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First Reversible Electrogeneration of Triply Oxidized Nickel Porphyrins and Porphycenes. Formation of Nickel(III) π Dications

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The site of electrooxidation in nickel(II) porphyrins and related macrocycles has been a point of controversy[1,2] since the first report of nickel(III) porphyrin electrogeneration by Wolberg and Manassen almost 25 years ago.[3,4] Since then, the electrochemistry of a variety of different nickel porphyrins,[5–10] chlorins,[2,8] isobacteriochlorins,[2] and porphycenes[11,12] in nonaqueous media has been reported. Two reversible one-electron oxidations are seen for most neutral complexes, and these have generally been interpreted in terms of two basic types of electrode mechanisms.[1] One corresponds to the reversible formation of a Ni(II) porphyrin π cation radical followed by generation of the Ni(III) derivative while the other involves an initial electrogeneration of the Ni(III) porphyrin followed by π cation radical formation. Surprisingly, the electrogeneration of a Ni(III) porphyrin dication has never been experimentally observed by the global three-electron oxidation of a neutral Ni(II) complex. This is perhaps unusual, since Ni(III) macrocycles are very well-known,[13–16] as are porphyrin dications for a variety of complexes with metals in the +3 oxidation state.[1]

As part of our studies on redox behavior of transition metal complexes of porphyrin macrocycles, we recently began investigating two types of complexes which differ quite substantially in their planarity. These are highly ruffled porphyrins bearing alkyl groups on the pyrrole β positions[17] and planar porphycenes,[18] which are porphyrin structural isomers. Both sets of compounds are easy to oxidize,[11,12,19] and we expected that previously inaccessible high oxidation states of transition metal derivatives might possibly be obtained for these compounds under appropriate experimental solution conditions. This is indeed the case, as demonstrated in the present communication, which reports the first nickel porphyrins and porphycenes to undergo three well-defined one-electron oxidations. The investigated compounds, whose synthesis and spectroscopic properties are reported in the literature,[11,19,20] are represented as (P)Ni and (OEPc)Ni where P = the dianion of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin (OMTPP) or 2,3,7,8,12,13,17,18-tetracyclohexenyl-5,10,15,20-tetraphenylporphyrin (TC$_6$TPP) and OEPc = the dianion of 2,3,6,7,12,13,16,17-octaethylporphycene.

Each Ni(II) compound shows three reversible oxidations by cyclic voltammetry at a Pt or glassy carbon electrode. There is no evidence for coupled chemical reactions, and the electrode reactions are all diffusion-controlled under the given experimental conditions. The initial oxidations of (TC$_6$TPP)Ni and (OMTPP)Ni occur at virtually identical potentials in benzonitrile containing 0.1 M TBAP (see Figure 1), and these values are shifted negatively by about 100 mV from $E_{1/2}$ for oxidation in butyronitrile containing the same supporting electrolyte.[19] The second oxidation occurs at +0.90 V for both compounds while the third is located at +1.56 V (TC$_6$TPP) or 1.63 V (OMTPP). The TC$_6$TPP derivative was also investigated in CH$_2$Cl$_2$, 0.1 M TBAP and undergoes three one-electron oxidations at $E_{1/2}$ = +0.66, +0.97, and +1.51 V under these solution conditions.

Similar redox behavior is observed for (OEPc)Ni. The first two oxidations occur at $E_{1/2}$ = +0.82 and +1.11 V in PhCN and are within experimental error of potentials reported for oxidation of the same compound in CH$_2$Cl$_2$, 0.1 M TBAP (0.81 and 1.12 V vs SCE).[11] A third oxidation of (OEPc)Ni is also observed under our experimental conditions, and this occurs at $E_{1/2}$ = 1.68 V (CH$_2$Cl$_2$) or 1.73 V (PhCN).

The data in Figure 1 might be rationalized in terms of porphyrin or porphycene trication formation after the abstraction of three electrons, but a more likely interpretation involves electrogeneration of a Ni(III) derivative after the first, the second, or the third one-electron oxidation. Data in the literature have been interpreted in terms of π cation radical formation after the first oxidation of (TC$_6$TPP)Ni[19] and dication formation after the second oxidation of (OEPc)Ni.[11] These assignments are also suggested in the present study where spectroscopic data for the doubly oxidized complexes are consistent with those for porphyrin and porphycene dications,[21] thus implying that the third rather

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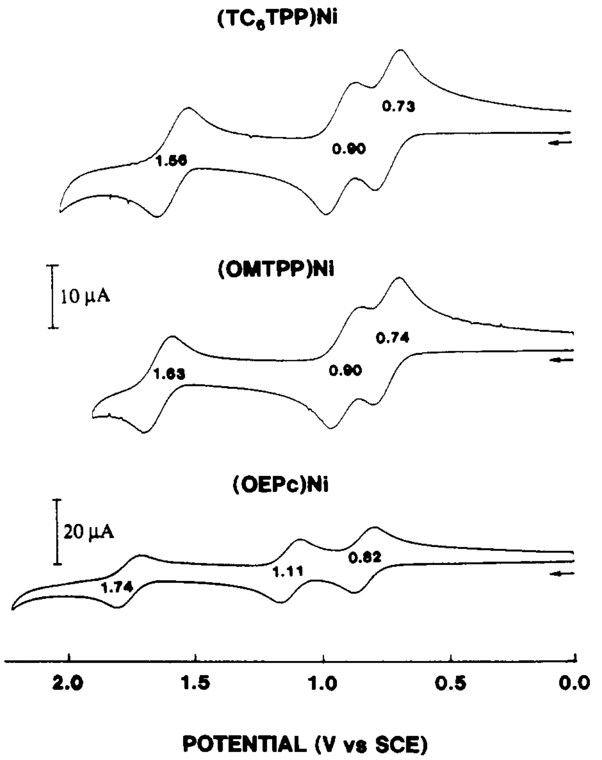

Figure 1. Cyclic voltammograms of (TC$_6$TPP)Ni, (OMTPP)Ni, and (OEPc)Ni in benzonitrile, 0.1 M TBAP. Scan rate = 0.1 V/s.

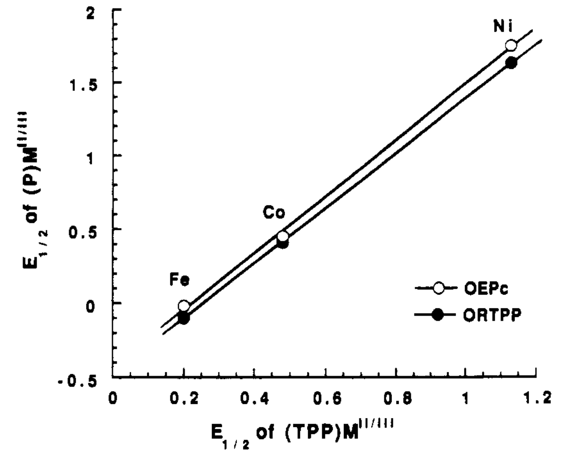

Figure 2. Plots of $E_{1/2}$ for the M(II)/M(III) reactions of (TPP)M versus the same reactions of (ORTPP)M and (OEPc)M where M = Fe(II), Co(II), or Ni(II) and R = CH_3 or C_2H_5 (in the case of iron).

Table I. Half-Wave Potentials (V vs SCE) and Structural Parameters of Nickel(II) Macrocycles in Benzonitrile, 0.1 M TBAP

	$E_{1/2}$			
compd	1st	2nd	3rd	Ni–N, Å
(OEPc)Ni	0.82	1.11	1.73	1.915[a]
(TC$_6$TPP)Ni	0.73	0.90	1.56	1.914(9)[b]
(OMTPP)Ni	0.74	0.90	1.63	1.906(2)[b]
(OEP)Ni	0.78	1.21	1.88[c]	1.952[b]
(EtioI)Ni	0.76	1.24	1.93[c]	1.957[d]

[a] Data from Ph.D. Dissertation: Pütz, C. Universität zu Köln, 1990. [b] Reference 19. [c] E_{pa} at 0.1 V/s. [d] Reference 25b.

than the first or second one-electron oxidation involves formation of the Ni(III) porphyrin or porphycene dication.

A Ni(II)/Ni(III) electrode reaction for the third process is also suggested by comparison of redox potentials for the third oxidation of (OMTPP)Ni, (TC$_6$TPP)Ni, and (OEPc)Ni with potentials for the M$^{II/III}$ redox reactions of other transition metal porphyrin and porphycene derivatives. For example, the metal-centered oxidations of (TPP)M^{II} (M = Ni, Co, Fe) vary linearly with the third-ionization potential of the metal ion,[4] and similar correlations are also obtained for complexes of (ORTPP)M[22] or (OEPc)M[24] where M = Ni, Co, or Fe and R = CH_3 or CH_2CH_3. Since potentials for all three series of compounds (TPP, ORTPP, and OEPc) vary with the third-ionization potential of the metal, one would expect a linear relationship between potentials for the known metal-centered reactions of (TPP)M^{II} and those for similar M$^{II/III}$ reactions of complexes with ORTPP or OEPc macrocycles. This is indeed the case, and these plots are shown in Figure 2.

All of the results are self-consistent and leave little doubt that a Ni(III) porphyrin or porphycene dication is generated after a global three-electron oxidation of the initial Ni(II) complex. It also appears that the degree of macrocycle planarity does not directly affect the electrochemical behavior, since both the ruffled (OMTPP) and planar (OEPc) derivatives have almost identical oxidation potentials. However, the data say little as to why the redox behavior of the three investigated compounds seems to differ from that of all previously characterized Ni(II) porphyrins.[1] One reason may be related to purely structural factors. The Ni–N distances in (TC$_6$TPP)Ni, (OMTPP)Ni, and (OEPc)Ni are all shorter than those in Ni(II) porphyrins such as (OEP)Ni[19] and (EtioI)Ni[25b] (see Table I) or Ni(II) hydroporphyrins,[25] all of which are easily oxidizable.[2,7b] On the other hand, it might be suggested that all easily oxidizable nickel porphyrins can actually be oxidized by three electrons under appropriate solution conditions, and in order to verify this hypothesis, we have reexamined the electrochemistry of (OEP)Ni[26,27] and (EtioI)Ni[26] as part of this study. To our surprise, each compound undergoes three one-electron oxidations. The $E_{1/2}$ values for the first oxidation of these two complexes are almost identical to those of (OMTPP)Ni and (TC$_6$TPP)Ni while the second oxidation of (OEP)Ni and (EtioI)Ni are shifted in a positive direction by more than 300 mV with respect to values for the other two porphyrins (see Table I). The first two oxidations of the OEP and Etiol complexes are also reversible while the third is irreversible and close to the limit of the solvent cutoff. It is, however, very well-defined and seems to involve an EC type mechanism, i.e., a chemical reaction following a reversible one-electron transfer. This result might imply that all easily oxidizable Ni(II) porphyrins and porphycenes could be ultimately converted to a nickel(III) dication. Further studies along these lines are needed in order to confirm this assumption, and these are now in progress in our laboratory.

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(21) Doubly oxidized [(OEPc)Ni]$^{2+}$ in benzonitrile is characterized by a single absorption band at 350 nm and no additional spectral detail up to 900 nm. This spectrum is almost superimposable on that of the [(OEPc)Zn]$^{2+}$ dication, which has a single band at 354 nm. Likewise, the UV–vis spectrum of [(OMTPP)Ni]$^{2+}$ has bands at 350 and 410 nm and may be compared to a spectrum of the [(OMTPP)Cu]$^{2+}$ dication which has bands at 360 and 430 nm in the same solvent.

(22) The synthesis and spectral data of these complexes are given in ref 20. The electrochemical characterization of the Co and Fe complexes will be published elsewhere.[23]

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(26) OEP and EtioI represent the dianions of octaethylporphyrin and etioporphyrin I, respectively.

(27) An earlier study of (OEP)Ni complexes reported only one oxidation.[7b]