Rapid and Selective Oxidation of Metallosulfophthalocyanines Prior to Their Usefulness as Precatalysts in Oxidation Reactions

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Two metallosulfophthalocyanines, RuPcS and FePcS, used in many catalytic oxidation reactions, were readily oxidized by hydrogen peroxide or monopersulfate, under acidic or neutral conditions in water, to form novel metal complexes derived from the facile oxidation of the PcS ring. Meso-nitrogen-oxide derivatives and metal-biliverdin-like derivatives were identified among the products at early reaction times, whereas at longer times fragmentation of the phthalocyanine ring occurred, with formation of sulfophthalimide and metal complexes containing the resulting tridentate ligand. The oxidative degradation of the MPcS complexes has been investigated by ESI-MS, UV/Vis-NIR and ^{1}H, ^{13}C and ^{15}N NMR spectroscopy. These rapidly formed, coordinatively unsaturated complexes represent the dominant species in oxidizing media, at least in the case of the Ru derivative, and must be the real catalyst precursors in previously published oxidation reactions using MPcS complexes. The oxidative degradation reactions occurred with selective mono-denitrogenation of one meso-nitrogen atom and formation of ammonia, thus recalling the celebrated selective degradation of heme to verdoheme and/or biliverdin and CO.

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Introduction

Metalloporphyrins and -phthalocyanines are close structural and functional models for the ubiquitous mono-oxygenase or peroxidase heme enzymes, of principal importance on a global scale for the oxidation of xenobiotics in biological systems. Metalloporphyrins are often very effective systems for the catalytic oxidation of a variety of organic substrates, including alkanes, alkenes and aromatic hydrocarbons.[1] Metallophthalocyanines, despite their cheap and facile preparation, have been studied much less intensively as oxidation catalysts, the main drawback being their extensive insolubility in common organic solvents, which considerably limits the scope of the investigations.[2] Introduction of suitable substituents at the periphery of the molecule can make the metallophthalocyanine complexes soluble, and therefore, suitable for homogeneous catalysis; in this context, tetrasulfonated metallophthalocyanines MPcS (**1** in Scheme 1) are of particular interest, since they make possible catalysis in aqueous media,[3] an obvious green alternative to organic solvents.[4] During the last decade, iron or manganese sulfophthalocyanines have been successfully employed by Meunier et al. for the oxidative dechlorination of chlorophenols[5] and the oxidation of other organic substrates[6] in the presence of hydrogen peroxide and mono-persulfate.

We have also reported on the catalytic activity of ruthenium sulfophthalocyanine, with particular regard to the oxidation of chloro-organics[7,8] and alcohols,[9] and, more recently, of cyclohexanone, cyclohexanol or cyclohexane to adipic acid with hydrogen peroxide and mono-persulfate.[10] During these studies, we become aware that, contrary to common belief, the metallophthalocyanine core does not possess an intrinsic chemical stability in oxidizing media, even under very mild conditions. Indeed, among the few reports found in the literature, we can quote only two examples where the macrocycle is reported to undergo a facile oxidative cleavage in the presence of either oxygen (and sulfite as the sacrificial reductant)[11] or *tert*-butyl hydroperoxide.[12] Many of the MPcS complexes examined during our studies, and particularly the catalytically active ones, were found to be extremely sensitive to oxidants, such as hydrogen peroxide or mono-persulfate, giving rise to dramatic changes in their physical properties, and thus, truly behaving as pre-catalysts. These observations prompted us to conduct a spectroscopic study in aqueous solution, focused on defining the fate of a selected choice of metallosul-

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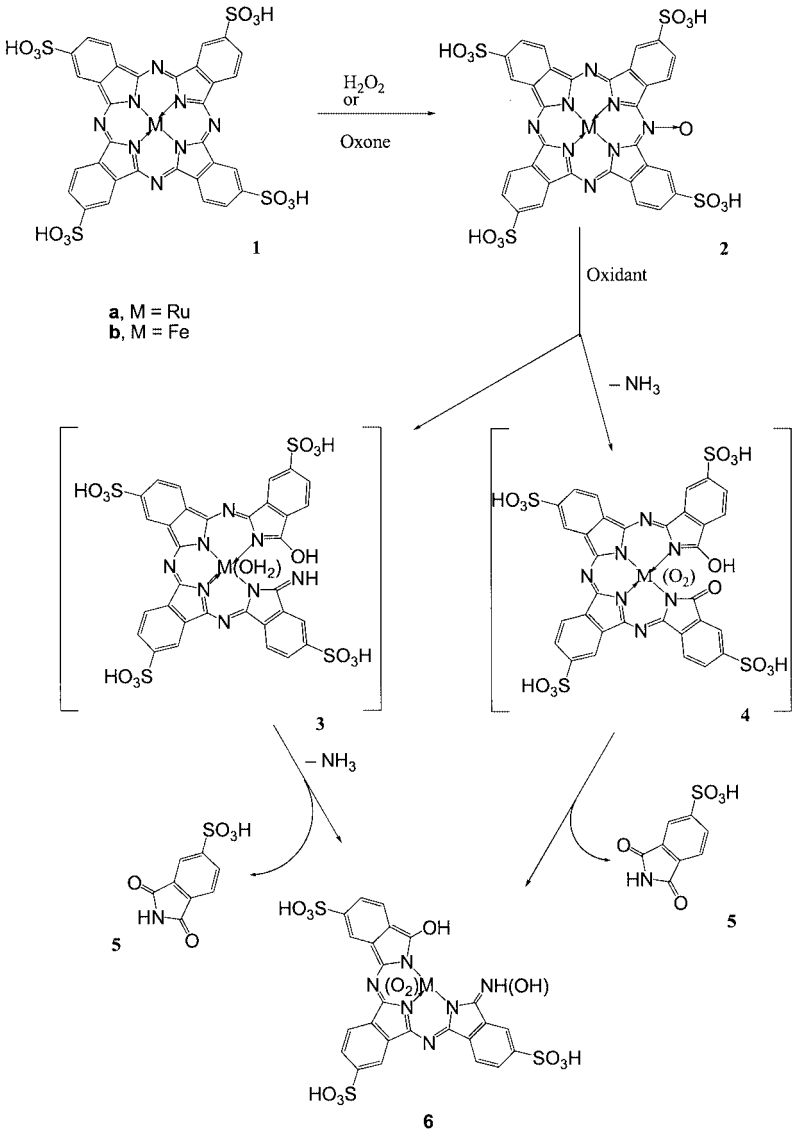

Scheme 1. Proposed pathway for the oxidation of MPcS by H_2O_2 or $KHSO_5$

fophthalocyanines, and the nature of the metal species formed during their mild oxidation by hydrogen peroxide or mono-persulfate.

Results and Discussion

General

The MPcS complexes (M = Fe, Ru and Cu) dissolved in water in the 1−50 mM concentration range were treated with various amounts of H_2O_2 or oxone (from 0.5 to 10 equivalent per mol) in acidic or neutral media and at room temperature. The electronic spectra (300−1500 nm) of the starting MPcS complexes show the diagnostic Q bands in the 620−670 nm region, which arise from the $\pi \rightarrow \pi^*$ transition within the heteroaromatic ring (Table 1). The intensely green/blue solutions became rapidly yellow/colorless (M = Fe and Ru) in the presence of an excess (≥10-fold) of oxidants, with complete disappearance of the corresponding Q band. In most cases, a series of distinct steps could be recognized during the oxidation of the MPcS complexes, leading to the formation of a number of intermediate products, which could be characterized spectroscopic ally. In strongly alkaline media (pH 13), the MPcS complexes, or more likely their hydroxo- and/or oxo-bridged derivatives, are almost insensitive to the oxidizing media, except RuPcS, for which, in the presence of $KHSO_5$ (but not of H_2O_2), a very slow decoloration was observed. The rate of the transformations depends upon the nature of the central ion. The CuPcS complex was found to be completely insensitive to the oxidation, even in acidic media.

The oxidation reactions were followed by ^1H and ^{13}C NMR spectroscopy with the aim of characterizing the metal species resulting from the oxidative degradation. We also recorded the ^{15}N NMR spectra of ^{15}N-RuPcS, but no signals were observed that were attributable to either meso- or metal-coordinating nitrogen atoms, in agreement with literature data, which often report insignificant ^{15}N NMR

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Table 1. Visible spectra of MPcS complexes

Compound	λ_{max}, nm (ε_M)[a]
FePcS	634 (40000)
CuPcS	624 (48000)
RuPcS	638 (26000)

[a] 3.33 μM aqueous solutions at pH 7 (phosphate buffer 0.2 M); the experiments were repeated at pH 2 (H_2SO_4 0.01 M), pH 9 (borate buffer 0.2 M) and pH 12 (NaOH 0.01 M) with no appreciable changes.

spectra for non-symmetrical nitrogen-containing compounds, even if labeled 100%.[13]

ESI-MS spectra, exhibiting the diagnostic isotopic patterns of the metal derivatives, offered the possibility of distinguishing between the metal-containing and purely organic species, and also between monomeric and oligomeric metal-containing species. Quite unexpectedly, the ESI-MS spectra gave clear indications, in all examined cases, of the corresponding molecular ions, when conducted in the positive-ion mode; various sodium-containing clusters, replacing the protons up to complete substitution, were also observed, especially at higher cone voltages (see Exp. Sect.). Under these conditions, peaks at −80 and sometimes at −160 amu were detected, indicative of a loss of SO_3. Clearly, cleavage of the S-benzene bond occurs to give the corresponding trisulfophthalocyanine derivative [M − 80], although the S-aromatic bond was not as easily cleaved as the S-aliphatic analog; the fact that this fragmentation was observed only at very high cone voltages suggests strongly that this event is an example of collision induced dissociation (CID).[14]

All attempts to isolate solid compounds from the oxidized reaction mixtures were unsuccessful and evaporation in vacuo resulted in intractable waxy solids, which did not yield solid materials.

RuPcS

RuPcS is diamagnetic both in the solid state (Gouy's method) and in aqueous solution (Evans' method), in agreement with a low-spin configuration of ruthenium(II) (d^6). The visible spectra in water show the diagnostic Q band at 638 nm, and also exhibit a definite shoulder, at higher energies, indicative of aggregation in aqueous solution.[15] The intensely green solutions of RuPcS become rapidly yellow in the presence of oxone or H_2O_2, with complete disappearance of the Q band, whereas no other absorptions are detected in the visible or in the near infrared regions, up to 1500 nm, which represents the upper wavelength for aqueous solutions containing peroxides. Simple demetalation, a rare event for metallophthalocyanine complexes,[16] can be ruled out on the basis of direct experiments, since the UV spectra of an organic phase, purposely added to the reaction mixtures, do not exhibit the absorptions at 310 and 385 nm that are diagnostic for RuO_4, the expected dominant species for free ruthenium in acidic oxidizing media. The diamagnetism of the aqueous solutions of the starting RuPcS complex is maintained in the presence of excess of oxidant, whereas the ^{1}H NMR spectra, showing for the starting RuPcS only a broad signal in the δ = 8 ppm region, exhibit well resolved signals at δ = 8.1 and 7.9 ppm upon oxidation, clearly indicative of the expected AMX patterns of the 1,2,4-aromatic proton system, thus suggesting extensive removal of the strong intermolecular interaction occurring in polar media (stacking) that is probably responsible for the broad NMR signal.

The ^{1}H NMR spectra of the acidic reaction mixtures with mono-persulfate also exhibit three more signals, centered at δ = 7 ppm (J = 51 Hz), which, in the case of the ^{15}N-RuPcS derivative, were replaced by a doublet with $J(^1H\text{-}^{15}N)$ = 74 Hz; significantly, the ^{15}N NMR spectra (DEPT-45) exhibit five signals centered at δ = −360 ppm, having the same $J(^1H\text{-}^{15}N)$ reported above. These findings are diagnostic of the presence of ammonium ions, which, on the basis of the measured intensity ratios between benzene and ammonium protons, are found in a 1:1 molar ratio with the regards to the complex, even after longer reaction times (Table 2). Hydrogen peroxide in acidic media behaves similarly, giving rise to the ^{1}H NMR signals of the ammonium ion. In this case, however, because of the presence of oxygen, continuously formed upon dismutation of the oxidant, quantitation of the ammonia produced was performed with an ion-selective electrode; again, the quantity of ammonia never exceeded the 1:1 molar ratio (Table 2).

Table 2. Production of ammonia by oxidation of MPcS complexes

Compound	Time, h	NH_4^+ produced	
		$KHSO_5$[a]	H_2O_2[b]
RuPcS	1	1.1	1.1
	18	1.1	1.03
FePcS	1.5	n.d.	0.45
	16	n.d.	0.73
CuPcS	16	0	0

[a] mol/mol of MPcS; ^{1}H NMR measurements. Reaction conditions: aqueous solution of MPcS, 1 mM, and $KHSO_5$, 0.5 M; pH ca. 2; 20 °C. [b] mol/mol of MPcS, electrochemical measurements. Reaction conditions: aqueous solution of MPcS, 1 mM, and H_2O_2, 2 M; pH ca. 2 (H_2SO_4); 20 °C.

It should be noted that the oxidation appears to be highly selective, involving only one of the eight nitrogen atoms of the macrocycle: further treatment of the oxidized RuPcS complex with sodium hydroxide under strongly alkaline conditions and refluxing led to complete denitrogenation of the compound, with formation of ammonia in the expected 8:1 molar ratio. The oxidative denitrogenation of amines to ammonia is a known process in biochemistry, where it is catalyzed by amine oxidase, a non-heme copper-containing enzyme, and is also reported to occur in the presence of a biomimetic copper complex.[17]

The ^{13}C NMR spectrum of the RuPcS complex (60 mM) shows the expected eight signals, which arise from the three tertiary [δ = 121, 125 and 132 ppm (aromatic CH carbons)] and the five quaternary carbon atoms [δ = 133 and 135 ppm (β-C with respect to N); δ = 144 ppm (sulfonate-

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bonded carbon); δ = 174 and 179 ppm (α-C)]. The oxidized solutions exhibit closely related eight-signal ^{13}C NMR spectra, whose differences in chemical shift from the untreated samples are scarcely significant, although they do confirm the integrity of the organic backbone. Also, 3-sulfophthalimide exhibits a related ^{13}C NMR spectrum (see Exp. Sect.), with almost imperceptible differences in the positions of each signal, including those from the α-C's, and is therefore independent of the nature of the bonded heteroatoms (oxygen or nitrogen).

The ESI spectra of RuPcS were found to be highly sensitive to the applied cone voltage, thus making the interpretation of the data complicated (Figure 1). Under medium cone voltage (50−100 V), the penta-protonated species $Ru^{II}PcSH_5^+$ (*m*/*z* = 935), showing the diagnostic isotopic (metal) pattern of the monomer, is the dominant species (Figure 2). By further increasing the applied voltage, and therefore under very drastic conditions, significant changes of the fine structure of the signal were observed, with the peak at *m*/*z* = 934 (−1 amu) gaining intensity and thus pointing to the formation of the $Ru^{III}PcSH_4^+$ species, produced in the capillary tip upon the one-electron oxidation of the central metal ion. At lower cone voltage (5−50 V), the main feature is the appearance of a new species that is still monomeric, but with *m*/*z* = 969. This species becomes dominant at very low voltage; the observed *m*/*z* value fit with a Ru^{IV} species, such as $Ru^{IV}(OH)_2PcSH_5^+$, which might arise from an oxidation in the capillary tip, is rather surprising because it occurrs under such mild conditions. The ^{15}N-RuPcS complex gives the expected ESI signal at *m*/*z* = 943, i.e. +8 amu with respect to the unlabelled derivative, and at lower voltage than the above Ru^{IV} species at *m*/*z* = 977−979 (the presence of small amount of ^{14}N in the labeled compound led to some loss of the conventional isotopic pattern of ruthenium).

Upon treatment with the oxidants, a series of distinct intermediate species could be detected by ESI-MS spectra. At low oxidant-to-metal ratios (ca. 1:1), a new signal appears at *m*/*z* = 951 − an increase of 16 amu with respect to the starting species − that still retains the diagnostic isotopic pattern of the monomer; the ^{15}N-RuPcS derivative behaves similarly, leading to the appearance of an ion at *m*/*z* = 959.

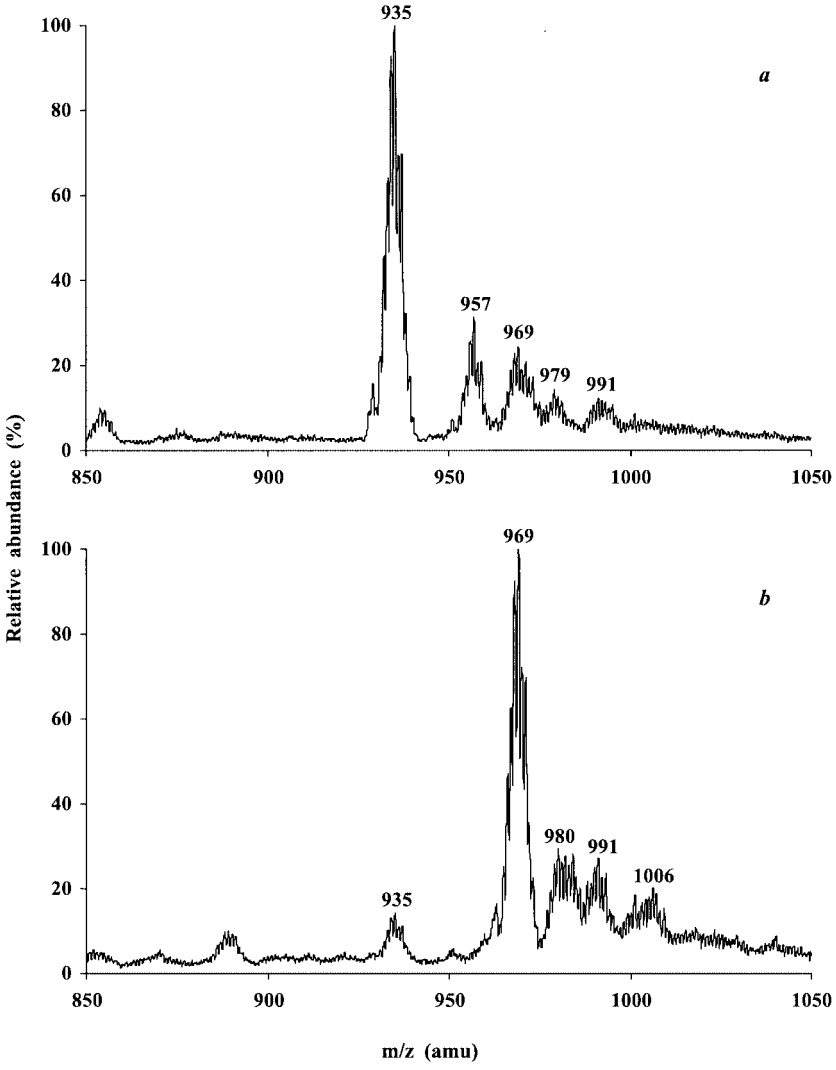

Figure 1. ESI-MS spectra of aqueous 5 mM solution of RuPcS, at high (150 V) (a) and low (30 V) (b) cone voltage

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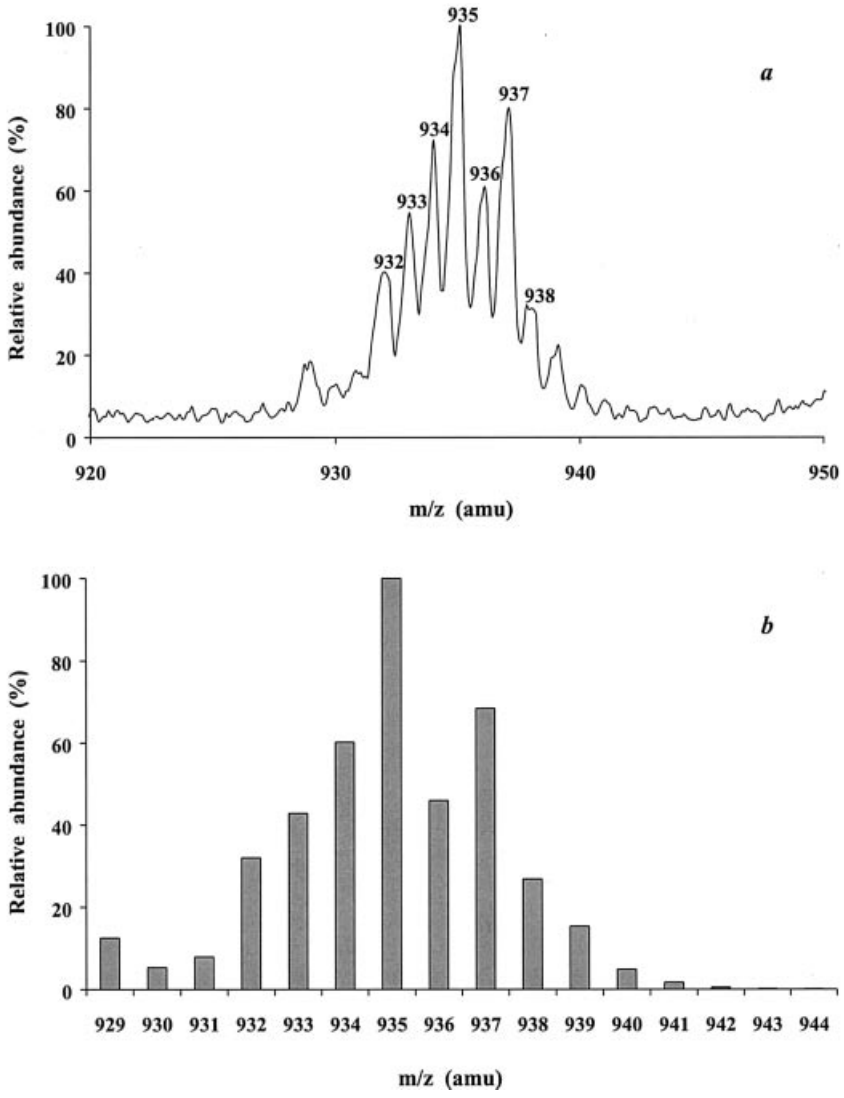

Figure 2. Fine structure of m/z = 935 peak of RuPcS (50 V) (a) vs. calculated isotopic pattern (b)

As in the case of the starting RuPcS discussed above, these signals are replaced at lower voltage by a signal at m/z = 985 (993 for the labeled derivative), again attributed to oxidation of the complex at the capillary tip. Both signals could be detected in the ESI spectra, when the measurements were performed at intermediate voltage, in order to achieve maximum sensitivity (Figure 3). The species detected at m/z = 951 (959 for ^{15}N) and clearly incorporating one oxygen atom, can be attributed to either an oxometal derivative Ru^{IV}(O)PcS or, more likely, a complex with a mono-oxygenated ligand, where the metal is still in a lower oxidation state, for example a Ru^{II}PcOS species (**2a** in Chart 1), where PcOS is the mono-nitrogen-oxide derivative in the meso position of the PcS ligand. An immediate explanation for the ready formation of the nitrogen-oxide derivative could be provided by the conventional chemistry of nitrogen-containing heteroaromatics towards inorganic peroxidic reagents.[18] However, the fact that some of the MPcS derivatives, such as CuPcS, are totally resistant to the oxidative treatment, suggests a direct involvement of the central metal atom in the oxygenation process, rather than an uncatalyzed attack by the peroxidic oxidant on a meso-nitrogen atom of the PcS ring. Under this hypothesis the oxygenation of a meso-nitrogen is highly reminiscent of the first step of the oxidation of heme (to hydroxyheme).[19]

Upon addition of further oxidant to RuPcS (up to 10:1), a fast and almost complete disappearance of the oxygenated species occurred; the ESI-MS spectra shows the presence of strong signals both at higher (m/z around 1003, 1022 and 1040) and lower molecular weights (m/z around 778, 796, 814 and 833), most of them apparently lacking the diagnostic isotopic pattern of ruthenium and possibly indicating the presence of closely related ions differing by a few amu. At longer reaction times, only the species with lower molecular weights were observed (Figure 3). ^{15}N-RuPcS behaved similarly, leading to the formation of ions with m/z centered at ca. 1010, 1030 and 1048 and at 784, 802, 817 and 838 amu. A direct comparison of the masses of the ions from the ^{14}N or the ^{15}N samples might make possible, in principle, an evaluation of the nitrogen content of the various species; unfortunately most of the signals did not exhibit the standard isotopic pattern of ruthenium, and therefore the exact

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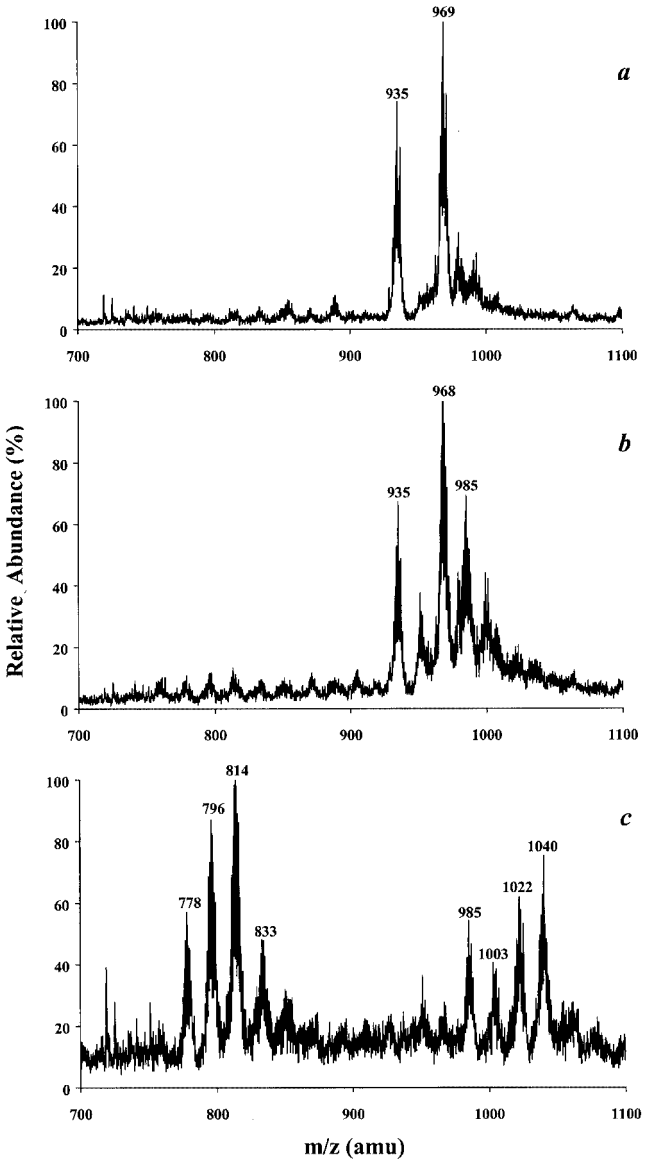

Figure 3. ESI-MS spectra of aqueous 5 mM solution of RuPcS (50 V) (a) and after addition of $KHSO_5$: in equimolar amount (50 V) (b) and twofold molar excess (50 V) (c); (in both cases reaction time 10 min)

masses were too uncertain to allow unequivocal conclusions. The intermediate species around *m*/*z* = 1003, 1022 and 1040 (1010, 1030 and 1048 for the ^{15}N-labeled derivative) were tentatively attributed to the aqua clusters (mono-, di- and tri-) of ions from compounds **3a** or **4a**, i.e., dioxoruthenium(VI) complexes with biliverdin-like ligands, either containing all the starting nitrogen atoms or lacking one of them, respectively; on this basis, the corresponding non-aquated cations might come at *m*/*z* = 985 and 986, respectively (992 and 993 for the ^{15}N-labeled derivative), and are therefore superimposed on the species formed in the initial stages of the reaction and discussed previously. Biliverdin- and verdoheme-like derivatives of phthalocyanines have been reported in the literature, although they were prepared upon photolysis of a triazatetrabenzocorrole and not directly from a phthalocyanine ring;[20] significantly, these derivatives were reported to lack not only the diagnostic Q-band, but also other absorptions of comparable intensity, and are thus in agreement with the observed quenching of the $\pi\rightarrow\pi^*$ bands in oxidized RuPcS complexes. The peaks at *m*/*z* = 778, 796, 814 and 833 (784, 802, 817 and 838 for the ^{15}N-labeled derivative) fit well with a series of aquated cations (from none to three molecules of water) from compound **6a**, i.e., a dioxoruthenium(VI) complex of a tridentate ligand formed upon fragmentation of the PcS ring (Scheme 1). Accordingly, the resulting organic fragment 3-sulfophthalimide (**5**) was detected as a single peak at *m*/*z* = 228 (positive ionization mode; 229 for the ^{15}N-labeled derivative) or at *m*/*z* = 227 (negative ionization mode); an original sample of the compound exhibited the same spectral behavior. One molecule of ammonia was also produced, during either the first or the second step (Scheme 1); to the best of our knowledge, fragmentation of a phthalocyanine ring with production of ammonia has never been reported.

FePcS

In the presence of small amounts of added mono-persulfate or hydrogen peroxide (1:1 molar ratio), a distinct shift of the Q-band of FePcS towards lower energies was observed, whose blue solutions (λ_{max} = 634 nm) turned green (λ_{max} = 670 nm; Figure 4) and finally, in the presence of increasing amounts of the oxidant (10-fold), almost colorless. The oxidized solutions became paramagnetic almost immediately (Evans' method), whereas, and quite surprisingly, the starting paramagnetic (Gouy's method) iron(II) (d^6) derivative,[21] was apparently diamagnetic by Evans' method, once dissolved in water. If it is conceivable that the expected strong stacking of the MPcS moieties occurring in the aqueous solutions does not allow reliable measurements of the magnetic moments by the Evans method, the fact that the oxidized complex was found to be clearly paramagnetic also points to an extensive removal of stacking upon oxidation. The benzene protons were still observed as a large unstructured signal at δ = 8−10 ppm (^1H NMR spectra), but most significantly, and as in the ruthenium case

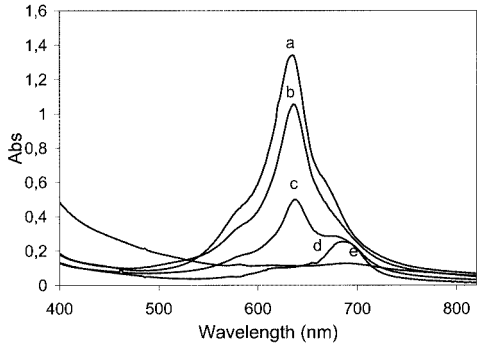

Figure 4. Vis spectra of aqueous 3.33 μM solution of FePcS (a) and after addition of $KHSO_5$: in equimolar amount (b); threefold molar excess (c); fourfold molar excess (d); 10-fold molar excess (e). In all the experiments no difference was observed between 1 and 10 minutes of wait before the recording, following the dilution, of the spectra

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discussed above, ammonia was produced upon oxidation, again, at least with hydrogen peroxide, in a 1:1 molar ratio with the metal (Table 2). In the presence of oxone the ammonia signals were also clearly detected by ^{1}H NMR spectroscopy, although accurate quantitation was not possible neither by NMR measurements, because of the paramagnetism of the solution, or by electrochemical measurements, since the selective ion electrode requires a constant ionic strength. Furthermore, in the presence of increasing amounts of the oxidants (10-fold), almost colorless solutions were obtained.

The oxidized solution showed, even during the early stages of the reaction, the complete disappearance of the ESI-MS signal (positive pattern) of the starting complex at m/z = 888 and the diagnostic isotopic pattern of an iron monomer, which corresponds to a $Fe^{III}PcSH_4^+$ ion, probably because of an easy oxidation of iron(II) to iron(III) in the capillary tip of the spectrometer. However, and unlike RuPcS, no important peaks were detected in the ESI spectra of the oxidized solutions, although the visible spectra gave clear evidence of transformation products: instead, only very weak and confusing signals were observed in the 700−750 and 500−550 amu regions, even under milder ionization conditions, together with sharp signals at m/z = 228 and 250, clearly attributable to sulfophthalimide (**5**) and the corresponding sodium cluster. These results suggest a very fast and extensive fragmentation of the oxidation products, indicative of a high sensitivity of the system either to the ionization conditions or to the chemical oxidation itself.

Conclusions

The most important finding in these experiments is that it is clearly evident that the rapid and irreversible oxidative degradation of the MPcS complexes studied with H_2O_2 or mono-persulfate occurs under very mild conditions, and prior to any role as precatalysts for oxidation reactions. A mechanism is tentatively proposed, involving the initial formation of oxidizing metal species in higher oxidation states, followed by a selective intra- (or inter) molecular attack at one meso-nitrogen atom of the phthalocyanine ring, with formation of a mono N-oxide derivative (compound **2**). As a consequence of the disruption of the aromaticity of the PcS macrocycle, a facile hydrolysis can be envisaged with ring opening and production of ammonia (compounds **3** and **4**). These biliverdin-like complexes then undergo further oxidative fragmentation, with loss of sulfophthalimide (detected) or 3-iminosulfoisoindoline (not detected), to tridentate ligands (compound **6**) that are still coordinated to the metal ions. It is fairly conclusive that this event results in the in situ formation of coordinatively unsaturated metal complexes, now thought to be candidate precatalysts for the oxidation reactions previously reported.[5a,7] Although the efficacy of each precatalyst also depends upon the intrinsic reactivity of the metal species towards the specific substrate, it is interesting to note that the different catalytic behaviors of the two MPcS complexes strictly reflect the degree of degradation in the oxidizing media. RuPcS gave rise to relatively long-lived coordinatively unsaturated metal species and was indeed shown to be an effective and efficient precatalyst in the $KHSO_5$ oxidation of caprolactone to adipic acid; in contrast, FePcS, which underwent fast and extensive demetalative fragmentation, provided to be a far less effective catalyst.[10] The fast and quantitative transformation of the MPcS complexes into catalytically active species, when in oxidizing media, could be a new paradigm for the general behavior of related classes of metallomacrocycles in oxidation catalysis.

Experimental Section

General Procedures: The reactions were typically carried out at 20 °C in a 5 mL vial, by stirring magnetically 2 mL of an aqueous solution containing the complexes (0.1−10 mM) and suitable amounts of H_2O_2 or $KHSO_5$ (from 0.5:1 to 10:1). Ammonia analysis was performed electrochemically (Orion, model 420A) with an ion-selective electrode (Orion, model 95−12; a glass electrode with a gas diffusion membrane); calibration curve was performed by a 1 M solution of NH_4Cl.

Materials: RuPcS[8] was prepared by template synthesis starting from $RuCl_3{\cdot}3H_2O$, sodium 4-sulfophthalate and urea, following early general procedures for the synthesis of metallosulfophthalocyanines.[21] The ^{15}N-RuPcS derivative was prepared similarly, starting from commercially available ^{15}N-urea (99% isotopic purity, Isotec Inc.). $FePcS{\cdot}3H_2O$ (monosodium salt) and CuPcS (tetrasodium salt) were purchased from Aldrich.

NMR Measurements: NMR spectra were recorded on a Bruker Avance 300 MHz (Karlsruhe, Germany) equipped with a BBO 5 mm probe; the frequencies of the observed nuclei were 300.13, 75.47 and 30.42 MHz respectively for ^{1}H, ^{13}C and ^{15}N. In the case of ^{1}H spectra a water suppression (Bruker made − zgcppr) pulse sequence was used; in addition a reference consisting of a co-axial capillary, inside the NMR tube, filled with a 30 mM D_2O solution of the sodium salt of 3-(trimethylsilyl)propionic acid-2,2′,3,3′-d_4 (TSP) was used.

FTIR spectra were acquired on a Perkin−Elmer Spectrum 2000 equipped with an MIR source and a MIR-TDGS detector; to record the spectra the samples were suspended in anhydrous KBr pellets; spectral width, for all the experiments, was 5000−370 cm^{-1}.

Vis spectra was carried out on a Perkin−Elmer Lambda 2 series 3300; the spectral window was 350−800 nm.

ESI-MS Measurements: The HPLC apparatus used was a Perkin−Elmer series 200 quaternary pump system (Norwalk, CT, USA). Analyses were performed at room temperature using a reversed phase Supelcosil LC-PAH column (250 × 4.6 mm; 5 μm) purchased from Supelco (Bellefonte, PA, USA). Samples were automatically injected using a Perkin−Elmer series 200 autosampler (thermostatted at 4 °C) with a 20 μL injection-loop. Isocratic separations were carried out using a mobile phase consisting of methanol (50%) and water (50%), both with 0.5% of formic acid at the flow rate of 200 μL/min. The HPLC system was connected to a Perkin−Elmer mod. 785A UV/Vis detector (Norwalk, CT, USA) set at the wavelength 280 nm and then to a PE Sciex Turboionspray source (2.1 L/min NEB gas). Acquisitions were carried out in positive ion mode over the mass range 700−1100 amu (or

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100−1500 amu when the detection of 3-sulfophthalimide was necessary), using a step size of 0.1 amu and a dwell time of 0.350 ms. The nebulizer gas (air) and the curtain gas (N_2) flows were set at 1.7 L/min and 2.7 L/min, respectively. The ionization voltage was set at +5200 V and the orifice and ring potentials were normally set at +50 V and +280 V, respectively; higher and lower voltage condition are referred to orifice potentials varied between 5 and 180 V and ring potentials between 100 and 360 V. Instrument control and data acquisition were performed with Macintosh System 7600/132 (Apple, Copertino, CA, USA) using Masschrom 1.1.1 software (PE Sciex, Foster City, CA, USA). The Mass Spectrometer was calibrated with polypropylene glycol (PPG) obtained from PE Sciex and the resolution was set in the range 0.6−0.8 amu.

Magnetic Moments Measurements: Magnetic moments were measured by Gouy's method (solid state) or Evans' method, performed as follows: a coaxial NMR tube (5 mm i.d.) was filled with a 0.31 M solution of *tert*-butanol in D_2O (tube) and with a 0.31 M solution of *tert*-butanol also containing ca. 30 mM of the MPcS complexes in D_2O (external capillary); the calculations for the susceptivity were performed according to the literature.[22]

Synthesis of 3-Sulfophthalimide (5): 3-Sulfophthalic acid (30 g, 0.122 mol) was heated at 150 °C in vacuo for 3 h; after cooling, urea (3.6 g, 0.06 mol) was added under nitrogen atmosphere and the mixture heated again to 130 °C until evolution of gas had finished (yield: 2.5%). ^{1}H NMR (300.13 MHz, D_2O, 25 °C: δ = 8.08 (d, 1 H, 1-CH), 7.93 (dd, 1 H, 3-CH), 7.77 (d, $J_{3,4}$ = 7.9, $J_{1,3}$ = 1.7 Hz, 1 H, 4-CH) ppm. ^{13}C NMR (75.47 MHz, D_2O, 25 °C): δ = 126.4, 129.1, 129.7 (CH); 132.4, 135.4 (β-C); 145.4 (sulfonate-C); 171.0, 172.0 (α-C) ppm. IR (KBr film): double peak at $\tilde{\nu}$ = 1714−1738 cm^{-1} (C=O). $C_8H_5NO_5S{\cdot}2.5H_2O$ (272.2): C 36.03, H 3.68, N 5.17, S 11.76; found C 35.14, H 3.16, N 5.16%, S 12.46.

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