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Thermal stability and photostability of water solutions of sulfophthalocyanines of Ru(II), Cu(II), Ni(II), Fe(III) and Co(II)

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Abstract

The thermal and photochemical stabilities were investigated for tetrasulfophthalocyanines of Cu, Co, Ni, Fe and Ru (MPcS) and for two monosulfophthalocyanines of Ru, either without (RuPcS1) or with the coordination of two units of DMSO in apical positions ([RuPcS1(DMSO)$_2$]DMSO). The thermal degradation of all of the studied complexes never showed the formation of spectroscopically detectable intermediates. CuPcS was the most stable complex, while all of the Ru-sulfophthalocyanines were particularly prone to thermal degradation. Photodegradation showed a better selectivity, and as with thermal degradation, the order of reactivity goes from the most stable CuPcS, to the least stable Ru-sulfophthalocyanines (RuPcS, RuPcS1 and [RuPcS(DMSO)$_2$]DMSO). In particular, when the RuPcS complex was irradiated, a stable intermediate was detected that had an absorption band at 532 nm and a mass spectrum attributable to the tetrasulfophthalocyanine from oxidative ring cleavage by the action of the singlet oxygen formed via ^{1}*RuPcS photosensitization. The most probable molecular formula demonstrates a new complex, with a cleaved ring containing an –N=O group and two –OH groups that are all bonded at the two extremities of the open-chain molecule.

Keywords: Phthalocyanine; Photostability; Electrospray mass spectrometry; Ruthenium; Ruthenium monosulfophthalocyanine

1. Introduction

The metal-phthalocyanines are close structural analogues of metal-porphyrins, although they are generally less catalytically active. They are characterized by an 18-electron system, which makes them particularly prone to photosensitization processes; indeed, they have been extensively used as photosensitizers in photodynamic therapies against cancer [1,2]. The important photochemical advantage of this class of compounds is due to their peculiar absorption spectra window in the visible region (red, 600–700 nm), which is also essentially independent of the nature of the central metal atom [3]. However, the metal-phthalocyanines can be degraded, with varying efficiencies, by the actions of temperature [4], UV light [5] and strong oxidants [6]. For example, we find that potassium monopersulfate and hydrogen peroxide are able to oxidize the phthalocyanine ring of several metallo phthalocyanines, which gives rise to *meso*-oxygenated intermediates that can arise from two different pathways: (i) the formation of a mono-oxygenated phthalocyanine ring (probably in the *meso* position), resulting in the ring opening and a rearrangement into a novel and relatively stable complex

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and (ii) the formation of a polyoxygenated phthalocyanine ring. In the first case, continuous addition of the oxidant leads to a mixture of degradation products, among which there are 4-sulfophthalimide, ammonia and the hydrated metal. In the second, the polyoxygenated derivative collapses directly into the hydrated metal and four phthalimide units, without the formation of any other detectable intermediate(s) [7].

Although the metal-phthalocyanines (either in solution or when anchored on solid supports) appear to be among the substrates of choice for redox and photoredox reactions, their scope has been considerably limited in the past because they generally form large and stable molecular aggregates. This is due to the strong attractive interactions (π stacking) that are favoured by the large and flat nature of their hydrophobic aromatic macrocyclic moieties [8–10].

Appropriate functionalizations of the phthalocyanine unit have demonstrated the possibilities of overcoming the problem of the solubilities of these compounds in common solvents and of significantly reducing the stacking, and therefore increasing the availability of active catalytic sites. Usually, the functionalization by carboxylic and sulfonic groups are used for water solubilization, while apolar tails make the solubilization in organic media possible.

In the present study, our aim was to investigate the early stages of the degradation of the metal-sulfophthalocyanines, i.e., to characterize the compounds that are obtained following a soft attack under aerobic conditions; namely, moderate thermal treatment, and irradiation by UV or visible light. The metal-sulfophthalocyanines taken into consideration were the tetrasulfophthalocyanines of Cu, Ru, Fe, Co and Ni (MPcS) and two monosulfophthalocyanine derivatives of Ru, always with the $-SO_3H$ group in position 3, in the absence (RuPcS1) and in the presence of DMSO ([RuPcS1(DMSO)$_2$]DMSO).

2. Experimental

2.1. Materials

All organic solvents and spectroscopic standards were reagent grade (Aldrich). D_2O (D $\geqslant$ 99%) was from Isotec Inc. Acetonitrile (HPLC grade), formic acid (analytical grade) (both from Carlo Erba Reagenti) and sterile deionized water (Laboratori Diaco Biomedicali) were used for the chromatographic analyses. Cu, Ni and Fe tetrasulfophthalocyanines (CuPcS, NiPcS and FePcS) were commercially available (Aldrich). Ru-tetrasulfophthalocyanine (RuPcS) [11], Co-tetrasulfophthalocyanine (CoPcS) [11] and Ru-monosulfophthalocyanines (RuPcS1 and [RuPcS1(DMSO)$_2$]DMSO) were prepared following the general procedures previously reported in [12]. All of the sulfophthalocyanines were kept for 2–4 h at 40 °C under vacuum before use.

2.1.1. Preparation of RuPcS1

Fifteen grams of 50 wt% solution of 4-sulfophthalic acid (30.5 mmol), 8.65 g (33.1 mmol) of $RuCl_3 \cdot 3H_2O$, 0.1 g (0.51 mmol) of ammonium molybdate and 15 ml of water were stirred together until all of the solids were dissolved. Forty parts of urea were added to this solution and the mixture was stirred until most of the urea was dissolved. This reaction mixture was poured into a reactor, to which 14 g (94.5 mmol) of phthalic anhydride had previously been added. The complete reaction mixture was then heated up to between 190 and 215 °C for 3 h. The temperature was then raised to 260–270 °C and maintained there for 3.5 h. After cooling and grinding, the reaction product was washed with water saturated with sodium chloride. The RuPcS1 was then extracted with ethanol from the crude mixture and dried in vacuo. Yield: 6.1 g (28%).

Anal. Calc. for $C_{32}H_{15}N_8O_3$ SNaRu: C, 53.72; H, 2.11; N, 15.65; S, 4.47; Found: C, 53.21; H, 2.42; N, 15.52; S, 4.31%. Vis(H_2O/CH_3CN): 640 nm. ESI-MS: *m*/*z* 717 (28%), attributed to $C_{32}H_{15}N_8RuSO_3Na(H)$; *m*/*z* 695 (20%), attributed to $C_{32}H_{16}N_8RuSO_3(H)$; *m*/*z* 614 (100%), attributed to the [MW – 80 (SO_3)]. ^{1}H NMR (CD_3CN/H_2O): broad and unresolved signal around 7–8 ppm, aromatic protons.

2.1.2. Preparation of [RuPcS1(DMSO)$_2$]DMSO

Three grams of RuPcS1 was suspended in 40 ml of dimethyl sulfoxide and the mixture was heated under N_2 for 4 h at 120 °C. The hot solution was filtered. After cooling, the dark blue crystals obtained from the filtrate were washed with ethanol and dried in vacuo at 50 °C. Yield: 0.870 g (22%).

Anal. Calc. for $C_{38}H_{33}N_8O_6S_4$ NaRu (RuPcS1 + 3 DMSO): C, 48.11; H, 3.40; N, 11.80; S, 13.49; Found: C, 47.93; H, 3.62; N, 11.68; S, 13.62%. IR (1052, 1069, 1091 cm^{-1}). Vis(H_2O): 582 nm (ε 1800); 642 nm (ε 3400). ESI-MS: *m*/*z* 717 (30%), attributed to $C_{32}H_{15}N_8RuSO_3Na(H)$; *m*/*z* 695 (20%), attributed to $C_{32}H_{16}N_8RuSO_3(H)$; *m*/*z* 614 (100%), attributed to the [MW – 80 (SO_3)]. ^{1}H NMR (CD_3CN/H_2O): 2.61 ppm (*s*.), DMSO protons; broad and unresolved signal around 7–8 ppm, aromatic protons.

2.2. Equipment

The ^{1}H NMR measurements were performed with a Bruker Avance 300 MHz spectrometer equipped with a 5-mm BBO probe, by adding small amounts of D_2O to the reaction mixtures (1:3); water suppression was determined by a presaturation sequence using a composite pulse (zgcppr Bruker sequence). A co-axial capillary tube containing a 30-mM solution of 3-(trimethyl-

silyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP) in water (D_2O) was used as reference.

The UV–Vis spectra were obtained using a Perkin Elmer Lambda 35 spectrophotometer (range of acquisition, 190–1100 nm). The solutions in the cuvette were kept at 10 μM or higher, according to the intensity of the Q band.

The HPLC apparatus for the LC/ESI-MS measurements was a Perkin–Elmer series 200 quaternary pump system. The analyses were performed at room temperature, using a reverse-phase Supelcosil LC-PAH column (250 × 4.6 mm, 5 μm; Supelco). The samples were automatically injected into the system using a Perkin–Elmer series 200 autosampler with a 20 μl injection loop. The isocratic separations were carried out using a mobile phase consisting of acetonitrile (50%) and water (50%), both with 0.5% formic acid, at a flow rate of 500 μl/min. The HPLC system was connected both to a Perkin–Elmer 785A UV/Vis detector set at a wavelength of 630 nm, and to a Sciex API 150 MCA single-quadrupole mass spectrometer through a Sciex TurboIonSpray source, after flow splitting (1:1). Acquisitions were carried out in positive ion mode over the mass range of 500–1100 u, using a step size of 0.1 u and a dwell time of 0.233 ms. The nebulizer gas (air) and the curtain gas (N_2) flows were set at 1.7 and 2.6 L/min, respectively. The TurboProbe temperature was set at 400 °C, with the heater gas (N_2) flow set at 6.0 L/min. The TurboIonSpray voltage was set at +5200 V and the orifice and ring potentials were normally set at +50 and +280 V, respectively; the high and low voltage conditions refer to orifice potentials that varied between 5 and 180 V, and ring potentials between 100 and 360 V. The instrument control and data acquisition were through a Macintosh System 7600/132 using Masschrom 1.1.1 software. The mass spectrometer was calibrated with a polypropylene glycol standard (PE Sciex), setting the resolution, as peak width at half peak height, in the range of 0.7 ± 0.1 u.

The Photochemical Multirays Apparatus (Helios Italquartz S.r.l., Milano, Italy) used for the UV–Vis experiments consisted of an airy radiation chamber, composed of one rotating carousel that contained 27 holes, allowing an equal number of potential sample solutions to be irradiated. Around the carousel, at the diameter of 285 mm, there were 10 lamps, each of which had a power of 15 W and a maximum wavelength emission at 254 nm (deuterium lamp) or 520 nm (daylight fluorescent tube; spectral window 450–600 nm). These lamps were fixed in a special lamp-holder with IP 44 protection, and they were equipped with a special aluminium reflector around them, to optimize their radiation power.

The FT-IR spectra were acquired on a Perkin–Elmer Spectrophotometer 2000 FT and recorded in nujol. The spectral width for all the experiments was 4000–200 cm^{-1}.

2.3. Typical procedure for the thermal treatment

One or 10 mM water solutions of the metal-phthalocyanines, at neutral and acidic (with H_2SO_4) pHs, was heated in closed vessels to 80 °C for 24 h. The absorption spectra (UV–Vis) and ESI-mass spectra were recorded at 1, 3, 6 and 24 h. Where possible, the thermal treatment was also followed using ^1H NMR.

2.4. Typical procedure for the photochemical treatment

One or 0.1 mM water solutions of the metal-phthalocyanines in a closed quartz tube was irradiated by UV (254 nm) or visible light (520 nm), either in the presence of air, or in a nitrogen atmosphere that was obtained by bubbling N_2 gas in a plugged tube for 6–8 h before the irradiation.

The degradation of the metal complexes was monitored by UV–Vis, ESI-MS and ^1H NMR spectroscopy at fixed times.

3. Results

The behaviours of the phthalocyanine derivatives were studied in pure water when they demonstrated sufficient solubility (up to 10 mM); otherwise, a 1:1 water/acetonitrile mixture was used.

The monosulfophthalocyanines of Ru were characterized by elemental analysis, UV–Vis, ESI-MS, NMR and IR spectroscopy. The IR spectra of the DMSO-crystallized complex exhibited diagnostic absorption bands at 1052, 1069 and 1091 cm^{-1}, which were attributed to the typical absorption of S=O (1052 cm^{-1}; due to the free DMSO) and S-bonded-to-metal moieties, respectively. This interpretation was supported by the information that the band typical of the O–M bonded moiety, which would be expected to be around 925 cm^{-1}, was never detected [13]. While clearly confirming the presence of DMSO, the DMSO proton signal of the ^1H NMR spectra also appeared in the same region as the uncomplexed ligand, thus suggesting that in the presence of water, the apical DMSO ligands were easily and quantitatively replaced. For the same reason, the mass spectra of RuPcS1 and of the [RuPcS1(DMSO)$_2$]DMSO were almost identical (Fig. 1).

The results of the thermal treatment at 80 °C provided a scale of stability of the substrates examined, while also allowing the evaluation of the effect of temperature on their molecular aggregation. CuPcS and NiPcS were apparently highly resistant to degradation, while RuPcS, CoPcS and FePcS showed definite changes in shape and intensity of the Q band (Table 1).

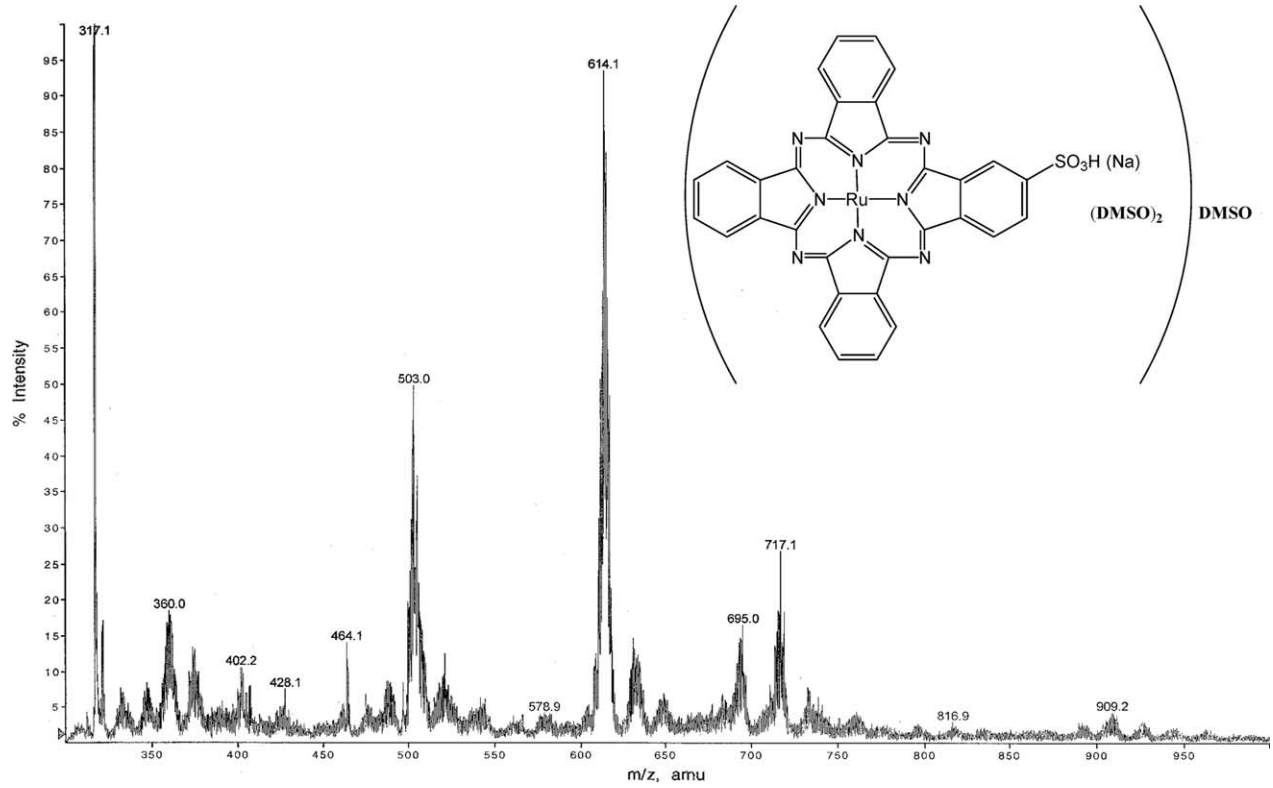

Fig. 1. ESI-MS spectrum of [RuPcS1(DMSO)$_2$]DMSO.

Table 1
Thermal degradation (80 °C) of a 1 mM solution of the MPcSs

MPcS	Time (h)	λ max Q band	$\Delta\lambda$ (nm)	Abs% (ε)
RuPcS	0	638	–	100 (29,400)
	24	633	5 bs	20–40
CoPcS	0	630; 657	–	100 (7400; 7800)
	24	630; 657	0; 0	85; 60
NiPcS	0	623	–	100 (48,000)
	24	623	0	100
FePcS	0	632	–	100 (33,200)
	24	635	3 rs	20–40
CuPcS	0	612; 692	–	100 (17,600; 9900)
	24	612; 692	0; 0	100
RuPcS1	0	640	–	100 (–)[a]
	24	640	0	200
[RuPcS1(DMSO)$_2$]DMSO	0	582; 642	–	100 (1800; 3400)[b]
	24	582; 640	0; 2 bs	Both 20–25

[a] For mono-RuPcS, the calculation of ε was difficult because of the poor, and not reproducible, solubility of the substrate; this is also the reason for the apparent increment in the Q-band intensity, i.e., it is probably due to the better solubilization of the not-completely homogeneous initial solution.
[b] The ε of [RuPcS1(DMSO)$_2$]DMSO was calculated taking into consideration the following formula weight: $C_{38}H_{33}N_8S_4O_6NaRu$.

The irradiations were performed in the presence or absence of oxygen (the air was removed by 6–8 h bubbling at room temperature with an inert gas, i.e., dinitrogen). Photochemical degradation of the phthalocyanines in solution is commonly considered to be a complex reaction due to the formation of several intermediates. These intermediates are mainly radicals, which can react with each other or with the unreacted substrate. With the phthalocyanines, it is widely accepted that the excited state is localized within the macrocyclic region

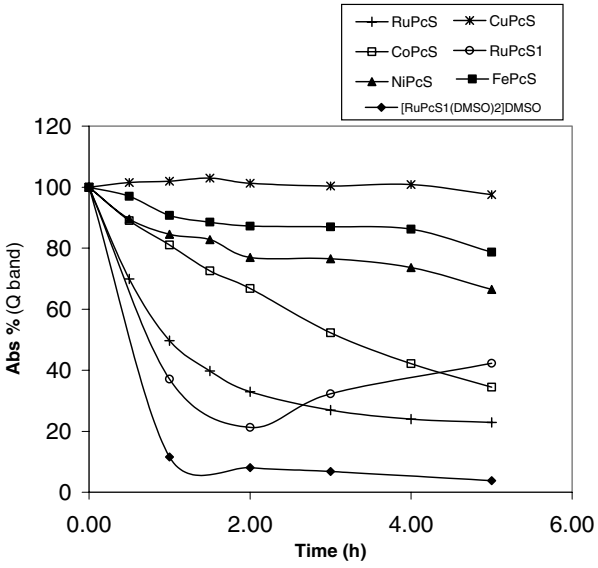

Fig. 2. Irradiation at 254 nm of a 1 mM solution of the MPcSs.

(rather than with the metal ion), which is why they are particularly sensitive to chemical degradation [14]. We carried out some preliminary irradiation tests to evaluate the efficiency of the photodegradation at 254 nm (near to the B band) and in the visible region (near to the Q band). As expected, degradation occurred mainly upon irradiation at 254 nm: usually the S2 state of the phthalocyanines (populated via irradiation in the near UV) is more active than the S1 state (populated by irradiation on the Q band), even if it has a shorter life time [15]. The presence of oxygen also has an important role. In the de-aerated solutions (as described above), the Q band was only slightly quenched (0–7% by visible light; 0–15% by UV; for an irradiation time of 24 h). In contrast, the oxygenated water solutions of the MPcSs underwent bleaching upon irradiation (always within 24–48 h), with almost complete degradation to phthalimide, ammonia and the hydrated metal (with the only exception being CuPcS). The distribution of the products observed in the presence of both UV and visible light were practically the same, but photolysis by UV light was faster by at least one order of magnitude, and therefore all of the later experiments were conducted at 254 nm.

Among the MPcSs considered in the present investigation, only CuPcS was totally resistant to photodegradation, even under oxygen. NiPcS and FePcS were degraded only in part, showing up to 25% with 5 h irradiation, while all of the remaining complexes were degraded more efficiently, in the following order: CoPcS < RuPcS < RuPcS1 < $[RuPcS1(DMSO)_2]DMSO$

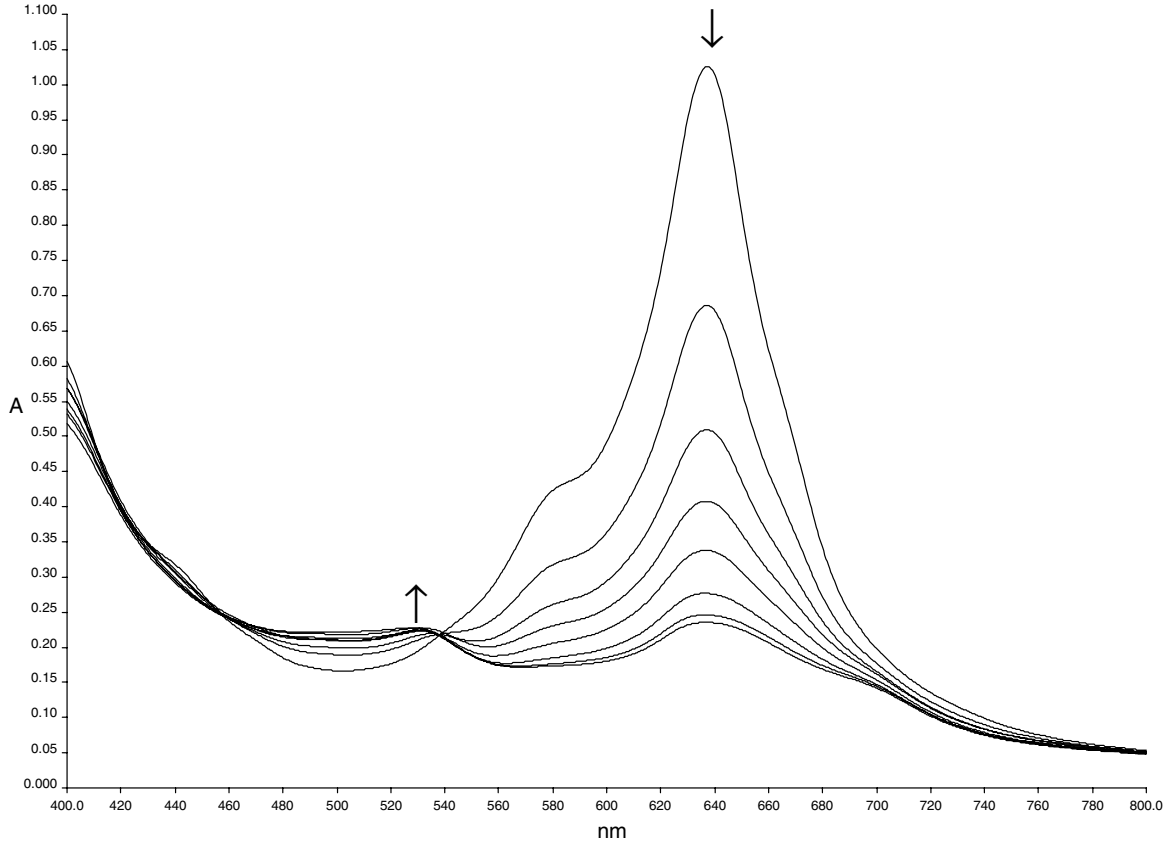

Fig. 3. Photolysis of 1 mM water solutions of RuPcS with 0–5 h of irradiation time.

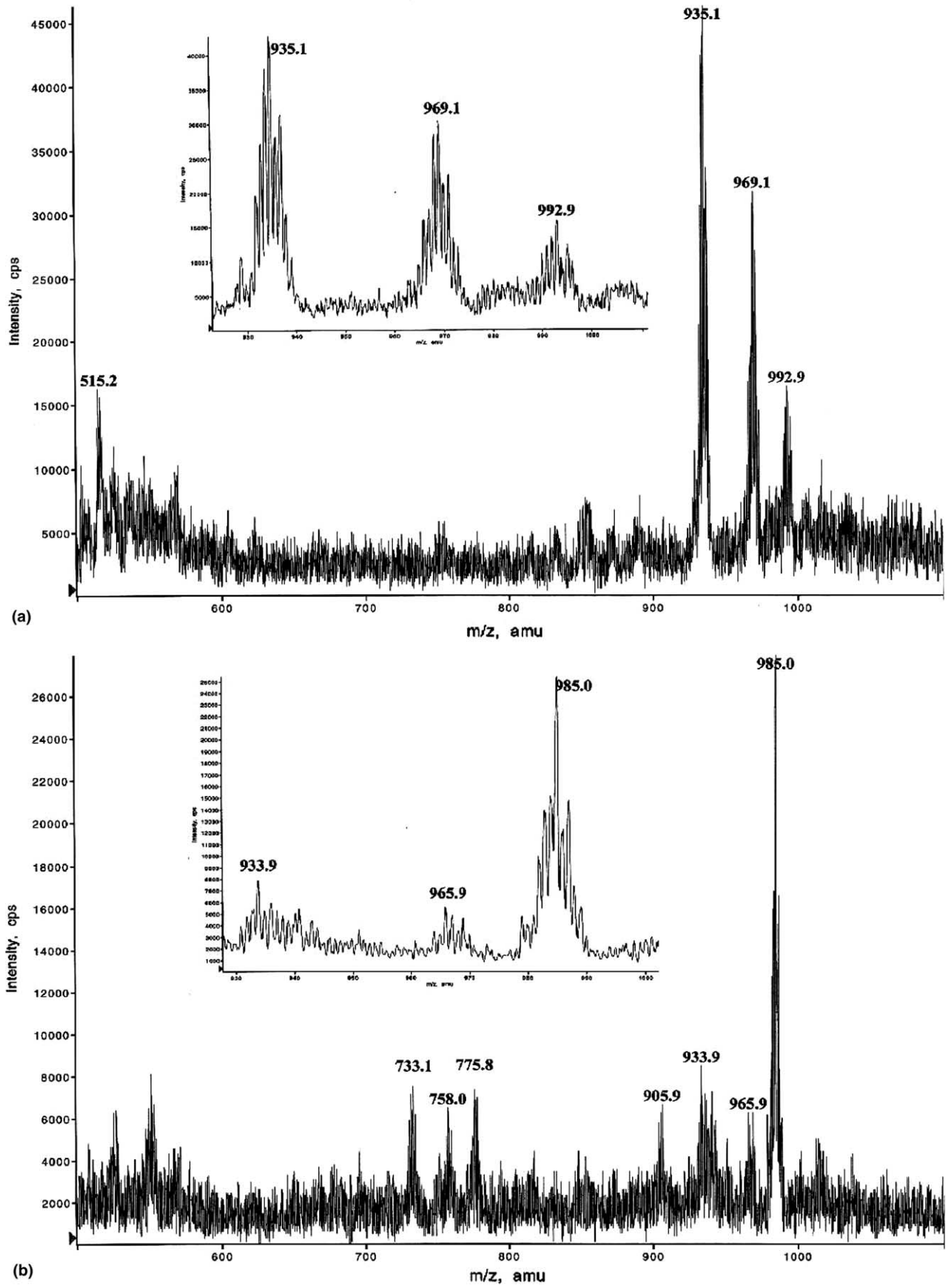

Fig. 4. LC/ESI-MS of non-irradiated (a) and irradiated (1 h) (b) 1 mM solutions of RuPcS.

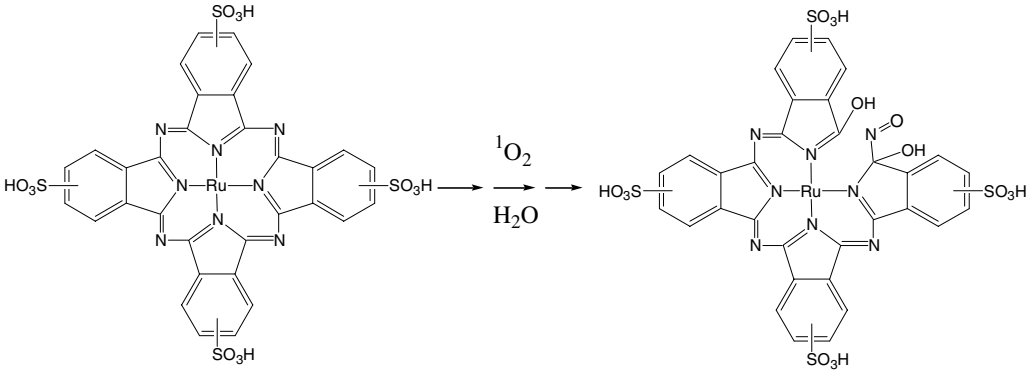

Chart 1. Proposed formula of the compound formed initially during the 254 nm irradiation of a water solution of RuPcS.

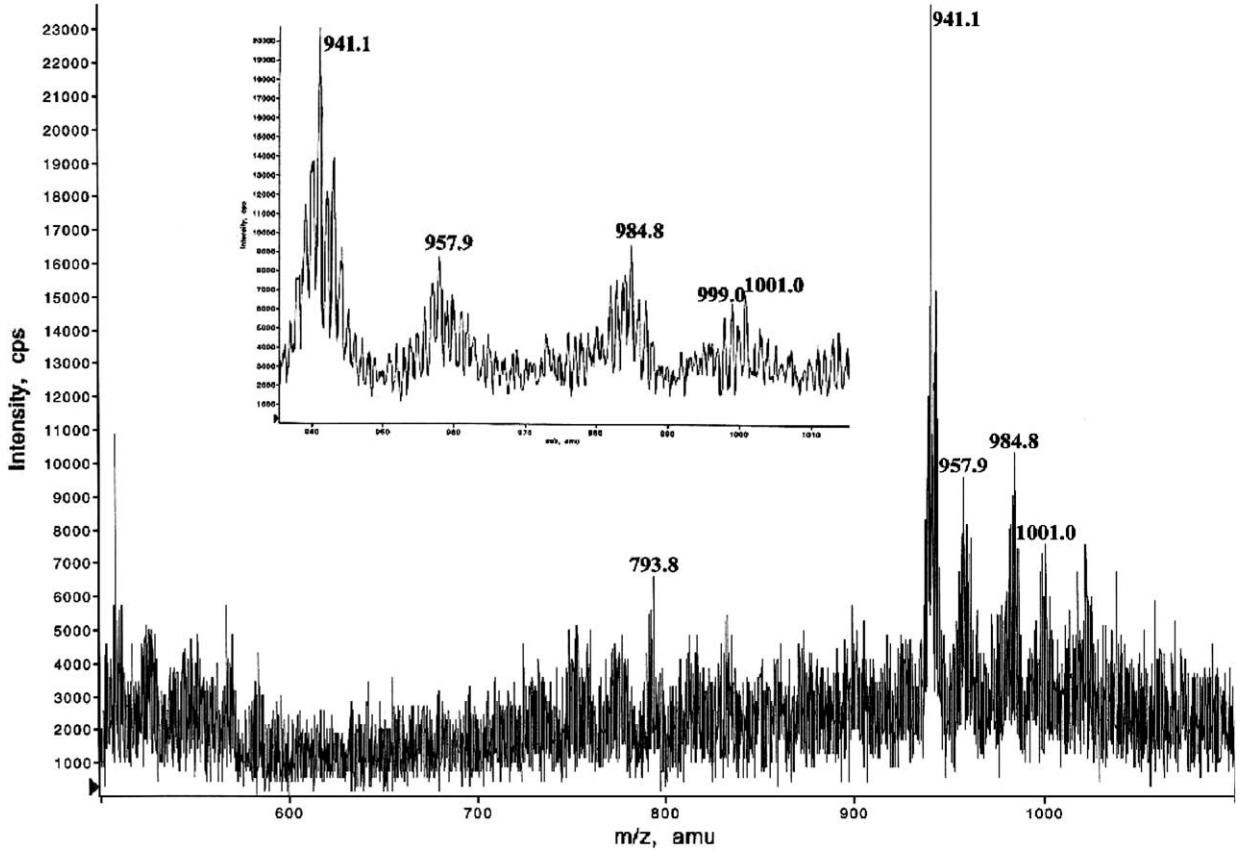

Fig. 5. LC/ESI-MS of the irradiated (15 h) 1 mM solution of RuPcS.

(Fig. 2). Interestingly, the substrates that were most sensitive to the degradation were all Ru derivatives. The anomalous behaviour of RuPcS1 (increased absorbance at later times) was not easy to explain. We believe that the apparent increment of the Q-band intensity after 2 h of irradiation was probably due to the better solubilization in the initial solution, which was not completely homogeneous.

A careful analysis of the visible spectra changes of the photolyzed MPcS solutions showed a general tendency to degrade into small fragments, which did not absorb in the visible region. From the ^{1}H NMR spectra, it is possible to detect sulfophthalimide and ammonia (as the ammonium cation, i.e., after acidification of the samples) as the main reaction products; no other products appeared to accumulated during the photoreaction. Only RuPcS showed the appearance of an absorption band in the visible region (aside from the initial substrates), which might indicate the presence of a stable intermediate. The Q band was completely replaced by a new band that was centred at 532 nm (Fig. 3), although a clear isosbestic point was not obtained,

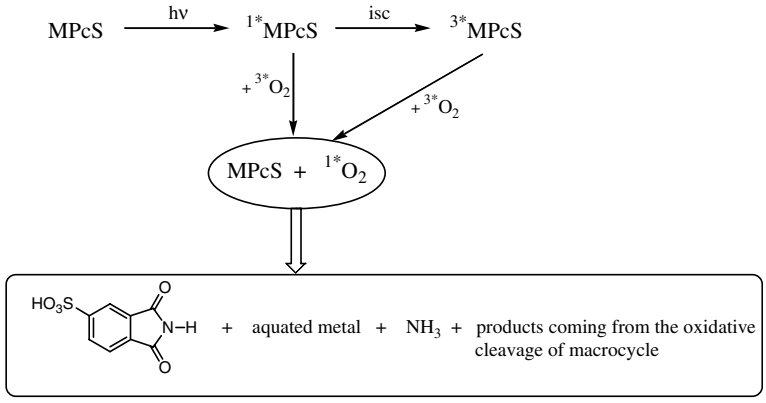

Chart 2. Proposed reaction scheme occurring during the 254-nm irradiation of the MPcSs.

probably because the intermediate also absorbs at the irradiation frequency, and is consequently liable to photodegradation. To better understand the nature of this intermediate, we carried out an LC/ESI-mass investigation on the photolyzed solutions (Fig. 4). The MS spectra clearly indicated the appearance of a new species, with the main peaks at *m*/*z* 985 (100%), 1019 (25%) and 1041 (16%), all of which clearly showed the expected isotopic pattern of the Ru derivatives. (Fig. 4B shows the spectrum at medium voltage, which does not show the high molecular weight peaks at *m*/*z* 1019 and 1041; see later.) The use of different voltage conditions, which is diagnostic for the detection of species that are formed either upon a photochemical reaction or a rearrangement during the electrospray ionization process, strongly suggested that *m*/*z* 1019 and its monosodium cluster derivative (*m*/*z* 1041) were attributable to the same compound. Indeed, the *m*/*z* 1019 signal only appears at low voltage conditions and is absent at medium/high voltage conditions, whereas the reverse is true for the *m*/*z* 985 signal. We would tentatively propose that the species formed under photolytic conditions is a species deriving from the formal addition of H_2O_2; this would in fact result from a singlet oxygen attack to the macrocycle, causing ring cleavage and forming a typical product of oxidative cleavage at the *meso* position [16], the species that contained both the –NO moiety and two –OH groups at the extremity of the breaking point (Chart 1). To support the concept of the presence of the *meso*-nitrogen still bonded at the cleaved phthalocyanine ring, we looked for ammonia inside the water solution by ^{1}H NMR. Indeed, in the 1-h-irradiated solution, where we detected only the species with *m*/*z* 985 (replaced by 1019 under very low voltage conditions) as reaction product, we did not find ammonia, while we found a very small amount of ammonium inside the 2-h-irradiated solution, where low amounts of other species were also present (see also Section 4).

Together with the *m*/*z* 985 signal, a careful analysis of the MS spectrum obtained after 2 h of irradiation also shows a typical sequence of signals that are attributable to species lacking one sulfophthalimide moiety (*m*/*z* 778, 796, 814, 834; data not shown) with respect to the initial substrate. However, irradiation for a long time (15 h) did not increase these peaks, instead selectively forming a completely new peak at *m*/*z* 941, which did not change under different voltage conditions (Fig. 5).

4. Discussion and conclusions

The thermal experiments show a poor selectivity towards any stable intermediate. None of the complexes showed any new absorption bands in the visible spectrum, and the attempt by ESI-MS to detect any new products also failed. Also, the behaviour of the shift of the Q band does not give us any interesting tools towards an understanding of the mechanism of degradation. The only certain data are that the rate of degradation depends both on the metal and on the degree of molecular aggregation. Indeed Ru, with its tendency to form octahedral derivatives and the possibility of forming numerous redox states, was the most reactive metal derivative in terms of temperature. Co and Fe also showed appreciable reactivities, since they also have the tendency to form octahedral derivatives. The behaviour of CoPcS is of particular note. When the solution was heated up to 80 °C for 24 h, the two visible bands at 630 and 657 nm showed different behaviours: the band at 657 nm (attributed to the monomer) showed larger attenuation than the other (at 630 nm; attributed to the dimer or to some other oligomeric form). That the monomer is much more sensitive to the thermal effect than the dimer is commonly accepted, but the difference for CoPcS is that it has a relative slow rate of dissociation towards the initial ratio between the two forms. We can conclude here that the thermal treatment is not selective and that the first products of degradation are likely to be degraded faster than the intact phthalocyanine.

The photostability of the metal-phthalocyanines depends mainly on the type of radiation; while they appear to be stable enough in the presence of visible light, they are very sensitive to UV irradiation [5,14,15]. The UV photostability depends on the π-electron bonding system: in the present example, we have three substrates, i.e., RuPcS, RuPcS1 and [RuPcS1$(DMSO)_2$]DMSO, with the same metal (Ru), but with very different electron densities (the $–SO_3H$ moiety is a strong electron withdrawing group). We believe that the different photostabilities exhibited by the various Ru phthalocyanine derivatives do not depend only on the different electron densities, but also on the degree of stacking of the compounds, which also involves the π-electron bonding system. The maximal value (wavelength) of the Q band followed the order: RuPcS < RuPcS1 < [RuPcS1-$(DMSO)_2$]DMSO, and these data can be used as a scale for the degree of stacking seen in the literature [17]. In fact, as RuPcS is more "symmetric" than the monosulfonated derivatives, it can exhibit a higher degree of stacking, which may protect the macrocycle from chemical and photochemical degradation; moreover, the presence of apical DMSO in the monosulfonated derivative (in the solid state) will reduce the initial degree of stacking, improving solubility and, consequently, resulting in a faster degradation. Indeed, [RuPcS$(DMSO)_2$]DMSO is the most sensitive compound to the irradiation. The results obtained upon thermal treatment are clearly different, with no substantial differences between the behaviours of RuPcS and [RuPcS$(DMSO)_2$]DMSO; here, we need to note that at 80 °C the stacking will be much lower, thus making their stabilities comparable.

The photochemical treatment was more selective only for RuPcS; when it was irradiated at 254 nm, the predominant species is a new compound with a band centred at 532 nm. Before analyzing the MS data, it needs to be remembered that the phthalocyanines are commonly classified as photosensitizers, and they are able to generate singlet oxygen (Chart 2). The ESI-MS spectrum of the above-mentioned species shows a peak at *m*/*z* 985 (1019), which we have tentatively attributed to a product coming from an oxidative attack by the singlet oxygen at the *meso*-nitrogen (Charts 1 and 2). The fact that we found ammonia only when the macrocycle started to lose a phthalimide unit fully confirms our interpretation (only for the 2-h-irradiation solution). However, when the irradiation time was increased, the products with only three units of phthalimide did not appear as the main products; they were instead replaced by a new compound with *m*/*z* 941. We believe that the pathway leading to the degradation products which have lost one phthalimide moiety is different from the alternative one leading to the *m*/*z* 941 compound. In the presence of oxygen, the reaction pathway leads to the degradation products, but since our reactions were performed in closed vessels, when the oxygen inside the solutions was consumed, the reaction pathway changed in favour of the product with *m*/*z* 941. At present, we are not able to propose a valid structure for this compound with *m*/*z* 941, but we intend to do this in the future with the aid of further specifically designed studies.

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