Acid−Base and Spectroelectrochemical Properties of Doubly N-Confused Porphyrins

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The *cis*-doubly N-confused porphyrin, H_2N_2CP, containing two adjacent confused pyrrole rings has been investigated from the point of view of its acid−base and electrochemical behavior in dichloromethane. This novel porphyrin isomer can form two metal−carbon bonds in the central core, stabilizing metal ions in unusually high oxidation states. Furthermore, the two outside *N*-pyrrole atoms remain available for acid−base and specific solvent interactions. Protonation of the pyrrole N atoms proceeds according to two successive steps, while only a single deprotonation step has been observed in the presence of bases. Similarly, in the case of the silver and copper complexes the protonation and deprotonation of the outer pyrrole rings have been detected, confirming the structure of the metalated species as $M^{III}{-}HN_2CP$. The electrochemical reduction of the metal ions (III/II redox process) and oxidation of the macrocycle ring have been detected respectively at −0.9 and 1.4 V based on spectroelectrochemical measurements in conjunction with the acid/base equilibrium studies. Additional waves observed around −0.5 and 1.3 V have been assigned to redox processes involving water molecules associated with the doubly N-confused porphyrins.

Introduction

The preparation and properties of new porphyrin analogues have been recently focused on the literature.[1] In particular, the N-confused porphyrin (NCP) was the first reported "true porphyrin isomer" containing one inverted pyrrole ring.[2,3] The presence of an inner carbon and outward-pointing nitrogen atoms conferred unique properties to this ligand.[4−10] For example, it can act as a dianionic or trianionic macrocyclic ligand, generating neutral complexes with Ni^{2+} and Ag^{3+} ions.[4,7,8] The Ni^{2+} complex can be easily oxidized to the Ni^{3+} species, but the reduction of the $Ag^{III}NCP$ complex in CH_2Cl_2 did not lead to the Ag^{2+} complex. Instead, there is evidence of reduction of the macrocyclic ligand,[4] confirming the high capability of NCP to stabilize metal ions in unusually high oxidation states. Recently, the synthesis and structural characterization of "*cis*-doubly N-confused porphyrin (N_2CP)" and its Cu^{3+}, Ag^{3+}, and Pd^{2+} complexes have been reported.[11,12] This porphyrin isomer has two adjacent, inverted pyrrole rings (Figure 1), such that it coordinates metal ions through two nitrogens and two carbon atoms. Functional density calculations have suggested the possibility of the N_2CP ligand to stabilize metal ions in the 4+ oxidation state.[13] It is important to notice that the outside *N*-pyrrole atoms are available for acid−base and specific solvent interactions, reflecting in a direct, strong influence on the porphyrin properties. In order to improve our understanding on the chemistry of N-confused porphyrins, we carried out a detailed acid−base and spectroelectrochemical investigation of the free-base species, H_2N_2CP, and its copper and silver complexes, i.e., $[Cu^{III}HN_2CP]$ and $[Ag^{III}HN_2CP]$, respectively (Figure 1).

Experimental Section

2-Ethoxy-5,10,15,20-tetrakis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (H_2N_2CP) was previously obtained[11] by the reaction of N-confused 5-(pentafluorophenyl)dipyrromethane, pentafluorobenzaldehyde, and Bu_4NBr in 0.5% $EtOH{-}CHCl_3$, in the presence of BF_3-OEt_2 at room temperature, after oxidation with DDQ and purification by silica gel column chromatography. $[AgHN_2CP]$ and $[CuHN_2CP]$ were obtained by metalation of free-base H_2N_2CP with silver acetate and copper acetate, respectively. These reactions were carried out at room temperature for 8 h (Ag) or 1 h (Cu).

The UV−vis spectra were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer. The solutions of H_2N_2CP, $[AgHN_2CP]$, and $[CuHN_2CP]$ and their protonated and deprotonated derivatives were stable at room temperature. A cutoff filter below 280 nm was used to prevent the photolysis of dichloromethane (DCM) and consequent formation of HCl, which interfered in the measurements.

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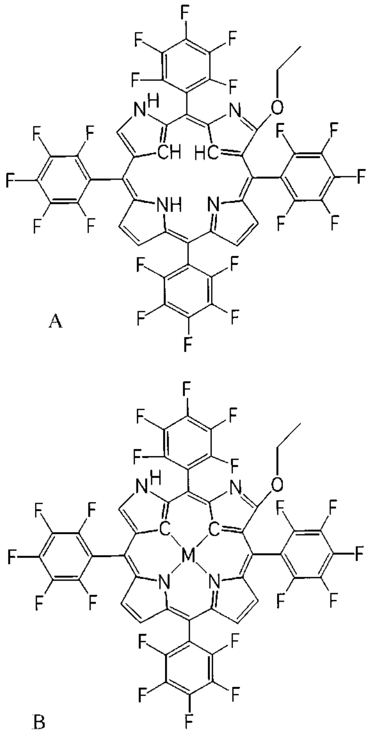

Figure 1. Structures of (A) H_2N_2CP and (B) $M^{III}HN_2CP$.

The electrochemistry was carried out in dichloromethane using a computer-driven PAR model 283 potentiostat/galvanostat and model 270/250 Research Electrochemistry Software version 4.30. A conventional three-electrode cell consisting of a platinum disk working electrode, Ag/Ag^+ (0.010 M) reference electrode in acetonitrile, and a coiled platinum wire auxiliary electrode was employed. Dichloromethane was distilled over CaH_2 immediately before use. $TBAPF_6$ Aldrich was used as electrolyte without further purification. All potentials were converted to the SHE scale by adding 0.503 V to the experimental data.

The spectroelectrochemical data were collected using a previously described homemade thin-layer cell[4,14,15] and a PAR model 173 potentiostat/galvanostat in parallel with a HP-8453A spectrophotometer.

Results and Discussion

The H_2N_2CP molecule is an isomer of perfluorinated *meso*-tetraphenylporphyrin compound, exhibiting two adjacent inverted pyrrole rings. In this case, a fully conjugated π structure is not possible, in contrast with porphyrins and analogous N-confused porphyrin species containing only one inverted pyrrole ring. Its electronic spectrum exhibits three major sets of bands in the 300−800 nm range, e.g., at 345, 424, and 670 nm, as one can see in Figure 2, keeping some similarity with the N, Soret (B), and Q bands in the porphyrin analogues.

The spectral data for the several species are shown in Table 1, for comparison purposes.

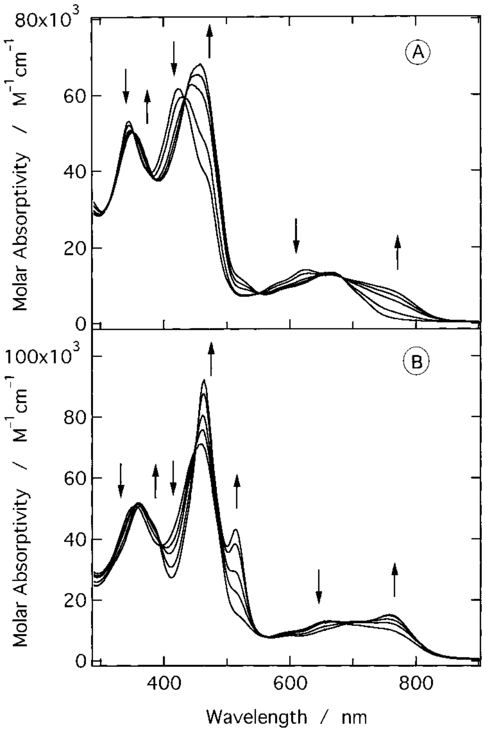

Figure 2. (A) Changes in the spectrum of free-base H_2N_2CP in DCM (2.1×10^{-5} M) after addition of successive aliquots of less than stoichiometric amount of trifluoroacetic acid. (B) Changes in the spectrum of the protonated species obtained after addition of more trifluoroacetic acid.

Table 1. Absorption Bands (nm) of the Neutral, Protonated, Deprotonated Free-Base and Metalated H_2N_2CP

H_2N_2CP	345, 424, 467, 580 (sh) 623, 670, 717 (sh)
$H_3N_2CP^+$	351, 455, 527 (sh), 594, 662, 757
$H_4N_2CP^{2+}$	361, 386 (sh), 464, 514, 599, 655, 698, 759
HN_2CP^-	343, 406, 454 (sh), 480, 510, 600, 660, 721
$AgHN_2CP$	366, 419 (sh) 440, 480, 517, 573, 620, 674
$AgH_2N_2CP^+$	367, 469, 520, 570, 614, 660, 764
AgN_2CP^-	367, 428, 474, 498, 560, 620, 678
$CuHN_2CP$	367, 417 (sh), 440, 480 (sh), 519 (w), 567, 612, 674
$CuH_2N_2CP^+$	368, 467, 520, 566, 612, 646, 765
CuN_2CP^-	355, 425, 471, 498, 552, 607, 687

The free-base H_2N_2CP species can be readily protonated, as observed by introducing small amounts of HCl or trifluoroacetic acid vapor into the DCM solution. However, since there are two pyrrolic nitrogen atoms available for protonation, a careful procedure is necessary in order to distinguish between the single and double protonation steps. To address this point, aliquots of trifluoroacetic acid (TFA, diluted in DCM), containing less than the stoichiometric amount of acid to monoprotonate the doubly N-confused porphyrin, were added to the H_2N_2CP solution, and the electronic spectra recorded in the visible−UV region. As the amount of TFA increased, the characteristic absorption bands at 345 and 424 nm for free-base species were shifted to 351 and 454 nm, while the composed Q type band at 670 nm was split into two main bands at 662 and 757 nm (Figure 2A). Simultaneous isosbestic points were observed at 353, 433, 553, and 683 nm, confirming the involvement of only two species in equilibrium. Addition of more TFA aliquots enhanced the absorption bands at 464 and 757 nm and led to the rise of a new band at 514 nm (Figure 2B). Simultaneous isosbestic points at 396, 449, and 690 nm indicated the presence of a second acid/base equilibrium process. The spectra obtained after addition of an excess of TFA or concentrated sulfuric acid were almost identical to that shown in Figure 2B, confirming that no further protonation is possible. Consequently, one can infer that the protonation of free-base H_2N_2CP occurs in two successive steps involving the two available pyrrole N atoms. This is analogous to the acid−base behavior of the NCP molecule in which two protonation steps were also observed. The basicity of N_2CP seems to be much higher, however, because in order to protonate NCP an excess of TFA was required.[2] In contrast with the Lash et al.[16] results, the absorption spectra of the samples obtained by using HCl or TFA were identical, showing no modulation effect induced by the counterion.

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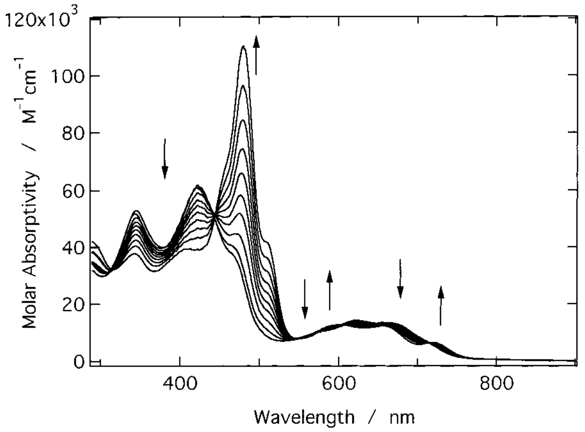

Figure 3. Changes in the spectrum of H_2N_2CP (2.1×10^{-5} M in DCM) as small aliquots of triethylamine were added into the solution.

The protonation sites were investigated by recording ^{1}H NMR spectra in the presence of 1 equiv and an excess (20 equiv) of TFA. The two broad signals at 15.28 and 13.37 ppm were assigned to the outer NH protons, strongly suggesting that the first protonation occurs at the peripheral pyrrole N atom. The addition of an excess of acid sharpened and shifted those peaks to 12.70 and 12.06 ppm. The possible association of the conjugate base with the protonated doubly N-confused porphyrin species was investigated, using $CHCl_2CO_2H$ (10 equiv) as probe. In this case, the peak of the dichloroacetate was found at 5.73 ppm, while the inner NH and CH peaks were found at 4.62 (NH), 2.39, and 1.48 ppm, respectively. The NMR signal of the counteranion of the protonated *meso*-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin sits above the porphyrin ring and was shifted around 3 ppm to higher field,[16] while the signal of our probe ion remained almost unchanged. This is evidence that the dichloroacetate (or TFA) should be around the periphery of N_2CP ring rather than above.

It is interesting to note that H_2N_2CP can undergo deprotonation reactions by addition of mild bases such as triethylamine, or strong bases like tetrabutylammonium hydroxide and sodium ethoxide. But, whatever the base used in the reaction, the final spectrum was exactly the same (Figure 3). The deprotonation reaction leads to the decay of the N band at 345 nm and enhancement of the Soret type band at 480 nm, and also at 510 nm (shoulder). The Q type bands were observed at 600, 660, and 721 nm. When the bases were added in a stepwise manner, the spectral changes were consistent with a single equilibrium, in contrast with the protonation process which occurred in two successive steps generating the $H_3N_2CP^+$ and $H_4N_2CP^{2+}$ species. In order to determine the amount of H^+ ions involved, the ^{1}H NMR spectrum of a H_2N_2CP solution was recorded after addition of an excess of Proton Sponge, revealing the band assigned to the inner N−H proton. Therefore, the deprotonation reaction involved only the removal of the outer N−H group. The acidity of the inner N−H bond should be very low, presumably lower than that of methanol, since even sodium methoxide was unable to react with it.

The silver and copper complexes of H_2N_2CP also are prone to react with acids and bases, generating the protonated and deprotonated species, as can be seen in Figure 4. The protonation of the inner carbon atoms was ruled out on the basis of the ^{1}H NMR, because only a broad peak at 15 ppm, assigned to the outer N−H protons, was found in the spectrum of doubly N-confused silver porphyrin complex, even in the presence of a 10 times excess of TFA.

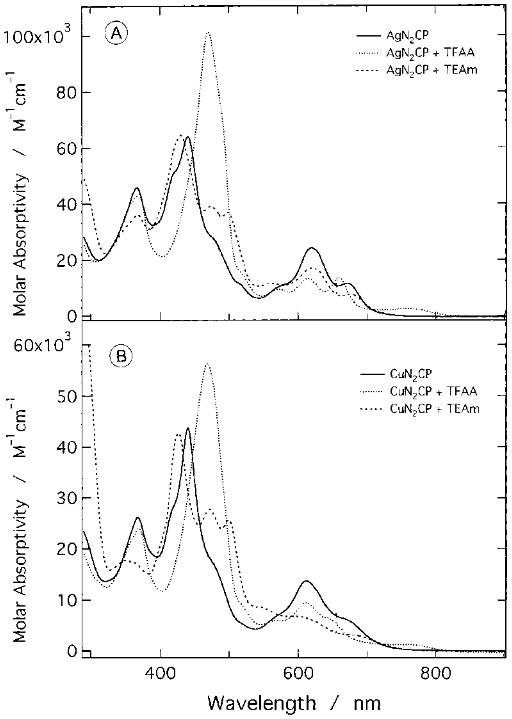

Figure 4. Spectra in DCM of the starting M−HN_2CP (solid line), the protonated M−$H_2N_2CP^+$ (dotted line), and the deprotonated M−N_2CP^- (dashed line) species obtained after the addition of TFA and triethylamine, respectively, to (A) $AgHN_2CP$ and (B) $CuHN_2CP$.

The [$AgHN_2CP$] solution in DCM (Figure 4A) exhibits major absorption bands at 366, 440, and 620 nm. Addition of TFA shifted the Soret type band to 469 nm, with significant changes in all other absorption bands. The spectrum of the deprotonated species generated by addition of triethylamine exhibited its characteristic bands at 367, 428, 560, 620, and 678 nm, in addition to the enhancement of the absorption shoulder at 500 nm (Figure 4A). The [$CuHN_2CP$] derivative exhibited a very similar spectral behavior (Figure 4B), displaying the characteristic absorption bands at 367, 440, and 612, while the protonated species absorption bands were found at 368, 467, and 612 nm. The absorption bands of the deprotonated species were found at 355, 425, and 607 nm, in addition to the enhancement of the shoulders at 471 and 498 nm.

As shown above, the acid−base and ^{1}H NMR studies confirmed the presence of one outer N atom in M−HN_2CP and two N atoms available for protonation in the free-base species, consistent with the structure shown in Figure 1.

Cyclic Voltammetry and Spectroelectrochemistry. (a) H_2N_2CP. The cyclic voltammograms (Figure 5) of H_2N_2CP, [$AgHN_2CP$], and [$CuHN_2CP$] exhibited four sets of waves around 1.5, 1.3, −0.5, and −1.0 V, as denoted by IV, I, II, and III, respectively. The assignment was carried out based on the cyclic voltammetric behavior after addition of excess of TFA or triethylamine, and on the spectroelectrochemistry results detailed below.

The voltammogram of H_2N_2CP is shown in Figure 5A. When trifluoroacetic acid was added to the solution, wave I shifted anodically from 1.24 to about 1.4 V generating a broad oxidation wave with maximum at 1.46 V. Concomitantly, wave II was intensified and shifted from −0.5 to 0.0 V, while wave III was shifted from −1.04 to −0.20 V and a new wave appeared at −1.17 V. In contrast, the addition of triethylamine did not

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[16] Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973.

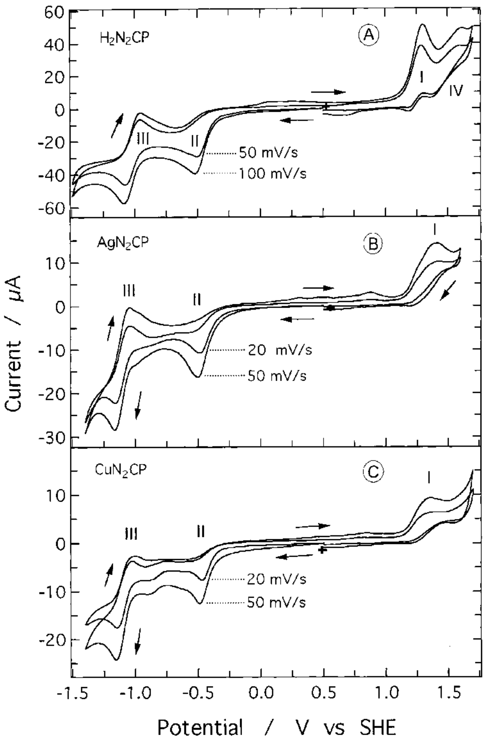

Figure 5. Cyclic voltammograms of 2.0 mM solutions of H_2N_2CP, $AgHN_2CP$, and $CuHN_2CP$ in dichloromethane with $TBAPF_6$ as electrolyte.

change the voltammetric behavior in the 0.0 to −1.3 V range. Nevertheless, waves I and IV were shifted from 1.24 and 1.45 V to 0.79 and 1.24 V, respectively.

In view of the similarity of the voltammetric behavior in the absence (shown in Figure 5A) and presence of triethylamine, the cathodic wave II was assigned to the reduction of small amounts of water present in solution, generating OH^- ions. Consequently, wave III was assigned to the first ring reduction of the HN_2CP^- species. The composite wave I of H_2N_2CP (Figure 5A) was assigned to the first ring oxidation (∼1.24 V) of the neutral H_2N_2CP species coupled with water oxidation, while wave IV (1.45 V) was assigned to the second monoelectronic ring oxidation process. The oxidation reactions of the deprotonated species were found in less positive potentials, at 0.79 and 1.24 V, respectively. Upon biprotonation, the first oxidation process (wave I coupled with water oxidation) shifted to more positive potentials, generating a broad irreversible wave with maximum at 1.46 V. As expected, the addition of TFA shifted wave II to ∼0.0 V and the first reduction of $H_4N_2CP^{2+}$ species was found at −0.20 V. The new reversible wave observed at −1.17 V was attributed to the second reduction of $H_4N_2CP^{2+}$ species.

Unfortunately, the complete removal of water could not be achieved. However, the addition of water to the solution led to the intensification of waves I and II, while waves III and IV became less reversible because of the enhancement of the corresponding coupled chemical reactions. This was particularly effective for the water reduction reaction by the reduced metalated species, reinforcing our assignment.

The spectroelectrochemistry of H_2N_2CP, in DCM solution containing 0.1 M $TBAPF_6$, is shown in Figure 6. When the potential was stepped from 0.5 to 1.20 V (Figure 6A), the absorption bands shifted to 351, 459 (sh), and 482 nm, while the absorbance at 640 nm decreased slightly in parallel with the rise of a band in 750 nm. These spectral changes are very similar to those observed for the first protonation of free-base to $H_3N_2CP^+$ species (Figure 2A). By applying 1.44 V, the rise of a band at 512 nm, accompanied by several other incipient changes, very similar to those observed for the protonation of $H_3N_2CP^+$ to $H_4N_2CP^{2+}$ species, was observed. Therefore, at 1.3−1.44 V (wave I) the electrochemical process should be generating H^+ ions, in order to account for the observed spectroelectrochemical changes. Since no wave was observed in the cyclic voltammograms of the pure electrolyte solution, we suggest that the H_2N_2CP species has water molecules associated with it, probably via hydrogen bonding with the nitrogen atoms of the inverted pyrrole rings. Oxidation of water is expected at 1.3 V and above, generating O_2 and H^+, responsible for the successive protonation reactions observed in the spectroelectrochemistry.

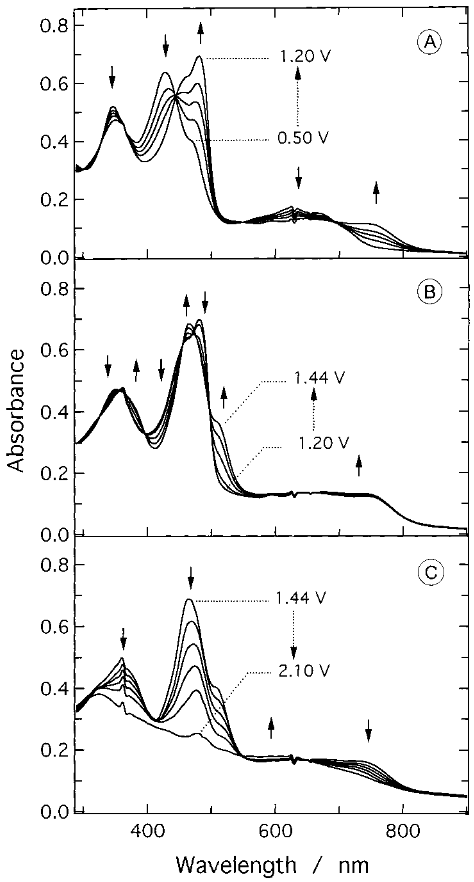

Figure 6. Spectroelectrochemistry of a 1.0 × 10^{-5} M H_2N_2CP solution in acetonitrile, $TBAPF_6$ 0.10 M. In all experiments the potential was stepped and the spectral changes registered as a function of the time: (A) 0.50−1.20 V; (B) 1.20−1.44 V; and (C) 1.44−2.10 V.

According to the spectroelectrochemical measurements, the oxidation of H_2N_2CP, or, more exactly, its diprotonated form, occurs only at more positive potentials. When the potential was stepped from 1.44 to 2.10 V (Figure 6C), the bands at 365, 466, 510, and 740 nm faded, giving rise to two broad bands around 323 and 610 nm.

After the oxidation step, the solution was renewed in order to investigate the spectroelectrochemical behavior at the cathodic region. When the potential was stepped from 0.00 to −0.70 V (Figure 7), the absorbance changes were identical to that for the formation of the HN_2CP^- species (Figure 3). Consequently, the redox process corresponding to wave II can be assigned to the reduction of water molecules generating H_2 and OH^- ions, responsible for the removal of protons from the doubly N-confused porphyrin ring.

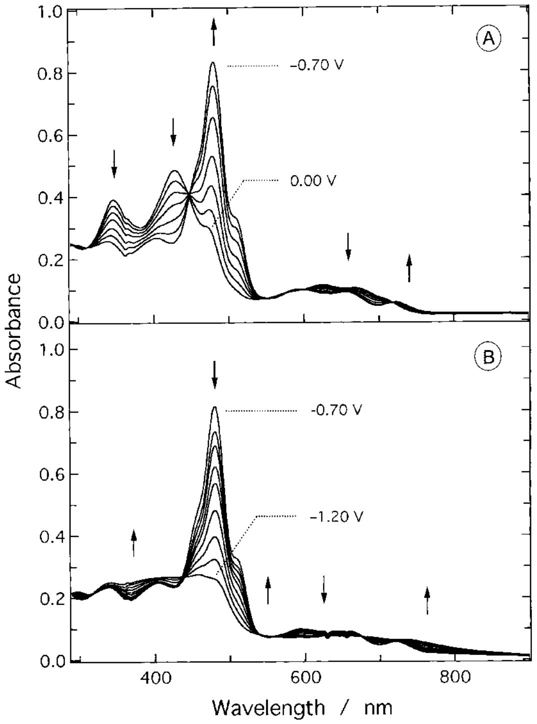

Figure 7. Spectroelectrochemistry of a 8.0 × 10^{-6} M H_2N_2CP solution in acetonitrile, $TBAPF_6$ 0.10 M. In all experiments the potential was stepped and the spectral changes registered as a function of the time: (A) 0.00 to −0.70 V and (B) −0.70 to −1.20 V.

Finally, when the potential was stepped from −0.70 to −1.20 V, the strong band at 480 nm and the weaker bands below and above 500 nm merged, giving rise to very broad spectral features (Figure 7B). These changes are consistent with the reduction of the HN_2CP^- species, generating a π radical anion. No further reduction processes could be observed at more negative potentials due to the exceedingly high currents involved.

The electrochemical behavior described above for H_2N_2CP is quite different from that observed for NCP.[4] In this case three reversible oxidation processes after an irreversible oxidation reaction and an irreversible reduction wave were observed in the same experimental conditions. Interestingly, no one of those electrochemical processes could be related to reactions involving water molecules as for doubly N-confused porphyrin.

(b) $AgHN_2CP$ and $CuHN_2CP$. The voltammetric profiles of $AgHN_2CP$ and $CuHN_2CP$ were similar, exhibiting waves II and III at −0.50 and −1.08 V, respectively. Interestingly, the effect of the coordination of Ag^{3+} and Cu^{3+} ions on the redox potentials seems to be rather small, in contrast with the typical behavior of metalloporphyrins,[17] in which case a significant shift of the redox processes is usually associated with the metalation of the porphyrin ring. Wave III is less reversible than in the H_2N_2CP, suggesting the occurrence of a chemical reaction coupled with the electrochemical process. In fact, the addition of small amounts of water made this wave completely irreversible, exhibiting a cathodic wave whose intensity increased as a function of the water content.

In the positive potential side, a broad wave I with features that suggested the occurrence of an electrochemical process with coupled chemical reaction was observed in the CV's of the silver and copper complexes. The first ring reduction wave was observed at −1.09 V besides an additional wave around −0.9 V, assigned to $M^{III/II}N_2CP$ couple. The addition of TFA or triethylamine shifted the redox waves in a way similar to that observed for the free base. The ring reduction of the protonated $[CuH_2N_2CP]^+$ was shifted to −0.5 V, and the $Cu^{III/II}N_2CP$ potential remained almost unchanged at −0.9 V, but wave III remained unchanged at 1.3 V. The addition of triethylamine did not change the voltammogram in the negative region, but the oxidation potential was lowered to 1.4 V. A similar behavior was observed for the silver such that the ring oxidation of the $[AgN_2CP]^-$ species was found at 1.0 V, while the ring reduction of $[AgH_2N_2CP]^+$ species was found at −0.6 V. Unfortunately the corresponding silver ion reduction could not be determined because of the appearance of a strong catalytic cathodic current next to the estimated reduction potential.

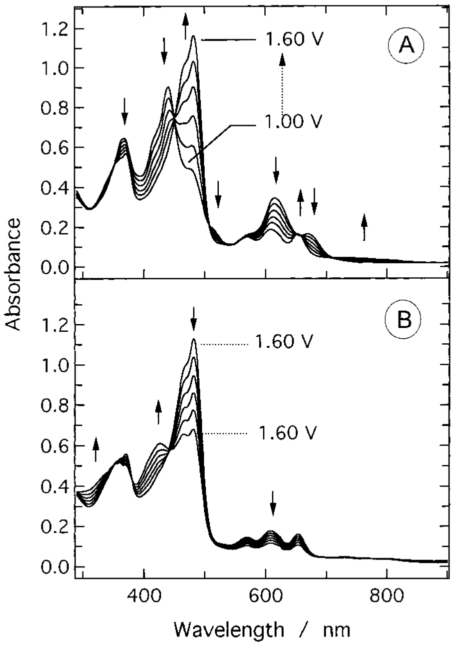

Figure 8. Spectroelectrochemistry of a 1.5 × 10^{-5} M solution of $AgHN_2CP$ in DCM, $[TBAPF_6]$ = 0.10 M, 25 °C: (A) potential stepped from 1.00 to 1.60 V; (B) further spectral changes as a function of the time at 1.60 V.

The spectroelectrochemical behavior of the silver complexes was very similar to that observed for the free-base species. After stepping the potential from 1.00 to 1.60 V, the spectral changes (Figure 8A) were very similar to those observed for the protonation reaction (Figure 4). This result suggests that the oxidation of adventitious water molecules generates O_2 and H^+ ions and protonates the silver and copper complexes, shifting their potential to the more positive side. In addition, the oxidized species acts as catalyst for that coupled oxidation reaction, precluding the observation of the first monoelectronic ring oxidation in its normal potential. After that, a decrease in the absorbance at 470 nm and in the bands around 600 nm, concomitantly with the increase in the absorbance at 310 and 425 nm, was observed (Figure 8B). These changes were assigned to the one electron ligand oxidation of protonated $[AgH_2N_2CP]^+$ species.

The reduction of the sample by stepping the potential from 0.00 to −0.70 V led to spectral changes (Figure 9A) very similar to those observed in the deprotonation reaction of $AgHN_2CP$, indicating that the electrochemical process at −0.50 V (wave II) is associated with the reduction of water. Further reduction at −1.00 V led to minor changes (Figure 9B) in the spectrum, a quite different spectroelectrochemical behavior when compared with the free base in the same potential range. We believe that the increase in the absorption at 318 nm and the decrease

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[17] Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435.

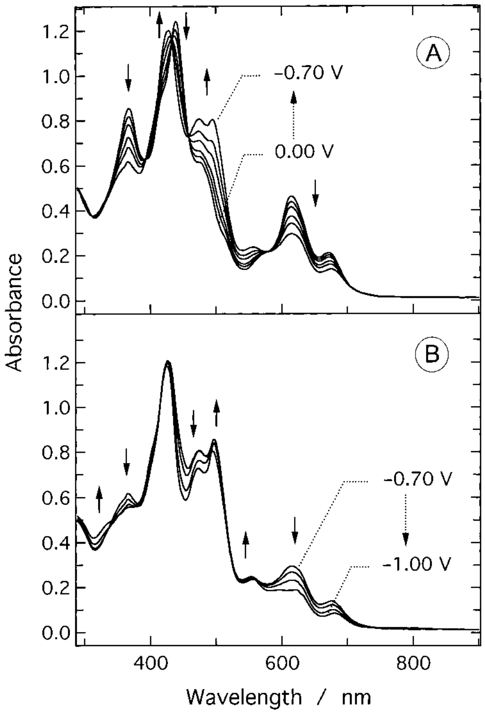

Figure 9. Spectroelectrochemistry of a 2.0×10^{-5} M solution of $AgHN_2CP$ in DCM, $[TBAPF_6] = 0.10$ M, 25 °C: (A) potential stepped from 0.00 to −0.70 V; (B) further spectral changes as a function of the time at −1.00 V.

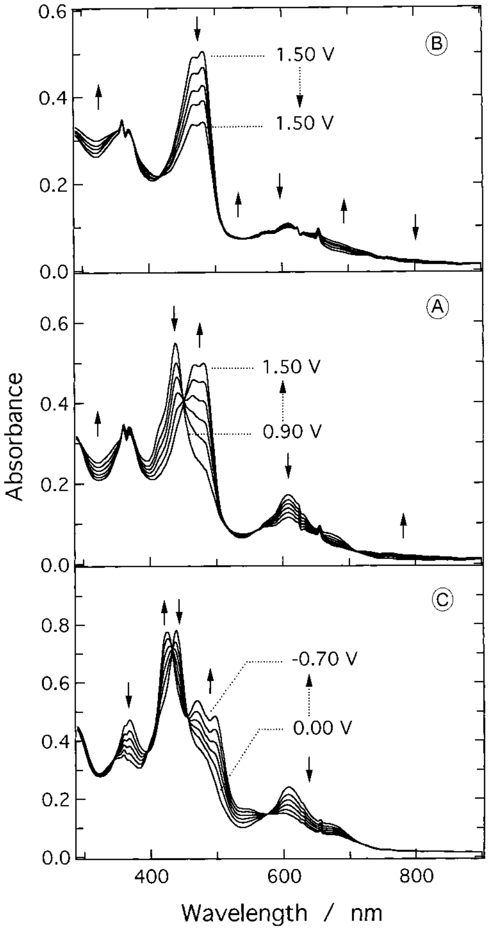

Figure 10. Spectroelectrochemistry of a 1.3×10^{-5} M solution of $CuHN_2CP$ in DCM, $[TBAPF_6] = 0.10$ M, 25 °C: (A) potential stepped from 0.90 to 1.50 V and changes associated with the protonation of $CuHN_2CP$; (B) oxidation of $CuH_2N_2CP^+$ species at 1.50 V; and (C) spectral changes after stepping the potential from 0.00 to −0.70 V. The changes were followed as a function of the time.

at 366, 474, 617, and 676 nm can be assigned to the $Ag^{III/II}N_2CP$ redox reaction, in contrast with $Ag^{III}NCP$.[4] This is followed by wave III, which probably is associated with the bielectronic reduction of the macrocycle ring, by comparison with free-base doubly N-confused porphyrin electrochemistry. The redox potential of about −0.95 V for the Ag(III/II) redox pair confirmed the high degree of stabilization of the metal ion in the unusual +3 oxidation state.

The copper complex exhibited a behavior similar to that of $AgHN_2CP$, as shown in Figure 10. When the potential was stepped from 0.90 to 1.50 V, the 439 nm band faded and an absorption band with maxima at 467 and 481 and a broad band at 785 appeared, concomitantly with the decrease in the absorbance at 608 and 674 nm (Figure 10A). This process is analogous to that observed in the protonation of $CuHN_2CP$ to $CuH_2N_2CP^+$ and was attributed to the oxidation of water. A second process was detected, in which the 467 and 481 nm bands decreased, leading to an increase of the absorbance at 325 and 690 nm, as shown in Figure 10B. This process was assigned to the oxidation of $CuH_2N_2CP^+$ species. The reduction of the sample by stepping the potential from 0.00 to −0.70 V led to spectral changes (Figure 10C) very similar to those for the deprotonation reaction of $CuHN_2CP$ to CuN_2CP^-, supporting the occurrence of water reduction. No further changes could be observed at more negative potentials because of current overflow.

Final Remarks

The H_2N_2CP molecule can be reversibly protonated in two successive steps at the pyrrole N atoms. From the results obtained with mild and strong bases and ^1H NMR spectroscopy results, the deprotonation process should involve only the removal of the sole outer H^+ ion. A similar behavior was observed for the silver and copper complexes. The spectroelectrochemistry in conjunction with the acid/base equilibrium studies showed that the first reduction and oxidation waves observed in the cyclic voltammograms (starting at 0.5 V) involves small amounts of water, probably associated with the outer N and N−H atoms of the inverted pyrrole rings. The exceptional influence of adventitious water on the electrochemical and spectroelectrochemical behavior was unexpected, considering the special care in using a dry solvent (DCM was distilled over CaH_2 immediately before use) and the use of a sealed electrochemical cell, in addition to our previous studies on the electrochemistry of NCP and AgNCP. Consequently, the interaction between the water molecules and doubly N-confused porphyrins seems to be quite strong influencing the redox reactions of water. The monoelectronic oxidation waves were found around 1.4 V and the reduction of the metal ions around −0.9 V. The more intense wave III in the CV's was assigned to the reduction of the doubly N-confused ligand.

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