

Table V for ligand identification) can be the precursors of polymeric chains of formula  $[\text{Cd}(\text{HA})_2]_n^{2n+}$  while the complexes  $\text{Cd}_3(\text{HA})_8$ ,  $\text{Cd}_4(\text{HA})_{10}$ , and  $\text{Cd}_5(\text{HA})_{12}$ , the last one analogous to  $[\text{Zn}_5(4\text{-MP})_{12}]^{10+}$ ,<sup>19a</sup> can be considered as the longest soluble fragments of an infinite polymeric chain, under our experimental conditions.

The IR spectra of solid cadmium complexes with the three ligands in their completely deprotonated form,  $[\text{Cd}(\text{MMA})_2]$ ,  $[\text{Cd}(4\text{-MP})_2]$ ,<sup>29,30</sup> and  $[\text{Cd}_3(\text{MPA})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>31</sup> show that only in the last case does chelation occur, which agrees well with the structural differences of the ligands. The chelating ability of MPA, although in solutions containing Cd(II) it is lower than that of MEA,<sup>14,21</sup> is the greatest among the  $\gamma$ -mercapto amines we have studied. A good example of this different behavior is provided by nickel complexes, where chelates of the same stoichiometry as those found with MEA<sup>32</sup> are formed with MPA<sup>33</sup> but coordination

occurs only through sulfur if the ligands are 4-MP<sup>18b</sup> or MMA.<sup>19a</sup> The same trend has been found in the solid cadmium complexes of the four ligands.<sup>29,31,34</sup> If solution equilibria studies are also taken into account,<sup>14,20,21</sup> where chelation has been proposed only in the case of MEA and MPA, it can be proposed that, other factors being equal, in order of increasing importance, the flexibility of the hydrocarbon chain linking both functional groups, the degree of substitution on the amine function, and the length of the hydrocarbon chain determine the tendency of mercapto amines to behave as chelating agents.

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## Does One-Electron Transfer to Nickel(II) Porphyrins Involve the Metal or the Porphyrin Ligand?

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Nickel("I") complexes can be reversibly produced by one-electron electrochemical reduction of nickel(II) porphyrins within the time scale of cyclic voltammetry as well as thin-layer and conventional cell electrolysis in solvents such as dimethylformamide and benzonitrile. UV-vis and ESR spectroscopies indicate the formation of a nickel(I) complex rather than the anion radical of the nickel(II) porphyrin. ESR data suggest an out-of-plane displacement of the nickel(I) ion caused by the insufficient size of the hole offered by the porphyrin ligand.

Nickel(I) macrocyclic complexes have attracted active attention during the last 10 years as powerful catalysts of the electrochemical reduction of electrophiles. The principle of the reaction consists in generating electrochemically the Ni(I) complex from the Ni(II) complex. The former then reacts with the electrophile, regenerating the latter. Main applications have concerned the reduction of alkyl halides<sup>2,3</sup> and of carbon dioxide.<sup>4</sup>

Another source of interest for nickel(I)-tetraazamacrocyclic complexes relates to coenzyme F430, an hydrocorphinoid nickel(II) complex involved in the reductive cleavage of *S*-methyl coenzyme M ((methylthio)ethanesulfonate) to coenzyme M (mercaptoethanesulfonate) and methane.<sup>5</sup> Recent findings point to the involvement of the corresponding Ni(I) complex in this reaction as indicated by the similarity of the ESR signal detected in whole

cells of *Methanobacterium thermoautotrophicum*<sup>6a</sup> and of the ESR spectrum of the reduced form of the pentamethyl ester of coenzyme F430.<sup>6b</sup>

In both cases, the ability of the starting nickel(II) complex to form, upon one-electron transfer, a nickel(I) complex rather than the anion radical of the macrocyclic ligand appears as a key point for obtaining an efficient catalysis. In the latter case, one indeed expects the formation of ring coupling products that would eventually stop the propagation of the catalytic reaction. Moreover, nickel(I) complexes are expected to react with electrophiles, halogen, or halonium donors by transfer of their unpaired electron in an inner-sphere manner, being thus more efficient and more specific than ring anion radicals, which are likely to function as outer-sphere electron donors.<sup>7,8</sup> In this connection, ESR and UV-vis spectroscopy are useful tools to assess the relative importance of the Ni(I) and Ni(II) anion radical resonant forms. The electrochemical and ESR study of an extended series of nickel-tetraazamacrocyclic complexes involving neutral ligands<sup>9a</sup> has shown that Ni(I) is obtained with saturated macrocycles and with macrocycles containing isolated imine groups whereas an

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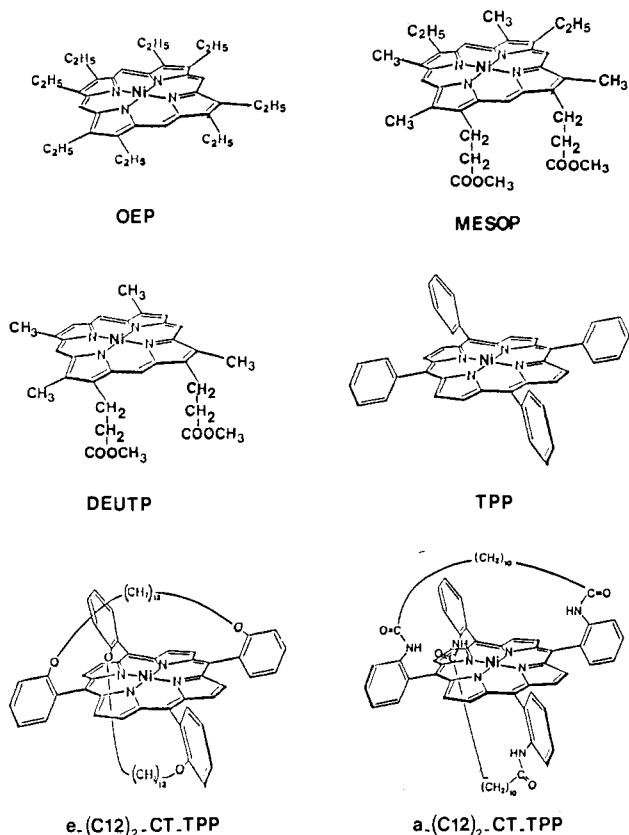


Figure 1. Nickel(II) porphyrins investigated in this work with their conventional designations.

anion radical signal was obtained with macrocycles containing  $\alpha$ -diimine bonding functions. However with mono- and dianionic ligands, the Ni(I) ESR signal is observed with partially or completely conjugated ligands (hydrocorphin<sup>6b</sup> and isobacteriochlorin<sup>9b</sup>).

Nickel(II) porphyrins are usually considered to give rise upon reduction to the corresponding anion radical based on<sup>9a</sup> extended Hückel quantum mechanical calculations of the orbital energy levels.<sup>10</sup> Experimental evidence supporting this assignment is however tenuous.<sup>11</sup> On the other hand, it has been recently shown that reduced nickel(II) octaethylporphyrin catalyzes the electrochemical reaction of vicinal dihalides into the corresponding olefin with a significantly higher rate constant than outer-sphere electron-transfer catalysts having the same standard potential,<sup>12</sup> thus pointing to the inner-sphere character of the reaction. This prompted us to reexamine the electrochemical reduction of an extended series of nickel(II) porphyrins and the nature of the

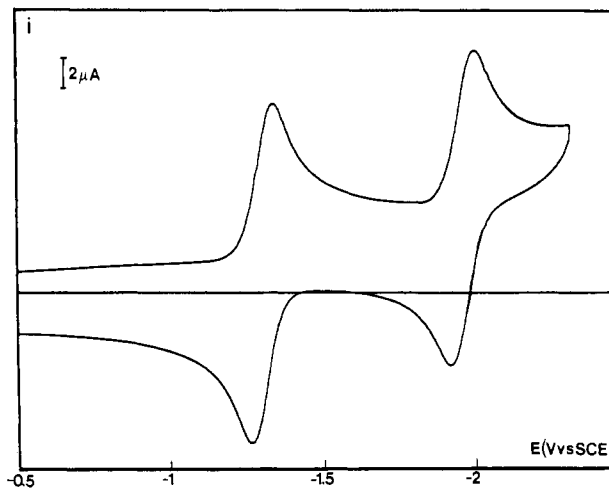


Figure 2. Cyclic voltammetry of Ni<sup>II</sup>e-(C12)<sub>2</sub>(CT-TPP) (1 mM) in DMF + 0.1 M NBu<sub>4</sub>PF<sub>6</sub> at a glassy carbon disk electrode. Temperature = 20 °C. Sweep rate = 0.1 V·s<sup>-1</sup>.

Table I. Standard Potentials<sup>a</sup> of the Ni(II)/Ni("I") Redox Couple<sup>b</sup>

porphyrin	solvent		
	DMF	PhCN	DCE
OEP	-1.38 <sub>0</sub>		
MESOP	-1.36 <sub>0</sub>		
DEUTP	-1.32 <sub>0</sub> <sup>c</sup>	-1.42 <sub>0</sub> <sup>c</sup>	
TPP	-1.11 <sub>0</sub> <sup>d</sup>		
e-(C12) <sub>2</sub> -CT-TPP	-1.29 <sub>0</sub> <sup>c</sup>	-1.45 <sub>0</sub> <sup>c</sup>	-1.58 <sub>5</sub>
a-(C12) <sub>2</sub> -CT-TPP	-1.09 <sub>5</sub>	-1.14 <sub>0</sub>	-1.19 <sub>0</sub>

<sup>a</sup>In V vs SCE. <sup>b</sup>Temperature = 20 °C; supporting electrolyte 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> unless otherwise stated. <sup>c</sup>Supporting electrolyte 0.1 M Et<sub>4</sub>NClO<sub>4</sub>. <sup>d</sup>0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.

one-electron-reduction product based on its ESR and UV-vis spectral characteristics.

## Results and Discussion

The various nickel(II) porphyrins investigated in this work, four simple porphyrins and two basket-handle porphyrins, are shown in Figure 1 together with their conventional designation.

**Cyclic Voltammetry.** All the investigated porphyrins exhibit, in dimethylformamide (DMF) and benzonitrile (PhCN), two reduction waves, in contrast with previous reports.<sup>9b,11b</sup> Only the first of the waves is visible in 1,2-dichloroethane (DCE). The first wave, corresponding to the Ni(II)/Ni("I") (formal oxidation state) is reversible in all three solvents even at a scan rate as low as 0.1 V·s<sup>-1</sup>. The reversibility of the second wave appears as critically dependent upon the purity of the solvent-supporting electrolyte mixture, particularly upon the presence of water and of alkylating agents contained in the tetraalkylammonium supporting salt. An example of the observance of two reversible reduction waves is shown in Figure 2.

The standard potentials of the Ni(II)/Ni("I") redox couple as derived from the cyclic voltammograms are listed in Table I. The variations seen in the simple porphyrins series reflect the electronic inductive effect of the ring substituent. The difference between the two basket-handle porphyrins comes partly also from inductive effect (ether vs NHCO linkage) and from through-space effects of the same nature as previously described in details in the case of iron porphyrins.<sup>13</sup> We cannot, however, infer from the sim-

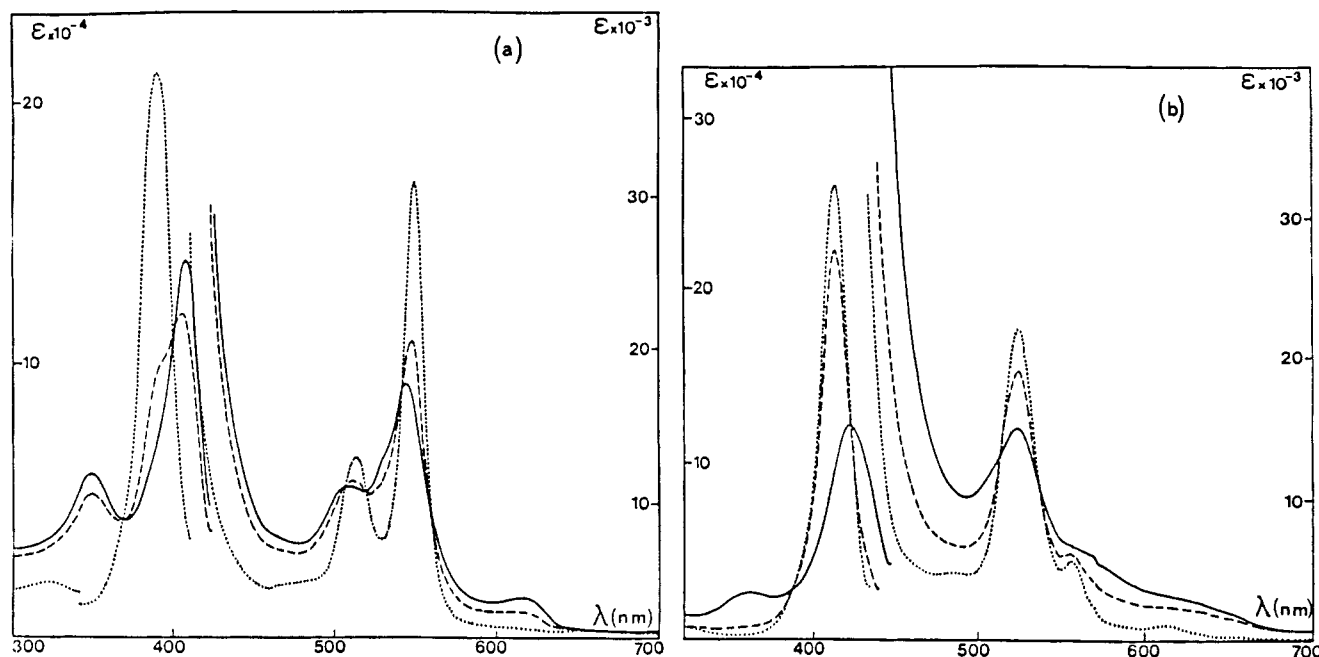
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(10) (a) Zerner, M.; Gouterman, M. *Theor. Chim. Acta* **1966**, *4*, 44. (b) Strictly speaking, ref 10a provides calculated energies of the top full and lowest empty orbitals of nickel(II) porphyrins, not of nickel(I) porphyrins. It therefore predicts that if one starts with Ni(II), injection of one electron will take place in the porphyrin ring  $\pi^*$  ( $e_g$ ) orbital rather than in the Ni  $d_{x^2-y^2}(b_{1g})$  orbital only if it is assumed that the geometry of the complex does not change simultaneously to any significant extent.

(11) (a) Difficulties were apparently encountered in generating a stable nickel(II) octaethylporphyrin one-electron reduction product in acetonitrile and tetrahydrofuran<sup>9b</sup> at variance with the data we obtained in DMF and benzonitrile as described in the following. The assignments based on ESR and UV-vis spectra recorded under these conditions are thus rather uncertain. It was also shown that the reduction product slowly reacts with dichloromethane when used as a solvent.<sup>9b</sup> Another study of the reduction of (TPP)Ni<sup>III</sup> and various phenyl ring substituted (TPP)Ni<sup>III</sup> complexes<sup>11b</sup> concluded that an anion radical was formed, on the basis of ESR and UV-vis spectra recorded in dichloromethane as a solvent. (b) Chang, D.; Malinski, T.; Ulman, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 317.

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(13) (a) Namely destabilization of the "I<sup>-</sup>" complex due to protection against solvation by the basket-handle chains in the case of e-(C12)<sub>2</sub>-CT-TPP, stabilization of "I<sup>-</sup>" due to NHCO dipole-charge interactions in the case of a-(C12)<sub>2</sub>-CT-TPP. The fact that the difference increases as the complexing power of the solvent decreases from DMF to PhCN and to DCE reflects the steric hindrance of solvent axial coordination by the chains as previously observed and rationalized in the case of iron porphyrins.<sup>13b,c</sup> (b) Lexa, D.; Momenteau, M.; Rentien, P.; Rytz, G.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1983**, *106*, 6755. (c) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J. M. *Inorg. Chem.* **1986**, *25*, 4294.



**Figure 3.** Thin-layer spectroelectrochemistry of (DEUTP)Ni<sup>II</sup> (a) and (e-(C<sub>12</sub>)<sub>2</sub>-CT-TPP)Ni<sup>II</sup> (b) in DMF + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at -1.6 (a) and -1.5 (b) V vs SCE, respectively. Temperature = 20 °C. Key: (—) final spectrum; (···) starting spectrum; (- -) intermediate spectrum.

ilarity of these effects with those found with the iron(II)/iron(I) porphyrin couple<sup>13</sup> that the negative charge is located more on the metal than on the porphyrin ring. This point will be discussed in the following sections on the basis of UV-vis and ESR spectroscopy data.

In DMF, the nickel("I") porphyrins are sufficiently stable to being obtained by *preparative scale electrolysis* at a potential 100 mV negative of the cathodic peak potential. The starting nickel(II) porphyrin is regenerated quantitatively upon reoxidation at a potential 100 mV positive of the anodic peak potential. In both cases, *coulometry* indicates the exchange of one electron per molecule.

**Thin-Layer UV-Vis Spectroelectrochemistry.** In DMF and PhCN, it is possible to generate reversibly the Ni("I") complex by electrolysis of the Ni(II) complex in a thin-layer cell. The reversibility of the process, i.e., the ability to regenerate quantitatively the Ni(II) complex by reoxidation, is an essential test of the actual obtention of the Ni("I") complex in the first part of the experiment rather than one of its possible decomposition products. Several examples of such experiments are shown in Figures 3 and 4. In all cases, well-defined isobestic points are obtained during reduction as well as during reoxidation (Figures 3 and 4). Table II summarizes the spectral characteristics of the various nickel("I") porphyrins as compared to those of the parent Ni(II) complexes. Table III shows a comparison between the spectral characteristics of (OEP)Ni("I") and those of (OEP)Co<sup>I</sup>, (OEP)Fe<sup>I</sup> and the anion radical of (OEP)Zn<sup>II</sup> from spectra recorded under the same conditions. The spectral characteristics of all the investigated nickel("I") porphyrins are very similar whatever the porphyrin ring, even when going from TPP to alkyl substitution on the pyrroles. It is also seen (Table II) that they are of the hyperporphyrin type, thus resembling those of the corresponding cobalt(I) and iron(I) porphyrins<sup>15</sup> and are clearly very different from those of a porphyrin anion radical as exemplified by Zn<sup>II</sup>OEP<sup>-</sup> (Table III) and Zn<sup>II</sup>TPP<sup>-</sup>.<sup>14</sup> This is the first indication that the nickel("I") porphyrins are better described as nickel(I) complexes (without quotation marks) than as porphyrin anion radicals.

**Table II.** Spectral Characteristics<sup>a</sup> of Nickel("I")<sup>b</sup>

Porphyrin	$\alpha$	$\beta$	$\gamma$
Ni("I")OEP	617 (0.27), 545 (2.15), 506 (1.01), 407 (12.09), 346 (4.30)		
Ni(II)OEP	550 (3.34), 515 (1.15), 391 (20.81)		
Ni("I")OEP <sup>c</sup>	620 (0.27), 545 (2.12), 512 (1.00), 408 (11.60), 345 (5.10)		
Ni(II)OEP	552 (3.05), 516 (1.06), 394 (18.10)		
Ni("I")MESOP	625 (0.30), 543 (1.80), 505 (0.83), 408 (9.00), 348 (4.50)		
Ni(II)MESOP	550 (3.10), 513 (1.00), 390 (23.20), 325 (1.90)		
Ni("I")DEUTP	615 (0.30), 542 (1.72), 506 (1.06), 407 (13.76), 348 (6.22)		
Ni(II)DEUTP	547 (3.10), 513 (1.15), 388 (21.17), 320 (1.00)		
Ni("I")TPP <sup>d</sup>		523, 418, 360	
Ni(II)TPP		527, 415	
Ni("I")e-(C <sub>12</sub> ) <sub>2</sub> -CT-TPP	620 (0.294), 560 (0.589), 521 (1.445), 422 (12.14), 360 (3.67)		
Ni(II)e-(C <sub>12</sub> ) <sub>2</sub> -CT-TPP	555 (0.490), 523 (2.24), 412 (26.00)		
Ni("I")a-(C <sub>12</sub> ) <sub>2</sub> -CT-TPP	610 (0.427), 560 (0.599), 524 (1.103), 419 (9.88), 360 (2.09)		
Ni(II)a-(C <sub>12</sub> ) <sub>2</sub> -CT-TPP	558 (0.477), 526 (1.540), 415 (17.80)		

<sup>a</sup>Wavelengths of the main bands are given in nm; values in parentheses are 10<sup>-4</sup> $\epsilon_M$  (molar extinction coefficient). Temperature = 20 °C. <sup>b</sup>In DMF, unless otherwise stated, plus 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. <sup>c</sup>In PhCN. <sup>d</sup>Not soluble enough for a meaningful determination of the  $\epsilon_M$  values to be possible.

**Table III.** Comparison of the Spectral Characteristics<sup>a</sup> of (OEP)Ni("I") with Those of (OEP)Co<sup>I</sup>, (OEP)Fe<sup>I</sup>, and the Anion Radical of (OEP)Zn<sup>II</sup><sup>b</sup>

Porphyrin	$\alpha$	$\beta$	$\gamma$
Ni("I")OEP	617 (0.27), 545 (2.18), 506 (1.01), 407 (12.09), 346 (4.30)		
Co(I)OEP	546 (2.33), 510 (0.73), 413 (5.65), 352 (7.01)		
Fe(I)OEP	684 (0.40), 565 (1.30), 524 (1.20), 493 (1.30), 400 (5.60), 374 (7.10)		
Zn(II)OEP <sup>-</sup>	750 (0.31), 624 (2.08)	421 (18.20), 410 (shoulder)	

<sup>a</sup>Wavelengths of the main bands are given in nm; values in parentheses are 10<sup>-4</sup> $\epsilon_M$  (molar extinction coefficient). Temperature = 20 °C. <sup>b</sup>In DMF + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

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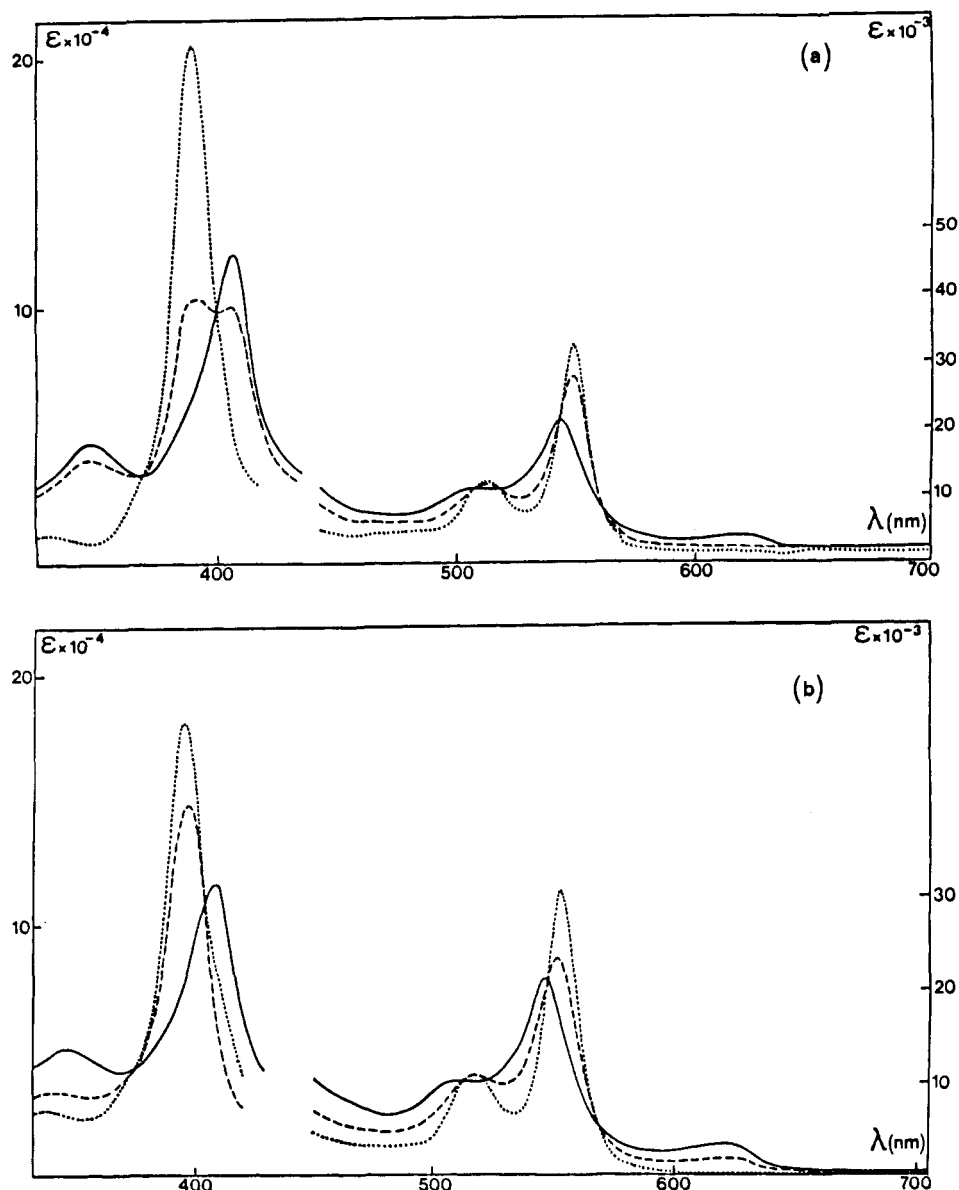


Figure 4. Thin-layer spectroelectrochemistry of OEPNi<sup>II</sup> in DMF (a) and PhCN (b) + 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>. Temperature = 20 °C. Key: (—) final spectrum; (---) starting spectrum; (· · ·) intermediate spectrum.

In DCE, the thin-layer reduction is not reversible even with Ni(a-(C<sub>12</sub>)<sub>2</sub>-CT-TPP), which has the most positive standard potential in the series and is hence expected to give rise to the most stable Ni("I") complex.<sup>16</sup> The spectrum thus obtained is completely different from that obtained with this porphyrin and others in DMF and PhCN. In dichloromethane also the thin-layer reduction is not reversible, as we observed for example in the case of NiOEP, and the resulting spectrum is again quite different from those obtained in DMF and PhCN.<sup>17</sup>

**ESR Spectroscopy.** Two series of experiments were carried out, one at room temperature (295 K) and the other at low temperatures (ranging from 10 to 140 K). In the first case, the nickel("I") porphyrin was generated on a platinum grid located inside the ESR cell whereas in the second the starting nickel(II) porphyrin solution was preelectrolyzed as described earlier and then

Table IV. ESR Spectroscopic Data for Nickel("I") Porphyrins and Porphyrin Anion Radicals<sup>a</sup>

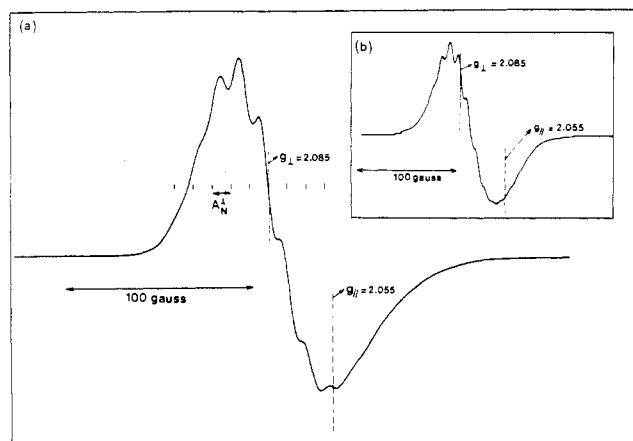
porphyrin	<i>g</i>	$\Delta H^b$
Ni <sup>I</sup> OEP	2.083	46
<sup>61</sup> Ni <sup>I</sup> OEP	2.085	55
Ni <sup>I</sup> MESOP	2.080	60
Ni <sup>I</sup> DEUTP <sup>c</sup>	2.085	64
Ni <sup>I</sup> TPP	2.081	99
Ni <sup>I</sup> a-(C <sub>12</sub> ) <sub>2</sub> -CT-TPP	2.083	70
Zn <sup>II</sup> TPP <sup>·-</sup> <sup>d</sup>	2.0026	5.3
H <sub>2</sub> TPP <sup>·-</sup> <sup>d</sup>	2.0027	8
H <sub>2</sub> OEP <sup>·-</sup>	2.0027	6

<sup>a</sup> In DMF + 0.1 M NBu<sub>4</sub>PF<sub>6</sub> at 77 K unless otherwise stated. <sup>b</sup> Peak to peak width in gauss. At 40 K a better resolved spectrum can be obtained (see Figure 4 and text). <sup>c</sup> at 295°K. <sup>d</sup> From ref 19.

- (16) (a) Ni<sup>I</sup>OEP has been shown to efficiently catalyze the electrochemical reduction of *trans*-1,2-dibromocyclohexane into cyclohexene.<sup>12</sup> By analogy, the instability of the Ni("I")-porphyrin complex in DCE that we observed here is likely to involve the reductive elimination of DCE to ethylene. See also a similar observation for Ni<sup>I</sup>OEP in ref 9b.
- (17) This is probably the reason why spectra different from those described here in DMF and PhCN were obtained in previous investigations of Ni("I")-porphyrin complexes in CH<sub>2</sub>Cl<sub>2</sub>, due, on this basis, to the radical anion nature of the species resulting from the one-electron reduction of nickel(II) porphyrins.<sup>12b</sup>

transferred under argon into a standard ESR tube.

With carefully purified nickel porphyrins no ESR signal was obtained at room temperature. A slightly anisotropic broad (50–80 G) signal centered around *g* = 2.08 is observed between 10 and 140 K, the characteristics of which are summarized in Table IV for the various porphyrins. The signal disappears upon increasing the temperature above 140 K and reappears reversibly upon cooling. At 40 K, a better resolved structure could be obtained

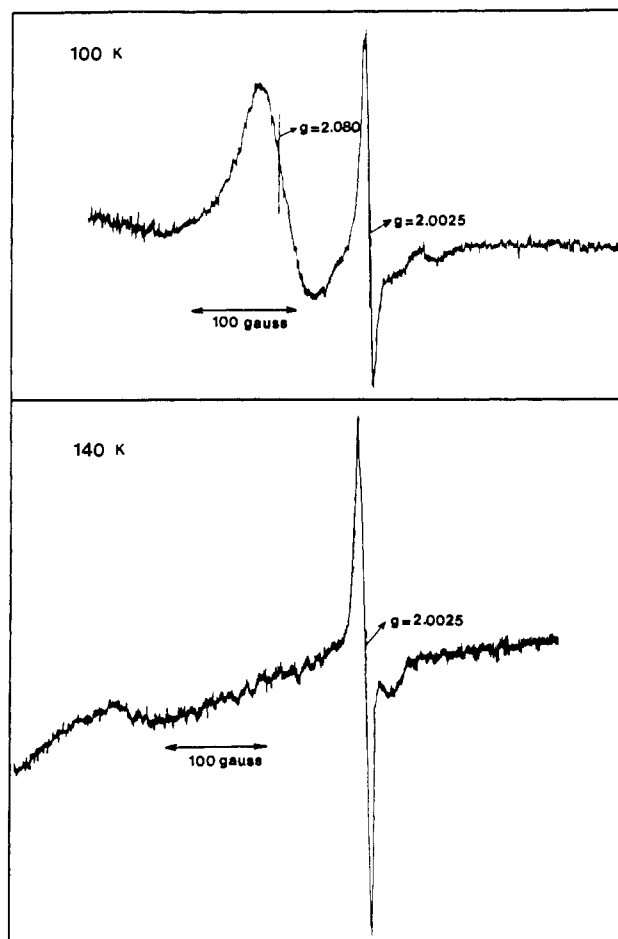


**Figure 5.** ESR spectra of Ni<sup>41</sup>DEUTP in DMF + 0.1 Bu<sub>4</sub>NPF<sub>6</sub> at 40 K: (a) experimental; (b) simulated.

as shown in Figure 5 for the case of Ni<sup>41</sup>DEUTP. This spectrum is consistent with two fine structure components at  $g_{\perp} = 2.085$  and  $g_{\parallel} = 2.055$  and nine hyperfine structure components of relative intensities 1:4:10:16:19:16:10:4:1 separated by  $A_{N_{\perp}} \approx A_{N_{\parallel}} = 8.5$  G. Clearly, this pattern arises from the hyperfine interaction of the electron spin with the four porphyrin nitrogen nuclear spins. Simulation (Figure 5b) was carried out by computing an anisotropic spectrum assuming axial symmetry, Lorentzian line shapes, and the aforementioned  $g$  values. Nine spectra with the required relative intensities, which were split by 8.5 G, were then added together. This is justified by computation of the resonance field taking into account the hyperfine coupling to second order,<sup>18</sup> resulting in an uniform splitting independent from the nuclear magnetic spin quantum number. Although this simulation is considered as sufficient for the purpose of the present discussion, it could probably be improved by assuming a slightly rhombic distortion as done in a related case.<sup>6b</sup> Introduction of <sup>61</sup>Ni (<sup>61</sup>NiOEP) did not result in the appearance of a resolved hyperfine coupling with the metal nuclear spin but did show an increase of the spectrum width from 46 to 55 G.

These characteristics as well as those of the relaxation times (no ESR spectrum at room temperature) point to a nickel(I) formulation rather than to a nickel(II) porphyrin anion radical. The latter would indeed be expected to give a much narrower signal centered at  $g = 2$  (see Table II for the characteristics of Zn<sup>II</sup>TPP, H<sub>2</sub>TPP, and H<sub>2</sub>OEP porphyrin radical anions) persisting at room temperature. The fact that  $g_{\parallel}$  and  $g_{\perp}$  are larger than 2 is consistent with a metallic ion spin-orbit interaction. The broadening observed with <sup>61</sup>Ni indicates a nonresolved hyperfine coupling of the same order of magnitude as that previously observed with other Ni(I) macrocyclic complexes.<sup>6a</sup> The coupling constant, 8.5 G, with the nitrogen is very similar to that observed earlier with other nickel(I) tetraaza complexes.<sup>6,20</sup> It clearly shows that the additional electron is located in the  $d_{x^2-y^2} b_{1g}$  orbital. As compared to more stable saturated nickel(I) tetraazamacrocyclic complexes,<sup>6,9,20</sup> the decrease in  $g_{\parallel}$  points to a destabilization of the  $d_{x^2-y^2}$  orbital, which is not sufficient however for its energy to become higher than that of the  $e_g \pi^*$  orbital of the porphyrin ring. This can be interpreted as resulting from an out-of-plane displacement of the Ni(I) ion caused by the insufficient hole size offered by the porphyrin ligand.<sup>9b</sup>

With insufficiently purified nickel porphyrins in the TPP and modified-TPP series as well as with nickel porphyrins from commercial origin, we found in the ESR spectra a sharp radical-like



**Figure 6.** ESR spectra of the one-electron reduction product of non-purified Ni<sup>II</sup>a-(C12)<sub>2</sub>-CT-TPP in DMF (+0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) at 100 (top) and 140 K (bottom).

signal mixed with the Ni(I) signal (Figure 6). It was observed at all temperatures and was thus the only visible signal at room temperature and more generally above 140 K.<sup>21</sup> As shown by fluorescence detection thin-layer chromatography, the impurity causing this additional signal is the corresponding porphyrin free base.

## Conclusion

The species reversibly generated by one-electron electrochemical reduction of nickel(II) porphyrins appears, on UV-vis and ESR spectroscopy grounds, to be a nickel(I) complex rather than the anion radical of the nickel(II) porphyrin. As compared to other nickel(I) tetraazamacrocyclic complexes, their ESR characteristics suggest an out-of-plane displacement of the Ni(I) ion caused by the insufficient size of the hole offered by the porphyrin ligand. This should be taken into account when contrasting the catalytic properties, in natural or artificial processes, of less conjugated macrocyclic complexes with those of reduced nickel(II) porphyrins.

## Experimental Section

**Chemicals.** DMF was vacuum distilled before use. PhCN was refluxed for 24 h on P<sub>2</sub>O<sub>5</sub> and then vacuum distilled. DCE was vacuum distilled on P<sub>2</sub>O<sub>5</sub> under argon flushing. Dichloromethane (uvasol, Merck) was stored on Na<sub>2</sub>CO<sub>3</sub>. The supporting electrolyte, Bu<sub>4</sub>NPF<sub>6</sub> (Fluka), was recrystallized three times in a 2:1 ethyl acetate-ethanol mixture.

The metal-free 5,10,15,20-tetraphenylporphyrin, octaethylporphyrin, deuteroporphyrin dimethyl ester, mesoporphyrin dimethyl ester, and basket-handle porphyrins were prepared as described in the literature.<sup>22a-e</sup>

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(21) This might be the reason why previous investigations of the ESR spectroscopy of electrochemically reduced nickel(II) porphyrins report the presence at room temperature of a sharp radical-like signal taken as evidence for the formation of a nickel(II) anion radical.<sup>11b</sup>

Nickel insertion was performed according to described procedures from nickel(II) acetate by boiling the porphyrin with the nickel source for 30 min in a mixture of glacial acetic acid and methylene chloride, followed by chromatography on silica gel (methylene chloride as eluant) and crystallization from methylene chloride–hexane.<sup>22d–f</sup>

Ni(a-BHP) and Ni(e-BHP) were prepared by reacting the corresponding free-base porphyrin (150 mg) and nickel chloride (300 mg) in refluxing dimethylformamide (10 mL) for 1 h. The organic solution was then evaporated to dryness. The remaining solid was washed with water (×3) and dried (Na<sub>2</sub>SO<sub>4</sub>). Chromatography on a silica gel column with methylene chloride–acetone (20:1 v/v) gave the expected compounds (120 mg), which were crystallized from methylene chloride–hexane.

**Preparation of <sup>61</sup>Ni(AcOH)<sub>2</sub>.** <sup>61</sup>Ni was purchased from CEA (France). HNO<sub>3</sub> was added with stirring to metallic Ni. The resulting green solution of nickel nitrate was then evaporated to dryness. Addition of 0.1 M NaOH to the green residue gave a gelatinous precipitate of Ni(OH)<sub>2</sub>, which was filtered off. Subsequent treatment of the solid with acetic acid afforded the desired product.

**Instrumentation and Procedures.** The instrumentation for cyclic voltammetry and thin-layer UV–vis spectroelectrochemistry was the same as previously described.<sup>23</sup> A similar thin-layer cell was used for room-temperature ESR experiments. In both cases the working electrode was a platinum grid. For low-temperature ESR experiments the nickel(“I”) porphyrin was prepared by electrolysis of 5 cm<sup>3</sup> of a 1–2 mM nickel(II) porphyrin solution in a 35 mm diameter–15 mm high carbon crucible serving as the working electrode. The electrolyzed solution was then transferred under argon pressure to a degazed ESR quartz tube, which was then cooled down to the desired temperature. The ESR spectra were obtained on an ER200E BandX ER 041 MR Bruker spectrometer. The magnetic field was measured with a ER 035 M NMR gaussmeter.

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**Registry No.** Ni<sup>II</sup>OEP, 24803-99-4; Ni<sup>II</sup>MESOP, 15892-09-8; Ni<sup>II</sup>DEUTP, 15892-10-1; Ni<sup>II</sup>TPP, 14172-92-0; Ni<sup>II</sup>(e-(C12)<sub>2</sub>-CT-TPP), 117687-99-7; Ni<sup>II</sup>(a-(C12)<sub>2</sub>-CT-TPP), 117688-00-3; Ni<sup>II</sup>OEP, 116025-40-2; Ni<sup>II</sup>MESOP, 117688-03-6; Ni<sup>II</sup>DEUTP, 117688-04-7; Ni<sup>II</sup>TPP, 88669-50-5; Ni<sup>II</sup>(e-(C12)<sub>2</sub>-CT-TPP), 117688-01-4; Ni<sup>II</sup>(a-(C12)<sub>2</sub>-CT-TPP), 117688-02-5.

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## The Pentacoordinate [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup> Cation: Its Structural Verification, Ligand Rearrangement, and Deceptive Reaction with Dioxygen

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Crystal structures of two cationic copper(I) complexes of a Schiff-base ligand in two isomeric forms, 2,6-bis[1-((2-imidazol-4-ylethyl)imino)ethyl]pyridine [(imidH)<sub>2</sub>DAP] and 4-methyl-4-[6-(1-((2-imidazol-4-ylethyl)imino)ethyl)pyridid-2-yl]-4,5,6,7-tetrahydro-1*H*-imidazo[4,5-*c*]pyridine [(imidH)(imidH')DAP] have been solved. The former species is pentacoordinate about copper, while the latter is tetracoordinate. Crystal data for [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)](BF<sub>4</sub>), CuF<sub>4</sub>N<sub>7</sub>C<sub>19</sub>BH<sub>23</sub> (A): *a* = 8.279 (5) Å, *b* = 24.243 (6) Å, *c* = 11.417 (3) Å, β = 96.18 (3)°, *Z* = 4 in the monoclinic space group *P*2<sub>1</sub>/*c*. Crystal data for [Cu<sup>I</sup>((imidH)(imidH')DAP)](BF<sub>4</sub>), CuF<sub>4</sub>N<sub>7</sub>C<sub>19</sub>BH<sub>23</sub> (B): *a* = 12.214 (5) Å, *b* = 12.638 (8) Å, *c* = 8.24 (2) Å, α = 104.1 (1)°, β = 93.4 (1)°, γ = 115.2 (1)°, *Z* = 2 in the triclinic space group *P* $\bar{1}$ . Distortions from an idealized trigonal-bipyramidal geometry for the pentacoordinate species are seen in elongated axial Cu–N average bond distances of 2.41 Å and in shorter in-plane Cu–N average bond distances of 1.91 Å. The tetracoordinate structure may be described as a flattened tetrahedron, having two large N–Cu–N bond angles of 132.8 and 140.4°. The pentacoordinate isomer has previously been proposed to form a dioxygen adduct at room temperature in nonaqueous solution, which, under removal of dioxygen, regenerates [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup>. In this work, this regeneration step has been determined by a Toepler pump experiment to proceed *without* significant release of dioxygen under the conditions of the experiment. Thus, the regeneration of copper(I) from oxygenated [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup> proceeds by a pathway more complex than simple release of O<sub>2</sub> from a dioxygen adduct of [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup>.

### Introduction

The coordination chemistry of simple copper(I) compounds is of longstanding interest to us because of the ubiquitous involvement of Cu(I) at cuproprotein active sites.<sup>1</sup> In particular, Cu(I) reactivity toward dioxygen<sup>2–4</sup> and Cu(I) participation in biological Cu(II) ⇌ Cu(I) redox chemistry<sup>5</sup> has stimulated our interest in the [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup> cation,<sup>6</sup> shown schematically in Figure 1A. About 10 years ago,<sup>7</sup> we first reported observations which indicated that the then-presumed pentacoordinate [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup> cation reacted reversibly with O<sub>2</sub> in solution under ambient conditions. Since then, additional reports by ourselves<sup>2–4</sup> and others<sup>8,9</sup> have further characterized this “reversible” reaction

of [Cu<sup>I</sup>((imidH)<sub>2</sub>DAP)]<sup>+</sup> (and its closely related derivatives) with O<sub>2</sub>. Meanwhile, other well-characterized synthetic copper(I)

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