, 4.6 mm × 10 mm) and eluted with a mixture of $MeCN/H_2O$ (70/30) at a rate of 1 mL min^{-1}. Elution times (min): methyl phenyl sulfoxide (1.03); methyl phenyl sulfone (1.03); anisole (1.80); thioanisole (2.25). All catalytic experiments were carried out under aerobic conditions.

Acknowledgements

We thank Prof. F. Banse for fruitful discussions about reactivity of mononuclear iron complexes and the “Agence Nationale de la Recherche” (ANR BIOXICAT), the “Région Ile de France” (“DIM développement soutenable”) and the Labex CHARMMMAT for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.09.030.

References

[1] C. Song, Catal. Today 86 (2003) 211.

[2] A. Röthlisberger, R. Prins, J. Catal. 235 (2005) 229.

[3] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. (1998) 345.

[4] Y. Shiraishi, K. Tachibana, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 41 (2002) 4362.

[5] J. Xu, S. Zhao, W. Chen, M. Wang, Y.-F. Song, Chem. Eur. J. 18 (2012) 4775.

[6] M. Carraro, G. Fiorani, L. Mognon, F. Caneva, M. Gardan, C. Maccato, M. Bonchio, Chem. Eur. J. 18 (2012) 13195.

[7] P.S. Kulkarni, C.A.M. Afonso, Green Chem. 12 (2010) 1139.

[8] C. Yansheng, L. Changping, J. Qingzhu, L. Qingshan, Y. Peifang, L. Xiumei, U. Welz-Biermann, Green Chem. 13 (2011) 1224.

[9] X. Zhou, X. Chen, Y. Jin, I.E. Markó, Chem. Asian J. 7 (2012) 2253.

[10] S.M.G. Pires, M.M.Q. Simões, I.C.M.S. Santos, S.L.H. Rebelo, M.M. Pereira, M.G.P.M.S. Neves, J.A.S. Cavaleiro, Appl. Catal. Gen. 439–440 (2012) 51.

[11] T.R. Simmons, G. Berggren, M. Bacchi, M. Fontecave, V. Artero, Front. Organomet. Chem. 127 (2014) 270–271.

[12] K. Ariga, Q. Ji, T. Mori, M. Naito, Y. Yamauchi, H. Abe, J.P. Hill, Chem. Soc. Rev. 42 (2013) 6322.

[13] J. Kaizer, E.J. Klinker, N.Y. Oh, J.-U. Rohde, W.J. Song, A. Stubna, J. Kim, E. Münck, W. Nam, L. Que, J. Am. Chem. Soc. 126 (2004) 472.

[14] A.K. Vardhaman, S. Sikdar, C.V. Sastri, Indian J. Chem. 50A (2011) 427.
[15] M. Merkx, D.A. Kopp, M.H. Sazinsky, J.L. Blazyk, J. Müller, S.J. Lippard, Angew. Chem. Int. Ed. 40 (2001) 2782.
[16] I. Siewert, C. Limberg, Chem. Eur. J. 15 (2009) 10316.
[17] M. Costas, K. Chen, L. Que, Coord. Chem. Rev. 200–202 (2000) 517.
[18] G. Xue, R. De Hont, E. Münck, L. Que, Nat. Chem. 2 (2010) 400.
[19] D. Wang, E. Farquhar, A. Stubna, E. Münck, L. Que, Nat. Chem. 1 (2009) 145.
[20] Y. Mekmouche, H. Hummel, R.Y.N. Ho, L. Que Jr., V. Schünemann, F. Thomas, A.X. Trautwein, C. Lebrun, K. Gorgy, J.-C. Leprêtre, M.-N. Collomb, A. Deronzier, M. Fontecave, S. Ménage, Chem. Eur. J. 8 (2002) 1196.
[21] M. Suzuki, T. Sugisawa, A. Uehara, Bull. Chem. Soc. Jpn. 63 (1990) 1115.
[22] A.L. Feig, M. Becker, S. Schindler, R. van Eldik, S.J. Lippard, Inorg. Chem. 35 (1996) 2590.
[23] M. Costas, C.W. Cady, S.V. Kryatov, M. Ray, M.J. Ryan, E.V. Rybak-Akimova, L. Que, Inorg. Chem. 42 (2003) 7519.
[24] Y. Hayashi, T. Kayatani, H. Sugimoto, M. Suzuki, K. Inomata, A. Uehara, Y. Mizutani, T. Kitagawa, Y. Maeda, J. Am. Chem. Soc. 117 (1995) 11220.
[25] S.V. Kryatov, E.V. Rybak-Akimova, S. Schindler, Chem. Rev. 105 (2005) 2175.
[26] T. Akamatsu, T. Kobayashi, Y. Sasaki, S. Ito, Y. Nishida, Polyhedron 16 (1997) 1497.
[27] L. Westerheide, F.K. Müller, R. Than, B. Krebs, J. Dietrich, S. Schindler, Inorg. Chem. 40 (2001) 1951.
[28] M.C. White, A.G. Doyle, E.N. Jacobsen, J. Am. Chem. Soc. 123 (2001) 7194.
[29] H. Toflund, E. Pedersen, S. Yde-Andersen, Acta Chem. Scand. 38 (1984) 693.
[30] S. Taktak, M. Flook, B.M. Foxman, J. Que, E.V. Rybak-Akimova, Chem. Commun. 42 (2005) 5301.
[31] S. Taktak, S.V. Kryatov, E.V. Rybak-Akimova, Inorg. Chem. 43 (2004) 7196.
[32] A.J. Simaan, F. Banse, P. Mialane, A. Boussac, S. Un, T. Kargar-Grisel, G. Bouchoux, J.-J. Girerd, Eur. J. Inorg. Chem. 1999 (1999) 993.
[33] E.A. Duban, K.P. Bryliakov, E.P. Talsi, Mendeleev Commun. 15 (2005) 12.
[34] J. Bernadou, B. Meunier, Chem. Commun. (1998) 2167.
[35] K. Chen, L. Que Jr., Chem. Commun. (1999) 1375.
[36] F. Avenier, L. Dubois, J.-M. Latour, N. J. Chem. 28 (2004) 782.
[37] O.V. Makhlynets, E.V. Rybak-Akimova, Chem. Eur. J. 16 (2010) 13995.
[38] W.N. Oloo, A.J. Fielding, L. Que, J. Am. Chem. Soc. 135 (2013) 6438.
[39] I. Prat, A. Company, V. Postils, X. Ribas, L. Que, J.M. Luis, M. Costas, Chem. Eur. J. 19 (2013) 6724.
[40] A.S. Ogunlaja, W. Chidawanyika, E. Antunes, M.A. Fernandes, T. Nyokong, N. Torto, Z.R. Tshentu, Dalton Trans. 41 (2012) 13908.
[41] Y. Hu, Q. He, Z. Zhang, N. Ding, B. Hu, Chem. Commun. 47 (2011) 12194.
[42] H. Li, W. Zhu, Y. Wang, J. Zhang, J. Lu, Y. Yan, Green Chem. 11 (2009) 810.
[43] S. Potash, S. Rozen, Chem. Eur. J. 19 (2013) 5289.
[44] G.M. Sheldrick, Program for Crystal Structure Solution, University of Gottingen, 1997.
[45] G.M. Sheldrick, Program for the Refinement of Crystal Structures from Diffraction Data, University of Gottingen, 1997.
[46] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.