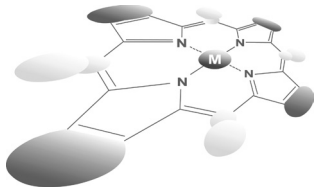
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2017; **21**: 1–9
DOI: 10.1142/S1088424617500274

Published at http://www.worldscinet.com/jpp/



Heteroleptic μ-nitrido diiron complex supported by phthalocyanine and octapropylporphyrazine ligands: Formation of oxo species and their reactivity with fluorinated compounds

Cédric Colomban[a], Evgeny V. Kudrik[a,b] and Alexander B. Sorokin*[a]

[a] *Institut de Recherches sur la Catalyse et l'Environnement de Lyon, IRCELYON, UMR 5256, CNRS-Universitè Lyon 1, 2 av. Albert Einstein, 69626 Villeurbanne Cedex, France*
[b] *Ivanovo State University of Chemistry and Technology 7, av F. Engels; 153000 Ivanovo, Russia*

Dedicated to Professor Claudio Ercolani on the occasion of his 80th birthday

Received 22 December 2016
Accepted 12 February 2017

ABSTRACT: The synthesis and reactivity of *N*-bridged diiron macrocyclic complexes have been a topic of increasing interest in recent years since the observation of particular catalytic properties of these complexes. Herein, we report a preparation of a novel heteroleptic μ-nitrido diiron complex with unsubstituted phthalocyanine and octapropylporphyrazine macrocycles. This complex reacts with *m*-chloroperbenzoic acid to form high-valent diiron oxo species showing strong oxidizing properties. The formation and structure of the transient oxo species was investigated by cryospray collision induced dissociation MS/MS technique. Analysis of fragmentation pattern showed that the attachment of oxo moiety occurred at either iron phthalocyanine or at iron porphyrazine site with slight preference for the phthalocyanine iron site. The catalytic properties of the heteroleptic μ-nitrido diiron complex were evaluated in the oxidative transformation of hexafluorobenzene and perfluoro(allylbenzene).

KEYWORDS: diiron complexes, phthalocyanine, porphyrazine, μ-nitrido, oxo species, C–F bonds.

INTRODUCTION

Fourty years ago, Summerville and Cohen have reported the first paper on the preparation of the *N*-bridged dimeric iron tetraphenylporphyrin [1]. This complex has attracted attention of many research groups due to unusual structure and properties [2–6]. The next important step was the synthesis of μ-nitrido diiron phthalocyanine complex by Goedken and Ercolani in 1984 [7] followed by the extensive studies of the structural and spectroscopic properties of μ-nitrido diiron homoleptic phthalocyanine [8, 9], porphyrin [10] and tetraazaporphyrin [11, 12] complexes as well as heteroleptic species [13–16]. Further progress in synthesis and spectroscopic characterization of single-atom bridged binuclear macrocyclic complexes was compehensively summarized by Ercolani and co-workers in 2003 [17]. Among μ-oxo, μ-carbido and μ-nitrido diiron macrocyclic complexes, the properties of the latter are particularly interesting. Metal sites in μ-nitrido dimers are strongly connected by the nitrogen bridge and their Mössbauer spectra show a single doublet signal indicating that both iron sites are identical, each in an +3.5 oxidation state. The iron–iron distance in μ-nitrido dimers is quite short, between 3.25 and 3.36 Å, indicating a significant π–π interaction between aromatic macrocycles. Several X-ray structures of μ-nitrido diiron complexes are available [18]. These formally Fe(III) Fe(IV) complexes bear one unpaired electron. Since 2000 only few papers on the synthesis and characterization of μ-nitrido dimers have been published.

Renewed interest in these complexes has been initiated by our recent observation of the remarkable catalytic properties of μ-nitrido diiron macrocyclic complexes [19, 20]. Of particular interest is the ability of the μ-nitrido

*Correspondence to: Alexander B. Sorokin, email: alexander.sorokin@ircelyon.univ-lyon1.fr; fax: +33 472-445-399; tel: +33 472-445-337

complexes to catalyze difficult reactions, such as the oxidation of methane [21–25] and ethane [26], benzene [27], formation of C–C bonds [28] and oxidative dehalogenation of chlorinated [29] and even fluorinated compounds [30]. Among single-atom bridged binuclear macrocyclic complexes, μ-nitrido diiron species are particularly active in catalysis due to their ability to form high-valent diiron oxo species [31]. Thus, the catalytic properties have been associated with transient high-valent oxo species which are very reactive and can be characterized by spectroscopic methods only at very low temperatures [19, 23, 32]. In order to understand the origin of unusual catalytic activity of μ-nitrido dimers, it is important to characterize the active species involved in these reactions and key reaction intermediates. It should be noted that a very limited number of high-valent iron oxo species on phthalocyanine platform have been obtained and characterized [21, 24, 33] compared with their counterparts supported by porphyrin ligands [34–37].

Both iron sites of the Fe(III)NFe(IV) construction responsible for the catalytic properties can be supported by porphyrin, phthalocyanine or porphyrazine ligands to form homoleptic complexes [17–19]. Another possible arrangement is a heteroleptic combination of two iron complexes bearing different macrocyclic ligands [13, 14] or the same type of macrocyclic ligands but with different substitution pattern [38]. Properties of the supporting ligands can influence the electronic properties of the dimers and their oxidation state [39–41]. Taking into account that the properties of the supporting ligands can influence the catalytic activity of the iron sites, this might open new interesting possibilities. Recently, we have prepared heteroleptic phthalocyanine μ-nitrido diiron complexes to probe the differences in chemical properties of the two iron centers within the same molecule [24]. One iron site was supported by an electron-deficient phthalocyanine ligand having four or eight alkylsulfonyl groups whereas the other iron site was coordinated with a much more electron-rich unsubstituted phthalocyanine. Using cryospray MS and collision induced dissociation MS/MS techniques as well as DFT calculations, we have shown that the oxidizing oxo unit was preferencially formed at the more electron-rich iron site. In the line with this finding, the increase of the electron density at iron site resulted in the significant gain in the catalytic activity [24]. It would be also interesting to evaluate whether the nature of the supporting ligand might influence the formation of active species. To this aim we have designed a heteroleptic μ-nitrido diiron complex with phthalocyanine and octapropylporphyrazine ligands (PcFe(μN)FePz, Fig. 1)

The focus of this work was to prepare a heteroleptic μ-nitrido diiron complex with different ligands having similar electronic properties in order to explore regioselectivity of the formation of the oxo species by collision induced dissociation MS/MS approach. Development of catalysts for challenging reactions showing new reactivity represents a major objective for chemists. Thus, the catalytic properties of PcFe(μN)FePz were evaluated in the oxidative transformation of hexafluorobenzene and perfluoro(allylbenzene).

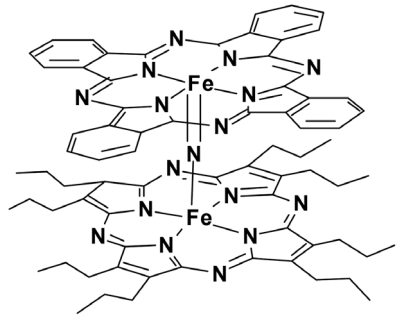


Fig. 1. Structure of heteroleptic μ-nitrido diiron complex with phthalocyanine and octaethylporphyrazine ligands, PcFe(μN)FePz

EXPERIMENTAL

Equipment and methods

UV-vis spectra of solutions were recorded on a Perkin–Elmer Lambda 35 or Agilent 8453 spectrophotometers. Infrared spectra were obtained using a Bruker Vector 22 FTIR spectrometer using KBr pellets. ^{1}H and ^{19}F NMR spectra were acquired on a AM 250 Bruker spectrometer. The reaction products were identified by GC-MS method (Hewlett Packard 5973/6890 system; electron impact at 70 eV, He carrier gas, 30 m × 0.25 mm HP-INNOWax capillary column, polyethylene glycol (0.25 μm coating). To analyze acidic organic products, the reaction mixtures were treated with 2.0 M solution of (trimethylsilyl)diazomethane in diethyl ether to transform carboxylic groups to the corresponding methyl esters.

The mass spectra of the complexes were recorded on a MicroTOF Q II, a quadrupole time of flight (Q-TOF) mass spectrometer (Bruker Daltonics, Bremen), equipped with a cold spray ionization source with a spray voltage of 5 kV. The temperature of the spray gas was -30 °C and that of the dry gas was -5 °C. The solutions of the complexes (~10^{-6} M) in acetonitrile in the presence of 1000 equiv. of *m*-chloroperbenzoic acid (*m*-CPBA) were introduced into the gas flow at 180 μL.h^{-1}. The *m*-CPBA oxidant was added to the frozen complex solution in acetonitrile and the sample was introduced immediately after melting. All mass spectra were recorded in the positive ion mode.

The molecular ions (M^{+}) of the oxo and peroxo diiron species observed in the regular MS experiment cannot be trapped in the quadrupole region due to the formation of multimers by π-stacking interactions. To overcome this problem, a low activation of ions during transmission

through the ion funnels was applied by In Source Collision Induced Dissociation (ISCID) at 20 eV, which enabled us to do MS/MS measurements. This activation allowed us to mass select the oxo and peroxo diiron species in the quadrupole part of the mass spectrometer. The collision energy applied in the collision cell was about 60 eV and the collision gas was nitrogen.

Materials

All chemicals were purchased from Alfa Aesar or Sigma-Aldrich and were used for the syntheses without further purification. Iron octapropylporphyrazine was prepared according to published procedure [42]. *m*-Chloroperbenzoic acid (*m*-CPBA, 85% peroxide content) purchased from Sigma-Aldrich was recrystallized from pentane prior to use. Hydrogen peroxide (35%) was obtained from Sigma-Aldrich.

Synthesis of heteroleptic μ-nitrido diiron complex with phthalocyanine and octapropylporphyrazine ligands, PcFe(μN)FePz. Iron phthalocyanine (300 mg, 0.53 mmol) and iron octapropylporphyrazine (50 mg, 0.07 mmol) were dissolved in deoxygenated 1-chloronaphthalene (30 mL) and NaN_3 (500 mg, 7.7 mmol) was added to the solution. The reaction mixture was stirred at 180 °C for 2 h. The cold solution was filtered to remove NaN_3 left and homoleptic $(FePc)_2N$. The solid was washed with benzene. Combined organic phases were submitted to column chromatography with basic alumina and benzene was used to remove 1-chloronaphthalene. Then, the impurities were eluted with CH_2Cl_2. The pure product was eluted with a 10:1 CH_2Cl_2:MeOH mixture. ESI-MS analysis showed neither presence of homoleptic $(FePc)_2N$ and $(FePz)_2N$ dimers nor FePc and FePz monomers. Yield 52 mg (54%). ESI-MS: *m/z* 1286.50 $[M]^+$ (100); calcd. for $C_{72}H_{72}N_{17}Fe_2$: 1286.48. IR (KBr): ν, cm^{-1} 920 (Fe=N–Fe). UV-vis (CH_2Cl_2): λ_{max}, nm 284, 314, 512 (sh), 608, 660 (sh).

Typical procedure for catalytic reactions with perfluorinated aromatic compounds. A 3 mL Teflon reactor was charged with 2 mL CD_3CN containing perfluorinated substrate (0.1 M), H_2O_2 (typically 1.6 M) and catalyst (0.4 mM). The catalyst:substrate:oxidant ratio was 1:250:4000. The reaction mixture was stirred at 60 °C for 6 h. The products were identified and quantified by GC-MS and ^{19}F NMR techniques.

RESULTS AND DISCUSSION

Preparation of heteroleptic complex

The synthesis of μ-nitrido diiron phthalocyanines is typically carried out by refluxing iron phthalocyanine in a high-temperature boiling solvent like xylenes or 1-chloronaphthalene in the presence of an excess of NaN_3 [1, 8, 17]. If an equimolar mixture of two different monomeric complexes is used, a mixture of the two corresponding homoleptic complexes and the desired heteroleptic complex can be usually obtained. To limit the amount of homoleptic by-products and to avoid tedious purification procedures, the heteroleptic complex PcFe(μN)FePz was prepared by using FePc/FePz mixture in a 7.5/1 ratio. These conditions favor the preferential formation of the targeted heteroleptic complex PcFe(μN)FePz together with the homoleptic unsubstituted $(FePc)_2N$ poorly soluble in common organic solvents which can be readily separated by filtration. A pure product was obtained by column chromatography using basic alumina applying CH_2Cl_2 and a 10:1 CH_2Cl_2:MeOH eluents in a 54% yield. The successful preparation of PcFe(μN)FePz was confirmed by IR, UV-vis and ESI-MS techniques. The ESI-MS spectrum of PcFe(μN)FePz showed a prominent molecular peak at *m/z* = 1286.50 corresponding to the expected value of the molecular ion. When the molecular ion PcFe(μN)FePz$^+$ was subjected to collision induced dissociation (CID), FePc (*m/z* = 568.1) and NFePz (*m/z* = 718.4) monomeric units were observed as principal fragments indicating that the bridging nitrogen atom was preferentially bound to more electron-rich iron octapropylporphyrazine moiety (Fig. 2). Only minor signals of NFePc (*m/z* = 582.1) and FePz (*m/z* = 704.4) were observed (Fig. 2, inset). This finding indicates that tandem ESI-MS/MS technique can be used for the determination of the fine structural features of these binuclear complexes.

The UV-vis spectrum of the heteroleptic PcFe(μN)FePz complex is compared with those of the monomeric FePz and homoleptic $(FePz)_2N$ in Fig. 3.

Similarly to the heterolytic tetraphenylporphyrin/tetra-*tert*-butylphthalocyanine complex (TPP)Fe(μN)Fe(Pc^{t}Bu$_4$) [16], only one broad Q-band at 608 nm was observed. The maximum of the PcFe(μN)FePz Q-band is in between those of the homogeneous $(FePz)_2N$ at 584 nm and $(FePc)_2N$ 625 nm (in py) [7]. This broad band results from the combination of Q-bands of both macrocycles [16]. As for Soret region, two bands at 284 and 314 nm were observed. The IR spectrum of PcFe(μN)FePz exhibits a typical anti-symmetric Fe–N–Fe stretch vibration at 920 cm^{-1} which is close to the corresponding Fe–N–Fe vibrations for the homoleptic complexes $FePc_2N$ at 915 cm^{-1} [17] and $FePz_2N$ at 914 cm^{-1} [42].

Preparation of high-valent diiron oxo complex and their ESI-MS analysis

Addition of active oxygen donors, *e.g.* peracids, hydrogen peroxide or organic hydroperoxides, to solutions of μ-nitrido diiron macrocyclic complexes leads to the formation of short-lived high-valent diiron oxo species which can be only detected at very low temperatures [19, 43]. These species exhibit very strong oxidizing properties and are capable of oxidizing the most recalcitrant organic molecules like methane [21–25], ethane [26], chlorinated [29, 44] or perfluorinated aromatic compounds [30].

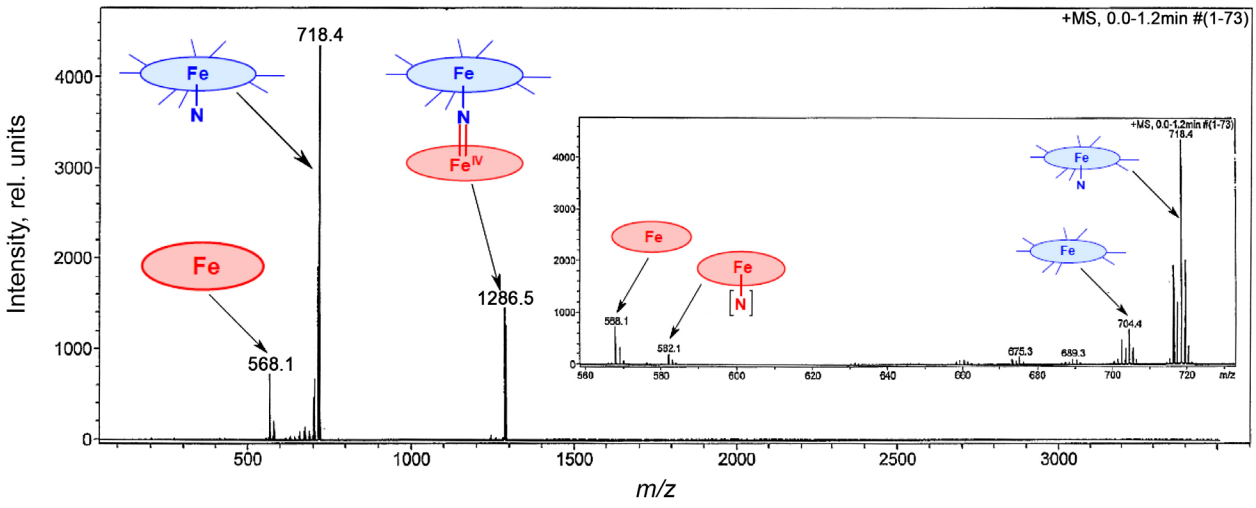


Fig. 2. CID MS/MS spectrum of the heteroleptic PcFe(μN)FePz complex. Phthalocyanine and octapropylporphyrazine ligands are shown as red and blue ovals, respectively. Inset: zoom of the fragmentation pattern of PcFe(μN)FePz

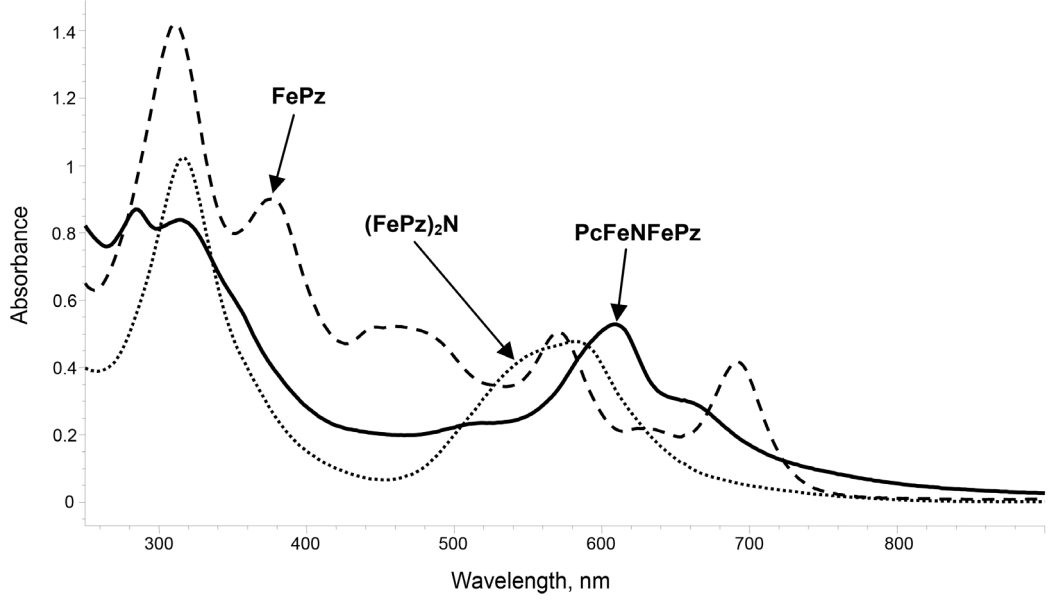


Fig. 3. UV-vis spectra of the monomeric FePz (---), homoleptic $(FePz)_2N$ (····) and heteroleptic PcFe(μN)FePz (—) complexes, 0.02 mM in CH_2Cl_2

Heteroleptic binuclear complexes having two Fe sites in the different ligand environment can form two isomeric high-valent diiron oxo species (Fig. 4).

We have previously shown that collision induced dissociation MS/MS (CID-MS/MS) technique can be used for the determination of the iron site where oxo group is attached *via* analysis of the fragmentation pattern [24] as shown in Fig. 4. μ-Nitrido high-valent diiron species can be prepared using H_2O_2 or *m*-chloroperbenzoic acid (*m*-CPBA) as active oxygen donors. In our previous research we have shown that using of both oxidants in combination with heteroleptic phthalocyanine complexes resulted in the formation of the same oxo species [24]. In this mass spectrometry study, *m*-CPBA was used as a convenient source of the oxo group.

An acetonitrile solution containing an excess of *m*-CPBA was added to the frozen ~1 μM solution of PcFeNFePz in acetonitrile. After melting of acetonitrile at -46 °C the resulting solution was immediately introduced into mass spectrometer. The mass spectrum of the reaction mixture showed the presence of several species (Fig. 5).

Along with a molecular peak of PcFeNFePz at *m/z* 1286.5, the signal centered at *m/z* = 1457.4 due to the formation of peroxo complex was observed. The mechanism of the formation of the identified species is proposed in Fig. 6.

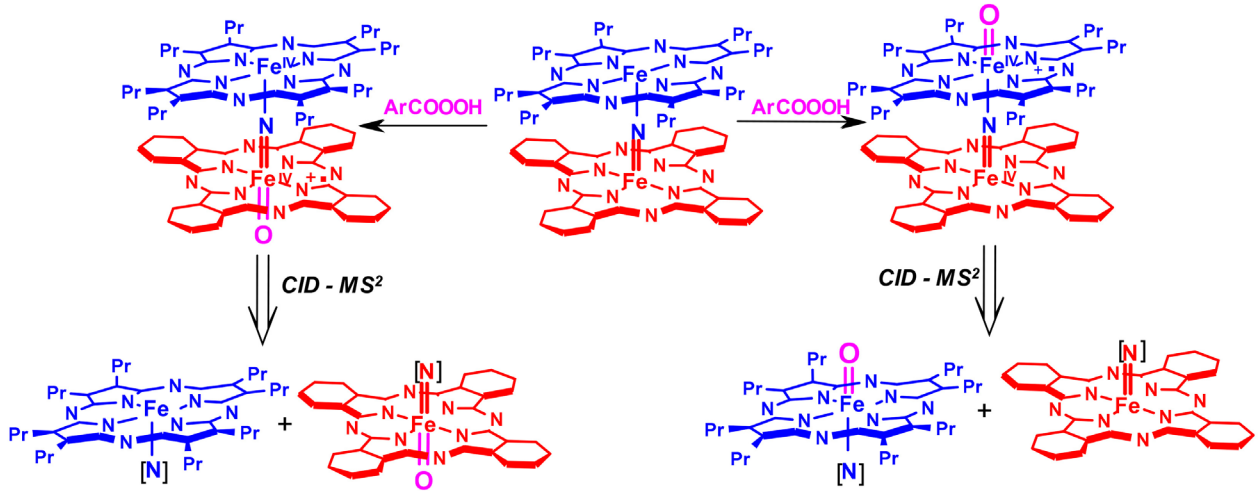


Fig. 4. Formation of two isomeric diiron oxo species at the heteroleptic PcFe(μN)FePz platform and the expected fragmentation under collision induced dissociation of the molecular peaks

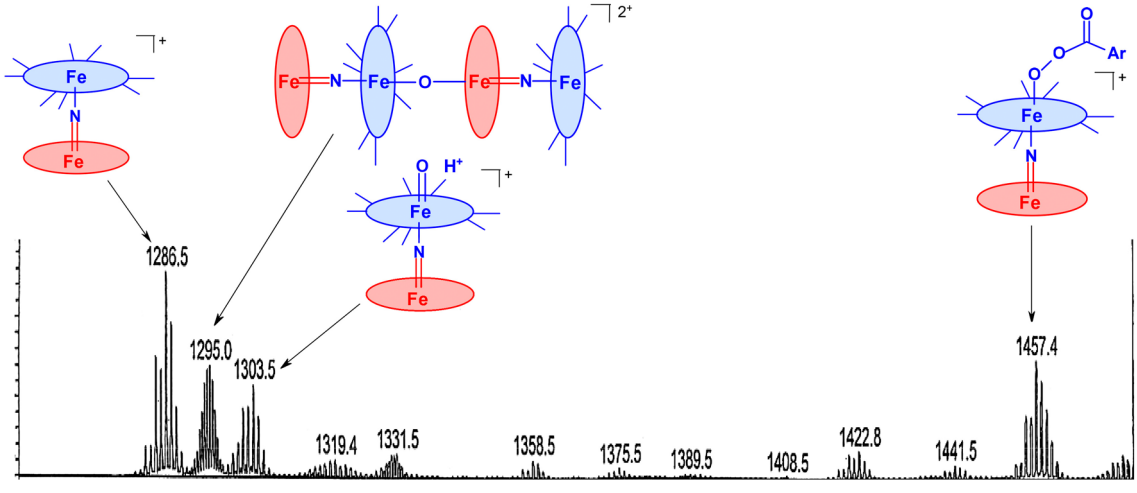


Fig. 5. Mass spectrum of the PcFeNFePz solution in MeCN recorded between 0.7 and 1.9 min after *m*-CPBA addition. Phthalocyanine and octapropylporphyrazine ligands are schematically shown as red and blue ovals, respectively. Only one possible isomer of each species issued from the interaction with *m*-CPBA is shown

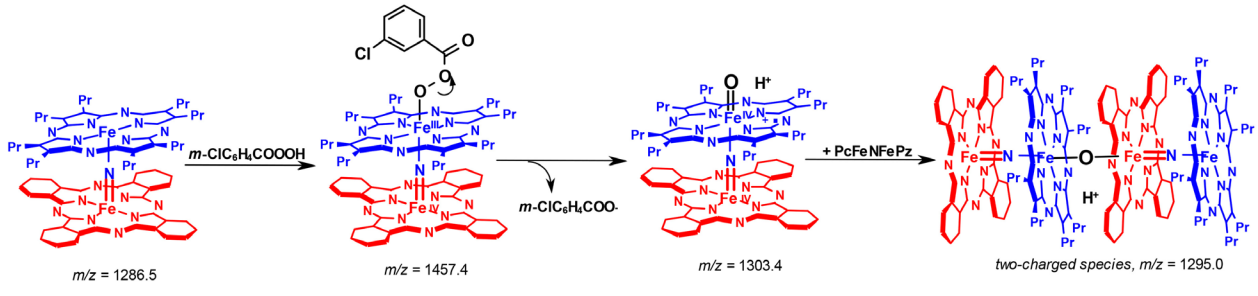


Fig. 6. Formation of peroxo-, oxo- and μ-oxo species of PcFe(μN)FePz in the presence of *m*-CPBA diiron oxo species detected by cryospray MS. Only one possible isomer of each species is shown

The peroxo complex (PcFeNFePz)-OOC(O)Ar undergoes a heterolytic cleavage of the O–O bond to generate oxo species (PcFeNFePz)=O. Due to the basicity of the oxo group in μ-nitrido diiron porphyrinoid complexes [25], this species is protonated and exhibits a molecular cluster peak centered at *m/z* = 1303.4. Interestingly, a two-charged species with *m/z* = 1295.0 was also observed. This signal was attributed to the protonated

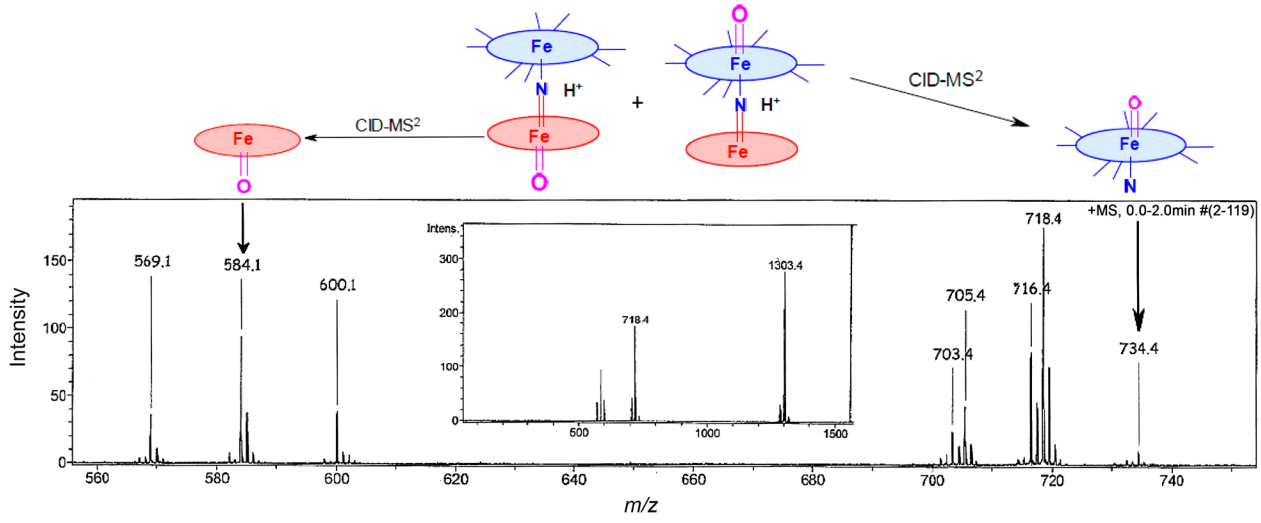


Fig. 7. Fragmentation pattern of the protonated isomeric diiron oxo species at the heteroleptic PcFe(μN)FePz platform and their experimental fragmentation pattern under collision induced dissociation of the molecular peaks. Phthalocyanine and octapropylporphyrazine ligands are shown as red and blue ovals, respectively

μ-oxo complex of μ-nitrido diiron dimer formed in the reaction of the oxo species (PcFeNFePz)=O with the starting complex PcFeNFePz. Related μ-oxo dimeric species of *monomeric* high-valent non-heme [45–47], porphyrazine [48], phthalocyanine [49–51] and porphyrin [52] iron complexes have been previously described. However, to the best of our knowledge, such a μ-oxo dimer of a binuclear diiron complex was observed for the first time. Alternative formulation as μ-hydroxo dimer of μ-nitrido dimeric complex cannot be excluded since μ-oxo species can be protonated. The protonation of μ-oxo iron porphyrin was previously reported [53].

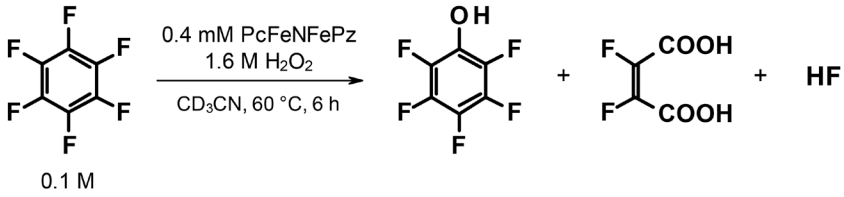
For the sake of simplicity, only one possible isomer of the high-valent μ-nitrido diiron oxo complex is depicted in Fig. 6 while two possible isomeric oxo species can be formed. In order to determine whether the site-specific formation of the oxo species occurs, *i.e.* wherther the chemical nature of the macrocyclic ligand can lead to the preferencial attachment of oxo ligand at one of the two possible iron sites, we used CID-MS/MS approach. The collision induced fragmentation of the parent molecular ion of the (PcFeNFePz)=O species results in the formation of mononuclear units containing or not oxo and/or nitrogen ligands. The analysis of the fragmentation pattern should allow to determine whether the oxo ligand is attached at phthalocyanine or porphyrazine iron site. To this aim, the mass-selected oxo species was studied by CID-MS/MS and results are shown in Fig. 7.

The abundant signals in the *m/z* ranges of 569–600 and 703–734 corresponding to iron phthalocyanine and iron porphyrazine fragments, respectively, were observed. Iron phthalocyanine fragments with *m/z* centered at 569.1, 584.1 and 600.1 are associated with $[PcFe + H]^+$, $[PcFe=O]^+$ and $[PcFe–OH(NH)]^+$ formulations, respectively. In turn, the signals with *m/z* 705.4, 718.4 and 734.4 belong to the iron porphyrazine fragments $[PzFe + H]^+$, $[PzFe=N]^+$ and $[PzFe=O(N)]^+$, respectively. Similarly to the initial PcFeNFePz complex (Fig. 2), iron porphyrazine moiety tends to keep the bridging nitrogen atom. It should be noted that the fragments containing oxo ligand were observed at both phthalocyanine and porphyrazine iron platforms: *m/z* = 584.1 and 600.1 and *m/z* = 734.4, respectively. The intensity of signals of $[PcFe=O]^+$ and $[PcFe-OH(NH)]^+$ fragments is higher than that of $[PzFe=O]^+$ suggesting a slight preference of the oxo group binding to iron phthalocyanine site.

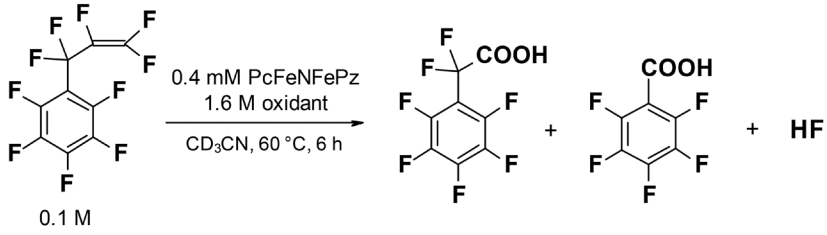
Oxidation of perfluorinated aromatic compounds catalyzed by PcFeNFePz

The catalytic potential of PcFeNFePz was evaluated in the oxidative transformation of hexafluorobenzene and perfluoro(allylbenzene). Although *m*-CPBA is a convenient active oxygen donor for obtaining oxo species for spectroscopic and mechanistic studies, it is not the best choice for the catalytic experiments, especially when potent oxidizing species can be formed. *m*-CPBA itself can be oxidized along with the substrate, especially in this particular case since *m*-CPBA is less deactivated toward an attack of a strong electrophilic high-valent oxo species than the electro-deficient perfluorinated aromatic substrates. For this reason, we used conventional H_2O_2 or ^{t}BuOOH oxidants. The reactions were performed at 60 °C in CD_3CN using catalyst:substrate:oxidant ratio = 1:250:4000 (Scheme 1).

When ^{t}BuOOH was used, no conversion of C_6F_6 was observed. In contrast, in the presence of H_2O_2 a 11% conversion of C_6F_6 and turnover number of 28 were achieved. The main product was pentafluorophenol accompanied by difluoromaleic acid and HF. Each catalyst molecule transformed 34.5 C–F bonds. This catalytic activity was



Scheme 1. Catalytic transformation of C_6F_6 by PcFeNFePz–H_2O_2 system



	Conversion	TON_{Sub}	Yield	Yield	TON_{F^-}
H_2O_2	58 %	145	37 %	6 %	538
^{t}BuOOH	97 %	241	12 %	51 %	1465

Scheme 2. Catalytic transformation of perfluoro(allylbenzene) by PcFeNFePz–H_2O_2 and PcFeNFePz–^{t}BuOOH systems. TON_{Sub} was calculated as molar amount of substate transformed per mole of the catalyst. TON_{F^-} was defined as molar amount of F^- formed per mole of the catalyst

slightly lower compared with that of previously obtained using $(FePc^tBu_4)_2N$ catalyst under the same conditions (29% conversion of C_6F_6) [30].

Perfluoro(allylbenzene) combining fluorinated aromatic cycle and fluorinated olefinic moiety is a useful substrate to study the selectivity of defluorination reaction. In contrast to hexafluorobenzene, both PcFeNFePz–H_2O_2 and PcFeNFePz–^{t}BuOOH catalytic systems were very efficient in the transformation of perfluoro(allylbenzene). Importantly, perfluorinated olefinic fragment exhibited significantly higher activity in the defluorination reaction (Scheme 2).

The PcFeNFePz–^{t}BuOOH catalytic system was even more active providing a 97% conversion of $C_6F_5CF_2CF{=}CF_2$ compared with a 58% conversion in the case of the PcFeNFePz–H_2O_2 system. Heptafluorobenzeneacetic and pentafluorobenzoic acids obtained *via* the cleavage of the double bond accompanied by defluorination were the principal products. Interestingly, the PcFeNFePz–H_2O_2 system was more selective to the formation of $C_6F_5CF_2COOH$ (37% yield) whereas the PcFeNFePz–^{t}BuOOH system provided C_6F_5COOH with a 51% yield. Very high turnover numbers in terms of the number of C–F bonds transformed by one catalyst molecule were achieved with both oxidants: 538 and 1465 using H_2O_2 and ^{t}BuOOH, respectively.

CONCLUSION

μ-Nitrido diiron macrocyclic complexes find increasing applications in catalysis, in particular, in different oxidation reactions, in dehalogenation transformations and in C–C bond formation [19]. It is expected that the scope of the catalytic applications of these complexes can be further increased. In this context, the synthesis of novel μ-nitrido diiron complexes will not only enlarge the choice and scope of these promising catalysts but also should provide a deeper insight into properties of μ-nitrido macrocyclic dimers important for their catalytic activity. Particular catalytic properties of μ-nitrido diiron platform can be associated with the formation of high-valent diiron oxo species having strong oxidizing properties. In this work, we have prepared and characterized a novel heteroleptic *N*-bridged diiron complex with phthalocyanine and porphyrazine ligands. We have studied in detail the formation of the high-valent diiron oxo complexes by cryospray mass spectrometry using *m*-CPBA as active oxygen donor. Initially formed isomeric peroxo complexes (PcFeNFePz)–OOC(O)Ar underwent to a heterolytic cleavage of O–O bond to form two isomeric oxo species, O=(Pc)FeNFePz and PcFeNFe(Pz)=O. The iron site of binding of the oxo group was determined by CID-MS/MS technique *via* analysis of the composition of fragments obtained after bombardment of the molecular ions of the oxo species. The fragments bearing oxo ligand were observed at both the monomeric iron phthalocyanine and porphyrazine units: $m/z = 584.1$ and 600.1 and $m/z = 734.4$, respectively. The intensity of signals of $[PcFe{=}O]^+$ and $[PcFe\text{-}OH(NH)]^+$ fragments is higher than that of $[PzFe{=}O]^+$ suggesting a slight preference of the oxo group binding to iron phthalocyanine site. In our previous study [24] we found that heteroleptic complex containing one electron-poor iron phthalocyanine site and one more electron-rich iron phthalocyanine site

formed high-valent diiron oxo species with oxo group bound exclusively at the electron-rich site of the dimer. In this work we observed comparable affinity of oxo group to iron phthalocianine and iron porphyrazine units with only slight preference for the former site. This result confirms that the properties of the supporting ligand of μ-nitrido diiron platform are important for the formation of high-valent diiron oxo catalytic species. The reaction of (PcFeNFePz)=O species with PcFeNFePz led to the formation of μ-oxo dimer complex of μ-nitrido dimer (PcFeNFePz)–O–(PcFeNFePz). Such a tetrairon complex was observed for the first time.

The PcFeNFePz complex in combination with H_2O_2 was active in oxidative transformation of hexafluorobenzene and perfluoro(allylbenzene). Perfluorinated olefinic fragment exhibited significantly higher activity in the defluorination reaction than perfluorinated aromatic moiety. Perfluorinated aromatic acids were obtained with moderate yields. Using perfluoro(allylbenzene), we have obtained the oxidative transformation of perfluorinated substrate by PcFeNFePz–^{t}BuOOH system for the first time. Moreover, PcFeNFePz–^{t}BuOOH system was even more efficient than PcFeNFePz–H_2O_2 system providing a 97% conversion of $C_6F_5CF_2CF{=}CF_2$. Very high turnover numbers defined as the number of C–F bonds transformed by one catalyst molecule were achieved with H_2O_2 and ^{t}BuOOH: 538 and 1465, respectively. It should be pointed out that transformation of C–F bonds involving oxidation pathways is a very difficult and rare reaction. Only a few papers describing the stoichiometric defluorination of 2-fluorophenolate with a bis(μ-oxo)dicopper(III) complex [54] and intramolecular C–F bond oxygenation of the complexes during formation of their oxo species [55, 56] have been published. The important feature of μ-nitrido diiron macrocyclic complexes is that they are capable of performing efficient catalytic oxidation of a variety of fluorinated aromatic and olefinic compounds with different fluorination degree and substitution pattern using industrially relevant H_2O_2 and ^{t}BuOOH oxidant [30]. Taking into account the constantly increasing large-scale production and application of fluorinated organic compounds (for example, ~40% of agrochemicals and ~20% of pharmaceuticals currently used are fluorinated molecules) and their exceptional stability in the environment, these compounds are considered as emerging pollutants. The development of practical methods for elimination of these contaminants of increasing concern is of great importance. We believe that further development of the catalytic systems based on μ-nitrido diiron macrocyclic complexes and industrially relevant peroxide oxidants might provide a solution to this environmental problem.

Acknowledgements

This research was supported by Agence National de Recherche (ANR, France, grants nos. ANR-08-BLANC-0183-01 and ANR-16-CE29-0018-01), by CNRS (PICS project 6295) and Russian Foundation of Basic Research (RFBR, project 14-03-91054). C.C. is grateful to Région Rhône-Alpes for PhD fellowship. We are grateful to Dr. F. Albrieux for the assistance with mass spectrometry experiments.

REFERENCES

1. Summerville DA and Cohen IA. *J. Am. Chem. Soc.* 1976; **98**: 1747–1752.
2. Scheidt WR, Summerville DA and Cohen IA. *J. Am. Chem. Soc.* 1976; **98**: 6623–6628.
3. Kadish KM, Bottomley LA, Brace JG and Winograd N. *J. Am. Chem. Soc.* 1980; **102**: 4341–4344.
4. Tatsumi K and Hoffmann R. *J. Am. Chem. Soc.* 1981; **103**: 3328–3341.
5. Schick GA and Bocian DF. *J. Am. Chem. Soc.* 1983; **105**: 1830–1838.
6. Bocian DF, Findsen EW, Hofmann JA, Schick GA, English DR, Hendrickson DN and Suslick KS. *Inorg. Chem.* 1984; **23**: 800–807.
7. Goedken VL and Ercolani C. *J. Chem. Soc. Chem. Commun.* 1984: 378–379.
8. Bottomley LA, Gorce J-N, Goedken VL and Ercolani C. *Inorg. Chem.* 1985; **24**: 3733–3737.
9. Kennedy BJ, Murray KS, Homborg H and Kalz W. *Inorg. Chem. Acta* 1987; **134**: 19–21.
10. Li M, Shang M, Ehlinger N, Schulz CE and Scheidt WR. *Inorg. Chem.* 2000; **39**: 580–583.
11. Stuzhin PA, Latos-Grazynski L and Jezierski A. *Trans. Met. Chem.* 1989; **14**: 341–346.
12. Stuzhin PA, Hamdush M and Homborg H. *Mendeleev Commun.* 1997; **7**: 196–198.
13. Ercolani C, Hewage S, Heucher R and Rossi G. *Inorg. Chem.* 1993; **32**: 2975–2977.
14. Ercolani C, Jubb J, Pennesi G, Russo U and Trigiante G. *Inorg. Chem.* 1995; **34**: 2535–2541.
15. Donzello MP, Ercolani C, Kadish KM, Ou Z and Russo U. *Inorg. Chem.* 1998; **37**: 3682–3688.
16. Zanotti G, Mattioli G, Notarantonio S, Paoletti AM, Rossi G, Bonapasta AA and Pennesi G. *Macroheterocycles* 2011; **4**: 161–163.
17. Floris B, Donzello MP and Ercolani C. In *The Porphyrin Handbook*, Vol. 18, Kadish KM, Smith KM and Guilard R. (Eds.) Elsevier Science: San Diego, 2003; pp. 1–62.
18. İşci Ü, Dumoulin F, Sorokin AB and Ahsen V. *Turk. J. Chem*. 2014; **38**: 923–949.
19. Afanasiev P and Sorokin AB. *Acc. Chem. Res.* 2016; **49**: 583–593.
20. Sorokin AB. *Chem. Rev.* 2013; **113**: 8152–8191.
21. Sorokin AB, Kudrik EV and Bouchu D. *Chem. Commun.* 2008; 2562–2564.
22. Sorokin AB, Kudrik EV, Alvarez LX, Afanasiev P, Millet JMM and Bouchu D. *Catal. Today* 2010; **157**: 149–154.

23. Kudrik EV, Afanasiev P, Alvarez LX, Dubourdeaux P, Clémancey M, Latour J-M, Blondin G, Bouchu D, Albrieux F, Nefedov SE and Sorokin AB. *Nat. Chem.* 2012; **4**: 1024–1029.
24. İşci Ü, Faponle AS, Afanasiev P, Albrieux F, Briois V, Ahsen V, Dumoulin F, Sorokin AB and de Visser SP. *Chem. Sci*. 2015; **6**: 5063–5075.
25. Quesne MG, Senthilnathan D, Singh D, Kumar D, Maldivi P, Sorokin AB and de Visser SP. *ACS Catal.* 2016; **6**: 2230–2243.
26. Alvarez LX and Sorokin AB. *J. Organomet. Chem.* 2015; **793**: 139–144.
27. Kudrik EV and Sorokin AB. *Chem Eur. J.* 2008; **14**: 7123–7126.
28. Alvarez LX, Kudrik EV and Sorokin AB. *Chem. Eur. J.* 2011; **17**: 9298–9301.
29. Afanasiev P, Bouchu D, Kudrik EV, Millet JMM and Sorokin AB. *Dalton Trans.* 2009: 9828–9836.
30. Colomban C, Kudrik EV, Afanasiev P and Sorokin AB. *J. Am. Chem. Soc.* 2014; **136**: 11321–11330.
31. Colomban C, Kudrik EV, Briois V, Shwarbrick JC, Sorokin AB and Afanasiev P. *Inorg. Chem.* 2014; **53**: 11517–11530.
32. Isci Ü, Afanasiev P, Millet JMM, Kudrik EV, Ahsen V and Sorokin AB. *Dalton Trans.* 2009; 7410–7420.
33. Afanasiev P, Kudrik EV, Albrieux F, Briois V, Koifman OI and Sorokin AB. *Chem. Commun.* 2012; **48**: 6088–6090.
34. Groves JT. In *Cytochrome P450: Structure, Mechanism and Biochemistry*, 3rd ed., Ortiz de Montellano PR. (Ed.) Kluwer Academic/Plenum Publishers: New York, 2005; Chap. 1, pp. 1–44.
35. Cong Z, Kinemuchi H, Kurahashi T and Fujii H. *Inorg. Chem.* 2014; **53**: 10632–10641.
36. Costas M. *Coord. Chem. Rev.* 2011; **255**: 2912–2932.
37. Jung C, de Vries S and Schünemann. *Arch. Biochem. Biophys.* 2011; **507**: 44–55.
38. İşci Ü. *J. Porphyrins Phthalocyanines* 2013; **17**: 1022–1026.
39. Kudrik EV, Afanasiev P, Bouchu D, Millet JMM and Sorokin AB. *J. Porphyrins Phthalocyanines* 2008; **12**: 1078–1089.
40. Isci Ü, Dumoulin F, Ahsen V and Sorokin AB. *J. Porphyrins Phthalocyanines* 2010; **14**: 324–334.
41. Kudrik EV, Afanasiev P, Bouchu D and Sorokin AB. *J. Porphyrins Phthalocyanines* 2011; **15**: 583–591.
42. Colomban C, Kudrik EV, Tyurin DV, Albrieux F, Nefedov SE, Afanasiev P and Sorokin AB. *Dalton Trans.* 2015; **44**: 2240–2251.
43. Afanasiev P, Kudrik EV, Millet JMM, Bouchu D and Sorokin AB. *Dalton Trans.* 2011; **40**: 701–710.
44. Colomban C, Kudrik EV, Afanasiev P and Sorokin AB. *Catal. Today* 2014; **235**: 14–19.
45. Kundu S, Thompson JVK, Shen LQ, Mills MR, Bominaar EL, Ryabov AD and Collins TJ. *Chem. Eur. J.* 2015; **21**: 1803–1810.
46. Ghosh M, Singh KK, Panda C, Weitz A, Hendrich MP, Collins TJ, Dhar BB and Sen Gupta S. *J. Am. Chem. Soc.* 2014; **136**: 9524–9527.
47. Lyakin OV, Zima AM, Samsoneneko DG, Bryliakov KP and Talsi EP. *ACS Catal.* 2015; **5**: 2702–2707.
48. Yusubov MS, Celik C, Geraskina MR, Yoshimura A, Zhdankin VV and Nemykin VN. *Tetrahedron Lett.* 2014; **55**: 5687–5690.
49. Neu HM, Zhdankin VV and Nemykin VN. *Tetrahedron Lett.* 2010; **51**: 6545–6548.
50. Pergrale C and Sorokin AB. C. R. Chim. 2000; **3**: 803–810.
51. Zalomaeva OV, Ivanchikova ID, Kholdeeva OA and Sorokin AB. *New J. Chem.* 2009; **33**: 1031–1037.
52. Sil D and Rath SP. *Dalton Trans.* 2015; **44**: 16195–16211.
53. Sainna MA, Sil D, Sahoo D, Martin B, Rath SP, Comba P and de Visser S. *Inorg. Chem.* 2015; **54**: 1919–1930.
54. Serran-Plana J, Garcia-Bosch I, Miyake R, Costas M and Company A. *Angew. Chem. Int. Ed.* 2014; **53**: 9608–9612.
55. de Ruiter G, Thompson NB, Takase MK and Agapie T. *J. Am. Chem. Soc.* 2016; **138**: 1486–1489.
56. Sahu S, Zhang B, Pollock CJ, Dürr M, Davies CG, Confer AM, Ivanovic-Burmazovic I, Siegler MA, Jameson GNL, Krebs K and Goldberg DP. *J. Am. Chem. Soc.* 2016; **138**: 12791–12802.