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Electrochemical Reduction and Demetalation of Silver and Thallium Porphyrins

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The electrochemical reduction of the metalloporphyrins $Ag^{II}P$ and $(Tl^{III}P)^+$ (P = TPP, $TPP(CN)_4$, OEP) has been analyzed and compared with that of the corresponding free bases and of other metalloporphyrins. It is observed that the reduction of silver(II) and thallium(III) porphyrins is easier than expected from earlier data obtained with metalloporphyrins in which the porphyrin ligand is the electron-accepting site. Also, the first reduction step of silver(II) and thallium(III) porphyrins results in the demetalation of the generated species. The first reduction step of Ag(II) and Tl(III) porphyrins involves an electron transfer to the metal, before demetalation to the corresponding free base and to uncomplexed metal ions in the solution.

Introduction

The porphyrin ligand plays a preponderant role in electron transportation in biological systems, justifying the keen interest shown in its properties. During recent years, studies[1c-7] involving the electrochemistry of porphyrins, metalloporphyrins and similar complexes such as phthalocyanines have contributed to improving the understanding of their redox reactivity, by the analysis of metal-ligand interactions on the one hand and of mechanisms of the electron transfer in these compounds on the other. Theoretical[8] as well as X-ray spectroscopic[9] studies of porphyrins and metalloporphyrins have shown that the pyrrolic nitrogens of the porphyrinic ligand carry a high negative charge density. In addition, calculations[8] have shown that the metal-nitrogen bond is mainly electrostatic in most of the metalloporphyrins. Given the size of the porphyrin ligands central cavity,[10] the extreme polarizability of this ligand, and the essentially Coulombic character of its metal bonding, it may be expected that the porphyrin ligand preferentially stabilizes the higher oxidation states of the metallic ions, and, as a matter of fact, numerous metalloporphyrins have been prepared that illustrate this trend. Thus, for instance, the silver porphyrins may be described as stable complexes of Ag(II); silver(III) porphyrin has also been isolated.[11] In addition, it has been shown, by absorption spectroscopy in the visible region, that a porphyrin of Ag(I)[12] exists, but that porphyrin is highly unstable and could not be isolated. Up to now, only a few papers[6,13,14] have been devoted to the study of the electrochemical reactivity of silver porphyrins. These studies have clearly demonstrated that, in oxidation, the first electron-transfer step corresponds to the monoelectronic oxidation of the central Ag(II) cation, the ligand being oxidized at a more anodic potential. In reduction, the only known electrochemical data concerning the first reduction step ascribed it to the reduction of the ligand without, however, having identified the reduction product.[14]

The present investigation of the electrochemical reduction of the silver porphyrins ($Ag^{II}TPP$, $Ag^{II}TPP(CN)_4$ which is the Ag^{II} metalloporphyrin substituted with four cyano groups on the β positions of pyrroles, $Ag^{II}OEP$) has been undertaken with the intention of obtaining new information on the electrochemical reactivity of these species and of comparing the mechanism of their reduction to that of corresponding free bases and of metalloporphyrins of other divalent metals. Analogous results will also be given on the reduction of the thallium porphyrins $Tl^{III}TPP(OCOCF_3)$ and $Tl^{III}OEP(OCOCF_3)$.

Experimental Section

The studied porphyrins, prepared according to known procedures, were $Ag^{II}TPP$,[12,15] $Ag^{II}OEP$,[14,15] $Ag^{II}TPP(CN)_4$,[7] $Tl^{III}TPP(OCOF_3)$, and $Tl^{III}OEP(OCOF_3)$.[16]

The electrochemical measurements have been carried out under argon at 25 °C on a dropping mercury electrode or on a disk electrode (Au; area 3.14 mm^2). For the rotating-disk electrode measurements, the rotation rate was 2000 rpm. All measurements have been performed with a classical three-electrode potentiostatic device (Solea-Tacussel), comprising a potentiostat (PRT 20-2 X), a voltage pilot unit (Servovit 2), a millivoltmeter with high-impedance input (S 6 B), and a potentiometric recorder (EPL 2). For cyclic voltammetric measurements, a signal generator (GSATP from Solea-Tacussel) was associated with the above units.

Coulometric measurements on the first reduction step were performed on a large mercury-pool electrode (area 6 cm^2). For the subsequent reduction steps, the number of electrons exchanged has been determined by comparing their respective reduction limiting current with that of the first reduction step.

Throughout the measurements, the reference electrode was a calomel electrode in a saturated aqueous solution of KCl (SCE), electrically connected with the studied solution by a junction bridge (0.1 M tetra-*n*-hexylammonium perchlorate (THAP) in the corresponding solvent). The supporting electrolyte (THAP) and the solvent *N,N*-dimethylformamide (DMF) were purified according to earlier reported methods.[17,18] Dichloromethane (CH_2Cl_2), pyridine, and benzonitrile (Merck and Aldrich puriss products) were used without further purification.

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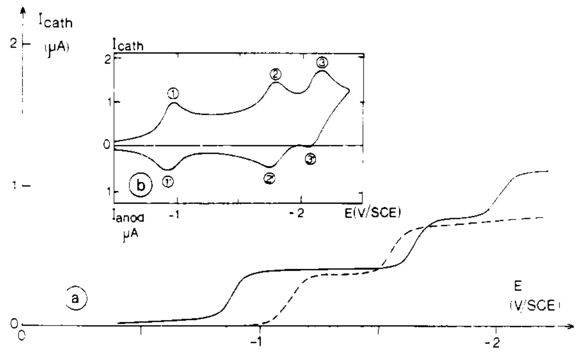

Figure 1. (a) Polarogram of $Ag^{II}TPP$ (—) and of H_2TPP (---) on DME in DMF–0.1 M THAP; $[Ag^{II}TPP] = 2.3 \times 10^{-4}$ M. (b) Cyclic voltammetry of $Ag^{II}TPP$ in DMF–0.1 M THAP (Hg electrode; scan rate 5 V s^{-1}).

Table I. Half-Wave Potentials (V/SCE) of $Ag^{II}TPP$ and H_2TPP in Various Solvents[a]

porphyrins	solvent	electrode	$E_{1/2}{}^{I}$	$E_{1/2}{}^{II}$	$E_{1/2}{}^{III}$	$\Delta E_{1/2}{}^{b}$
$Ag^{II}TPP$	DMF	Hg	−0.88	−1.65	−2.01	0.77
H_2TPP			−1.10	−1.51		0.41
$Ag^{II}TPP$	DMF	Au	−0.97	−1.67		0.70
H_2TPP			−1.15	−1.52		0.37
$Ag^{II}TPP$	pyridine	Au	−0.98	−1.70		0.72
H_2TPP			−1.21	−1.62		0.41
$Ag^{II}TPP$	CH_2Cl_2	Au	−1.10			
H_2TPP			−1.21			

[a] Supporting electrolyte THAP (0.1 M). [b] $\Delta E_{1/2} = E_{1/2}{}^{I} - E_{1/2}{}^{II}$.

The spectrophotometric measurements were carried out on a Beckman spectrophotometer (ACTA III) in cells with a 10-mm path length.

Results

I. Polarography and Stationary Voltammetry on a Rotating-Disk Electrode (RDE). (a) $Ag^{II}TPP$, $Ag^{II}TPP(CN)_4$, and $Ag^{II}OEP$. The electrochemical reduction of these metalloporphyrins was compared with that of the corresponding free bases in *N,N*-dimethylformamide, pyridine, dichloromethane, and benzonitrile as solvents.

Figure 1 shows a polarogram of $Ag^{II}TPP$ compared with that of H_2TPP from 0 to −2 V/SCE. Three well-defined polarographic reduction waves are observed, whose respective heights are in the ratio 1:1:1. The analysis of the limiting currents shows that each is diffusion controlled. Equivalent results are obtained on the solid electrode (Au) and in several other solvents: *N,N*-dimethylformamide, pyridine, dichloromethane, and benzonitrile. The values of the corresponding half-wave potentials, $E_{1/2}$, for $Ag^{II}TPP$ and H_2TPP are collected in Table I. Similar results are obtained with the complexes $Ag^{II}TPP(CN)_4$ and $Ag^{II}OEP$, whose half-wave potentials are given in Table II. Due to the poor solubility of $Ag^{II}OEP$, we reported only the first reduction step which gives a well-defined signal.

(b) $Tl^{III}TPP(OCOCF_3)$ and $Tl^{III}OEP(OCOCF_3)$. Two waves are observed whose respective heights are in the ratio 2:1. The corresponding potentials are given in Table II. Only the first, well-reproducible, wave was studied. For this first reduction step, the limiting current was diffusion controlled for the two metalloporphyrins.

II. Coulometry. Exhaustive electrolysis has been carried out on a mercury-pool electrode, in DMF–0.1 M THAP, and at an applied potential about 100 mV more cathodic than the half-wave potential for the first reduction step of these metalloporphyrins. In all cases this first reduction step has been found to be monoelectronic for the silver(II) porphyrins and dielectronic for the thallium(III) porphyrins.

Table II. Half-Wave Potentials (V/SCE) of Silver and Thallium Porphyrins Compared with Those of the Corresponding Free Bases[a]

porphyrins	$E_{1/2}{}^{I}$	$E_{1/2}{}^{II}$	$E_{1/2}{}^{III}$	$\Delta E_{1/2}{}^{c}$
H_2TPP	−1.10	−1.51		0.41
$Ag^{II}TPP$	−0.88	−1.65	−2.01	0.77
$(Tl^{III}TPP)^+$	−0.35	−1.00		0.65
$H_2TPP(CN)_4$	−0.12	−0.50	−2.01	0.38
$Ag^{II}TPP(CN)_4$	−0.08	−0.60	−0.95	0.52
H_2OEP[b]	−1.26	−1.65		0.39
$Ag^{II}OEP$[b]	−0.95			
$(Tl^{III}OEP)^+$	−0.47	−1.30		0.83

[a] These values were obtained on DME in DMF–0.1 M THAP. [b] Values obtained in benzonitrile due to the very poor solubility of these porphyrins in DMF. [c] $\Delta E_{1/2} = E_{1/2}{}^{I} - E_{1/2}{}^{II}$.

III. Cyclic Voltammetry. Silver porphyrins have been studied by this method on mercury or solid (Au) electrodes, in DMF–0.1 M THAP. The voltammograms show three successive reduction peaks, E_{pc}, and the three corresponding oxidation peaks, E_{pa}, for $Ag^{II}TPP$ and $Ag^{II}TPP(CN)_4$ (Figure 1), the anodic current of oxidation peak 3′ being smaller than those of anodic peaks 1′ and 2′. For the first two reduction steps 1 and 2, the potential difference, $\Delta E_p = E_{pc} - E_{pa}$, between corresponding cathodic and anodic peaks is constant and equal to about 57 mV at low sweep rates ($v < 0.1$ V s^{-1}), which indicates that these two monoelectronic reduction steps are reversible. On the contrary, the third reduction step exhibits a bad reversibility. $Ag^{II}OEP$ shows similar behavior for its first, identified, reduction step, with a difference ΔE_p of about 57 mV between the cathodic peak and the corresponding anodic peak.

In the first reduction step of these silver porphyrins, I_{pa}/I_{pc} and I_{pc} have been plotted vs. $v^{1/2}$ up to $v = 100$ V s^{-1}. The ratio I_{pa}/I_{pc} is smaller than unity at low scan rates ($v < 0.1$ V s^{-1}) and increases toward unity as the scan rate increases. Also, the ratio $I_{pc}/v^{1/2}$ decreases when the scan rate increases. These results indicate the occurrence of a chemical step following the electron transfer (EC mechanism).

With the thallium porphyrins, a single cathodic peak, E_{pc} (and no anodic signal), is observed for the first, well-defined, reduction step, which is indicative of an irreversible process.

Discussion

The only previous information[13,14] about the electrochemical reduction of silver and thallium porphyrins was limited to the indication of a first reduction wave of these complexes, which was attributed to the reduction of the porphyrin ligand. The results presented in the foregoing section provide new information on the reactivity of these complexes, and reconsideration of the mechanism of their electrochemical reduction becomes thereby necessary.

I. Silver Porphyrins. On the two studied series (TPP and OEP) the silver complexes exhibit a particular reactivity upon reduction.

(a) Redox Reactivity Compared to General Behavior of Divalent Metalloporphyrins. Numerous studies[3,14,17,18] of the porphyrins of divalent metals (Ca, Mg, Cd, Ni, Cu, Zn, Pd) have clearly demonstrated that their first reduction step occurs in the ligand to generate the monoanion radical

$$M^{II}P + e^- \rightleftarrows M^{II}P^{-\cdot}$$

For all these metalloporphyrins where the formally divalent metal is not electroreducible, the half-wave potential of the first reduction step is more cathodic than that of the corresponding free base. This observation has been interpreted[14,18] as being due to electrostatic action of the central metal ion on the conjugated (π) system of the ligand. Further, this potential shift has been determined as a function of the electronegativity of the metal.[14]

On the contrary in the reduction of $Ag^{II}TPP$ the first reduction step occurs at a more anodic potential (about 200 mV) than that of the corresponding free base H_2TPP, measured in the same experimental conditions. A similar anodic shift is also observed in the octaethylporphyrin series between $Ag^{II}OEP$ and H_2OEP. In the two cases—$Ag^{II}TPP$ and $Ag^{II}OEP$—the first reduction potential of the metalloporphyrin cannot be related to the electronegativity of the silver atom by using the diagram proposed by Kadish.[14] According to this diagram the expected redox potential for the first reduction step will be near those for the copper porphyrins CuTPP and CuOEP, which are known to be reduced at a more cathodic potential than is the corresponding free base.

More generally, earlier studies[4,5,14,18] of the redox reactivity of the porphyrins have established that there is a similar behavior of the free-base porphyrins and of the metalloporphyrins where only the ligand is electroreducible. In particular, the potential difference between the two first reduction waves of these porphyrins ($\Delta E_{1/2} = E_{1/2}{}^{I} - E_{1/2}{}^{II}$) is constant and equal to 0.42 ± 0.05 V. However, this potential difference is much larger ($\Delta E_{1/2} = 0.7 \pm 0.1$ V) for $Ag^{II}TPP$, and such behavior is reminiscent of that of known iron(II) and cobalt(II) porphyrins[18,19,20] which are reduced as

$$M^{II}P + e^- \rightleftarrows (M^{I}P)^-$$

Results obtained in various solvents are consistent with these observations (Table I).

(b) Effects of β Substitution. The study of the redox behavior of $Ag^{II}TPP(CN)_4$, which is the $Ag^{II}TPP$ complex substituted with four CN groups on the β positions of pyrroles, shows, as expected, that the CN groups facilitate the reduction. However, it has recently been shown[17,18] for the *meso*-tetraphenylporphyrin series that a shift of about 1 V is observed in the $E_{1/2}$ reduction potential in passing from the nonsubstituted to the tetracyano-substituted porphyrin, this shift being independent of the central cation when the electron transfer involves the porphyrin ligand. However, when the reduction occurs on the central cation, the shift is smaller and depends on the cation. The observed value $\Delta E_{1/2} = 0.8$ V between the first reduction wave of the nonsubstituted silver complex and that of the tetracyanated complex suggests that silver(II) is involved in the electronic transfer. This hypothesis is supported by an observed potential shift ($\Delta E_{1/2}$) of about 1 V in the second and third reduction waves, when passing from $Ag^{II}TPP$ to $Ag^{II}TPP(CN)_4$, thus indicating a reduction of the ligand in these second and third steps.

(c) Reduction Products. Exhaustive reduction of the studied silver metalloporphyrins indicates that the first reduction step is monoelectronic. The obtained final stable product is the corresponding free base, which has been identified by its very well-known absorption spectrum in the visible region as well as by polarographic measurements (half-wave potentials). In stationary voltammetry, when we carry out a cathodic followed by an anodic sweep on a solution of $Ag^{II}TPP$ after partial coulometry in pyridine on a solid (Au), small-surface electrode (slow electrolysis), we observe, in addition to the reduction waves of $Ag^{II}TPP$ and H_2TPP, a wave at −0.2 V which corresponds to the Ag^+/Ag^0 reduction and, also, the corresponding redissolution peak at +0.15 V. These reactions were identified by comparison with results obtained on silver(I) acetate solutions in the same experimental conditions. Therefore, it may be concluded that the primary reduction product of the silver(II) porphyrin undergoes a demetalation resulting in the Ag^+ cation and the porphyrin free base. Analogous demetalations are also observed with $Ag^{II}TPP(CN)_4$ and $Ag^{II}OEP$, from which the corresponding free bases $H_2TPP(CN)_4$ and H_2OEP are obtained.

(d) Interpretation. Gouterman et al.[13] recently presented a molecular orbital energy diagram of $Ag^{II}TPP$, which described well the results obtained in the oxidation of divalent silver porphyrins, where the metal becomes oxidized (Ag(II) → Ag(III)). This molecular orbital diagram shows that $Ag^{II}TPP$ possesses an unpaired electron in the last occupied orbital—b_{1g} ($d_{x^2-y^2}$), metal centered—which is lower in energy than the LUMO [e_g (π^*)] of the porphyrin ligand. Therefore, it is likely that the gain of one electron will be energetically more favorable by b_{1g} ($d_{x^2-y^2}$) level than by e_g (π^*) level. As a consequence, on the basis of the MO diagram of $Ag^{II}TPP$,[13] the electron given to the porphyrin during the first reduction step is expected to be transferred onto the half-filled metal-centered orbital (thus generating $(Ag^{I}P)^-$) rather than on the ligand-centered LUMO (what would produce the radical anion $Ag^{II}P^{-}\cdot$). Also, the demetalation observed after the first reduction step of the three silver porphyrins seems a logical consequence of the reduction Ag(II) → Ag(I), if the diameters of the metallic ions concerned are considered: 1.26 Å for Ag^+ vs. 0.89 Å for Ag^{2+}. The larger size of Ag^+ provides a good argument to explain its expulsion from the porphyrin core, Ag^{2+} being already one of the most voluminous cations to form stable complexes with the porphyrin ligand. This conclusion is also supported by the following established sequence of the increasing facility of demetalation for metalloporphyrins:[21] Pt(II) < Pd(II) < Ni(II) < Co(II) < Ag(II) < Cu(II) < Zn(II) < Mg(II) < Na^{I}_2 < Ag^{I}_2. Finally it should be remembered that the study[22] of the demetalation mechanism of $Ag^{II}T(p\text{-}C_6H_4SO_3)P$, in aqueous medium, has shown that the reaction takes place via intermediate monovalent silver complex, whose generation precedes the demetalation.

II. Thallium Porphyrins. As an analogue to the silver porphyrins, we also studied the electrochemical reduction of the thallium(III) porphyrins. These porphyrins are in effect at the limit of stability[16,23,24] (Tl^{3+}, 0.95 Å), and the Tl(III) ion is strongly out of the plane of the porphyrinic macrocycle. Further, preliminary indications suggest a reductive demetalation.[25] Published electrochemical results[14] mentioned the occurrence of a reduction wave (for $Tl^{III}OEP(OH)$) without further mechanistic details.

Our results indicate that the first observed reduction step is dielectronic and irreversible, which is quite unusual among the known $M^{III}P^+$ metalloporphyrins. The results show that, as with silver porphyrins, the electrochemical reduction is followed by a quantitative demetalation to the corresponding free base. One can say, therefore, that the first reduction step corresponds to the passage Tl(III) → Tl(I). The size of the Tl^+ ion (1.47 Å) is incompatible with complexation in the porphyrin ligand, and demetalation results.[26]

Conclusion

The results discussed above for silver(II) and thallium(III) porphyrins are inconsistent with a first reduction step on the porphyrin ligand. On the contrary, all results strongly support

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the theoretical predictions and the known chemical properties of the complexes, especially for silver porphyrins. The following reduction schemes account for these experimental observations.

$$Ag^{II}P + e^- \rightleftarrows \underset{\text{unstable}}{[Ag^{I}P]^-} \xrightarrow[(H^+)]{\text{demetalation}} Ag^+ + H_2P$$

$$[Tl^{III}P]^+ + 2e^- \rightarrow \underset{\text{unstable}}{[Tl^{I}P]^-} \xrightarrow[(H^+)]{\text{demetalation}} Tl^+ + H_2P$$

$$P = TPP,\ TPP(CN)_4,\ OEP$$

Even careful purification of the solvent and electrolytes used in the experiments leaves traces of water or other impurities able to generate protons.[27]

Registry No. $Ag^{II}TPP$, 14641-64-6; $Ag^{II}TPP(CN)_4$, 57948-05-7; $Ag^{II}OEP$, 36609-71-9; $Tl^{III}TPP(OCOCF_3)$, 76011-09-1; $Tl^{III}OEP(OCOCF_3)$, 51436-47-6; H_2TPP, 917-23-7; H_2OEP, 2683-82-1; $H_2TPP(CN)_4$, 52353-92-1.

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Mixed-Metal Complexes in Solution. 3. Thermodynamic Study of Heterobinuclear Copper(II)-L-Histidine and -Histamine Complexes in Aqueous Solution

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Potentiometric measurements have been used to characterize the equilibrium system containing copper(II), L-histidine (his) or histamine (hm), and M (M = Ni^{II}, Zn^{II}, or Cd^{II}). The results obtained provide evidence for heterobinuclear species containing Cu^{II}, M, and his or hm. The thermodynamic parameters of these complexes were determined by direct calorimetry. Some hypotheses for the structures of $[CuM(his)_2]^{2+}$ and $[CuM(hm)_2]^{4+}$ are discussed.

Introduction

In previous papers,[2,3] we reported the stability constants in aqueous solution of heteronuclear complexes formed by polyfunctional ligands such as L-histidinate or citrate with two different transition-metal ions. While quite a few qualitative studies can be found in the literature, as far as we know just some ten values of stability constants determined in aqueous solution, in addition to those reported by us, are available.[4-8] An attempt has been made to characterize the equilibrium systems and to determine the framework of a structure of some heterobinuclear species; unfortunately this EPR investigation,[9] carried out in nonaqueous solution, did not allow the authors to draw any definitive conclusions on the arrangement of the ligand around the metal ions. Considering that the thermodynamic parameters can give useful information on the bonding details, as shown for simple complexes[10-12] and for complexes containing two different ligands,[12-16] we thought it interesting to determine, by direct calorimetry, the heats of formation of the heteronuclear complexes and to calculate their $\Delta H°$ and $\Delta S°$ values.

Table I. Experimental Details of Potentiometric Measurements for Complex Formation at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)[a]

M	c_{Cu}	c_M	c_{H_2L}	no. of points	pH range
Zn^{2+}	3.5	7	3.5	35	3-7.3
	4	8	4	25	3-7.3
	3	6	3	24	3-7.3
	3	15	6	26	3-7.3
	4	12	8	28	3-7.3
	3	6	9	33	3-7.3
	5	6	7	41	7.3
Cd^{2+}	3	9	6	26	3-7.8
	3	15	6	27	3-7.8
	3	6	3	23	3-7.8
	4	6	4	29	3-7.8
	3	5	3	24	3-7.8
	3	6	9	31	3-7.8
	5	6	7	28	3-7.8
		3	10	45	5-10
		2.5	10	40	3-10
		4	12	39	3-10
		3.5	15	42	3-10
		4	4	20	5-6.5
		3	6	35	5-9
Ni^{2+}	4	6	3.8	27	3.0-7.5
	3	6	3	28	3.0-7.5
	3	4	3	31	3.0-7.5
	3	15	6	26	3.0-7.5
	2.5	15	4.8	23	3.0-7.5
	4	8	4	33	3.0-7.5
	3	6	9	30	3.0-7.5
	5	6	7	27	3.0-7.5

[a] The concentrations are expressed in mmol dm^{-3}.

We investigated the ternary complexes of L-histidinate (his) and histamine (hm) with all the possible pairs formed by the Cu^{II}, Zn^{II}, Ni^{II}, and Cd^{II} ions. Histamine forms heteronuclear complexes with copper(II)-zinc(II) and copper(II)-cadmi-

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