840 *Inorg. Chem.* **1997,** *36,* 840−845

EPR and ^{2}H NMR Studies on the Oxidation of Nickel(II) Tetraphenylcarbaporphyrin To Form Novel Organometallic Nickel(III) Complexes

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Received July 24, 1996[⊗]

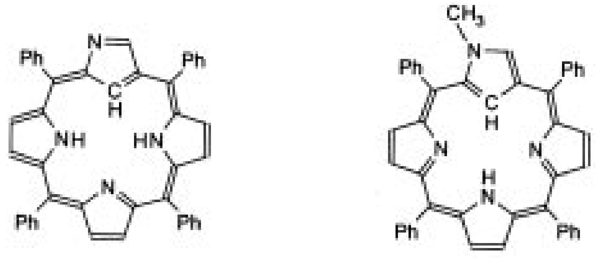
One-electron oxidation of nickel(II) 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin ((CTPP)Ni^{II}) and nickel(II) 2-methyl-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin ((MeCTPP)Ni^{II}) resulted in formation of rare organonickel(III) derivatives. The half-wave potential for the first oxidation of (CTPP)Ni^{II} and (MeCTPP)Ni^{II} equals 0.66 V and 0.72 V, respectively (*vs* SCE, CH_2Cl_2 solution, TBAP). The EPR spectral patterns of the one-electron-oxidized species have been determined at 293 and 77 K. In both temperatures the spectral parameters markedly depend on the axial ligand introduced by oxidants or in methathesis. In each case the spin-Hamiltonian parameters ($g_{av} > 2.1$ (77 K) or $g_{iso} > 2.1$ (293 K)) reveal a metal-centered oxidation rather than a cation radical formation ($g_{iso} \approx 2.002$). The localization of the one-electron oxidation on the nickel ion has been supported by the observation of ^{61}Ni hyperfine splitting. The ^{2}H NMR investigations, carried out for pyrrole deuterated derivatives: (CTPP-d_7)Ni^{III}Br, (CTPP-d_7)Ni^{III}(NO$_3$), and (Me-d_3-CTPP)Ni^{III}OH, confirmed independently by the nickel(III) electronic structure.

Introduction

Organometallic nickel(III) complexes are extremely rare.[1] To our knowledge the only previously reported examples of a nickel(III)−carbon bond were observed for nickel(III) complexes of a terdentate “pincer” N,C,N′-coordinating diamino monoanionic aryl ligand having bis(*o*-dimethylamino) substituents ($C_6H_3(CH_2NMe_2)$-*o,o*′). This tridentate molecule is able to form organometallic compounds with a Ni^{III}−C$_{aryl}$ σ-bond.[2] Moreover, the organonickel(III) species were previously considered as transient species in reaction mechanisms including the oxidative addition of aryl or alkyl halides to Ni(0) substrates[3] and the Karasch addition reaction of polyhalogenoalkanes to an olefinic double bond.[4] Nickel(I) macrocyclic complexes seem to react also with alkyl halides *via* Ni^{III}−alkyl intermediates.[5] Analogous organonickel(III) species were considered in the process of the pulse radiolysis.[6] It was also suggested that the last step of CH_4 formation in methanogenic bacteria may involve a Ni(III)−methyl form in its catalytic cycle.[7]

Recently we reported on synthesis and structure of two stable organometallic Ni(II) complexes of inverted porphyrins which are isomeric with respect to tetraarylporphyrin or *N*-methyltetraarylporphyrin, namely 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin (CTPPH$_2$)[8] and 2-methyl-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin (MeCTPPH) (Chart 1).[8,9] One Ni−C and three Ni−N bonds are formed within the inverted tetrapyrrole macrocycle of (CTPP)Ni^{II} or (MeCTPP)Ni^{II}. Both macrocycles act as four-coordinate dianionic ligands enforcing coordination of pyrrolic carbon to nickel(II). Potentially CTPPH$_2$ may also serve as a trianionic ligand in a situation when all three inner protons are removed and there is no proton attached to the outer nitrogen.[8,10] In the case of MeCTPPH that contains only two inner protons (21-CH and 23-NH) the dianionic structure can solely occur.[9] Recently we have extended the class of carbaporphyrin by means of a remarkable (CTPP)Ni^{II} internal carbon methylation. The considered intermediates of the methylation mechanism also include oxidized nickel carbaporphyrin.[11]

Chart 1



CTPPH$_2$ MeCTPPH

Here we present the spectroscopic identification of the novel group of organometallic nickel(III) complexes where a nickel(III)−carbon bond is encapsulated by inverted porphyrin.

Experimental Section

Solvents and Reagents. ^{61}Ni was obtained as the metallic powder (90.4% enriched) from Techsnabexport and converted into anhydrous

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

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S0020-1669(96)00876-2 CCC: $14.00

$^{61}NiCl_2$. All solvents were thoroughly dried and distilled under nitrogen prior to use. Tetrabutylammonium cyanide (TBA)CN and bis(triphenylphosphine)nitrogen(1+) cyanide (PPN)CN were used as a source of the cyanide ligand.

Preparation of Compounds. 5,10,15,20-Tetraphenyl-2-aza-21-carbaporphyrin ($CTPPH_2$), methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (MeCTPPH), and 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin-d_7 ($CTPPH_2$-d_7; 80% deuterated at pyrrole positions) and their nickel complexes were prepared by previously elaborated routes.[8,9,11] 2-Perdeuteromethyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (Me-d_3-CTPPH) was obtained in the same way as MeCTPPH using CD_3I.

Oxidation Procedures. Oxidation was performed in the glovebox by addition of aliquots of dichloromethane solutions of Br_2, $[PyH]Br_3$,, Cl_2, I_2, $[PyH]_2Cr_2O_7$, and $(CH_3COO)_4Pb^{IV}$ to a solution of nickel(II) carbaporphyrin (concentration of 5×10^{-3} M) in dichloromethane. The progress of the process was followed by respectively ^2H NMR, EPR, or UV−vis spectroscopy. The double integrated EPR spectra were used to estimate nickel(III) concentration by means of comparison with the spectrum of stable radical TEMPO solution (5×10^{-4} M) recorded in identical conditions. The UV−vis spectra were also used to assure complete oxidation. The full conversion into the oxidized species was observed instantly after addition of 1 equiv of the oxidant. The exception was iodine for which only about 10% of the complex could be oxidized. When the solid oxidant (i.e. $(NH_4)_2Ce(NO_3)_6$, AgO, PbO_2) was used, the solution of nickel carbaporphyrin was stirred with slurry of the oxidant in dichloromethane. The EPR signal of the nickel(III) species appeared after few minutes but complete oxidation (no traces of nickel(II) carbaporphyrin bands in the UV−vis spectrum) was accomplished after 2 h of stirring, and then the solid material was removed by filtration through a sintered glass frit.

Instrumentation. EPR spectra were obtained with a Bruker ESP 300E spectrometer. The magnetic field was calibrated with a proton magnetometer and EPR standards. The microwave frequency (9.4−9.8 GHz) was measured by means of a Hewlett-Packard 5350B frequency counter. The applied microwave power was 10 mW, and the modulation amplitude was 0.6 mT. For the quantitative measurements, which involved a stable radical standard, the power and modulation amplitude were set at 0.8 mW and 0.1 mT, respectively. The EPR spectra were simulated assuming orthorhombic symmetry. In the spectra of samples enriched in ^{61}Ni the 10% ^{58}Ni contribution was taken into account in the simulation procedure. The details of the EPR simulation have been given elsewhere.[12]

^2H NMR spectra were measured on a Bruker AMX 300 spectrometer (^2H 46.06 MHz). Usually 10000 scans were accumulated with a delay time of 50 ms for each ^2H NMR spectrum. The spectra were collected over a 30 kHz band width with 4K data points. The signal to noise ratio was improved by a apodization of the free induction decay which induced typically 25−100 Hz broadening. The peaks were referenced against residual solvent resonances.

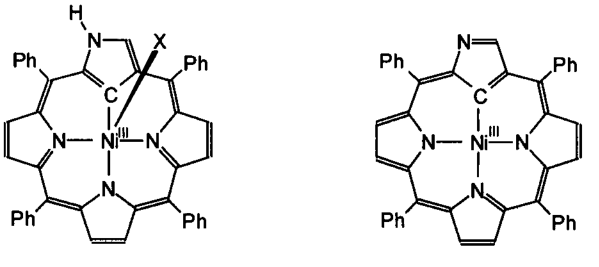
Absorption spectra were recorded on a diode array Hewlett-Packard 8453 spectrometer.

Electrochemical measurements were made in dichloromethane on a Bioanalytical System CV-50W apparatus with a platinum working electrode and silver reference electrode.

Results and Discussion

Electrochemical oxidation of $(CTPP)Ni^{II}$ in dichloromethane solution with 0.1M tetrabutylammonium perchlorate as supporting electrolyte shows a reversible oxidation at 0.66 V vs SCE. This value is located within a range 0.2−1.41 V (vs SCE, CH_2Cl_2 with TBAP) of analogous first oxidation potentials determined for nickel(II) porphyrins, nickel(II) chlorins, and nickel(II) β-oxoporphyrins.[13−15] For comparison the first oxidation potential of isomeric $(TPP)Ni^{II}$ occurs at 1.05 V (in CH_2Cl_2 vs SCE).[13] The oxidation of $(MeCTPP)Ni^{II}$ has been also examined. The methylated derivative undergoes one electron oxidation at 0.72 V, i.e. at the potential which is close to the one measured for $(CTPP)Ni^{II}$. For the likely metal-centered oxidation two modes of coordination by 21-carbaporphyrin can be taken into account as shown in Chart 2: dianionic **A** and trianionic **B**. A similarity of the first oxidation potential of $(CTPP)Ni^{II}$ and $(MeCTPP)Ni^{II}$ and reversibility of the redox process in the first case suggest that both inverted porphyrins act as the dianionic ligands. It also means that oxidation of the $(CTPP)Ni^{II}$ complex occurs without deprotonation of the outer nitrogen and an additional charge has to be compensated for by an anionic ligand (*vide infra*).

Chart 2



A **B**

A generation of nickel(III) complexes has been also accomplished *in situ* in dichloromethane solution by the chemical means using homogeneous (Br_2, $(PyH)_2Cr_2O_7$, $(PyH)Br_3$, I_2, Cl_2, $(CH_3COO)_4Pb^{IV}$), or heterogeneous ($(NH_4)_2Ce(NO_3)_6$, AgO, PbO_2) oxidants. At room temperature in dichloromethane solutions the one-electron oxidation products are stable enough to be investigated by spectroscopic methods. No nickel(III) EPR signal decay was observed for the fluid dichloromethane solution during 1 h. In the presence of the oxidant excess the respective spectra due to nickel(III) species have been observed after 1 week. However, attempts to isolate oxidized complex from the solution resulted in the product decay. Facile reduction to reform partially nickel(II) complexes appears to be a reason. In the presence of a proton scavenger (K_2CO_3) a slow oxidation of dichloromethane solution of $(CTPP)Ni^{II}$ by atmospheric dioxygen has been observed as well.

The oxidation processes are chemically reversible, and addition of typical reducing agents, e.g. sodium dithionite, results in a recovery of $(CTPP)Ni^{II}$ or $(MeCTPP)Ni^{II}$ respectively as examined by electronic and ^1H NMR spectra. The oxidation products have been concurrently characterized by UV−vis electronic spectra, EPR spectra, and ^2H NMR.

Figure 1 shows the representative comparison of the electronic spectra on nickel(II) carbaporphyrin and its one-electron oxidation product, i.e. $(CTPP)Ni^{II}$ and $(CTPP)Ni^{III}Br$. Oxidation results in a shift of the Soret and Q bands to lower energy. In addition Q bands have broadened. The similar changes have been found in the course of oxidation with other reagents.

The examined reactivity of the oxidized nickel(II) carbaporphyrin is summarized in Scheme 1.

The EPR spectra are particularly informative with regard to both electronic structure and ligation of the one-electron oxidation products (Figures 2 and 3 and Tables 1 and 2). The methathesis of $(CTPP)Ni^{III}Br$ to $(CTPP)Ni^{III}NO_3$ using $AgNO_3$ resulted in an EPR spectrum identical with one obtained by oxidation with $(NH_4)_2Ce(NO_3)_6$. Saturation of the dichloromethane solution of $(CTPP)Ni^{III}NO_3$ with water changes the **g** tensor values keeping general spectral pattern ($g_1 > g_2 \sim g_3 > 2.002$) unaltered. Addition of noncoordinating proton

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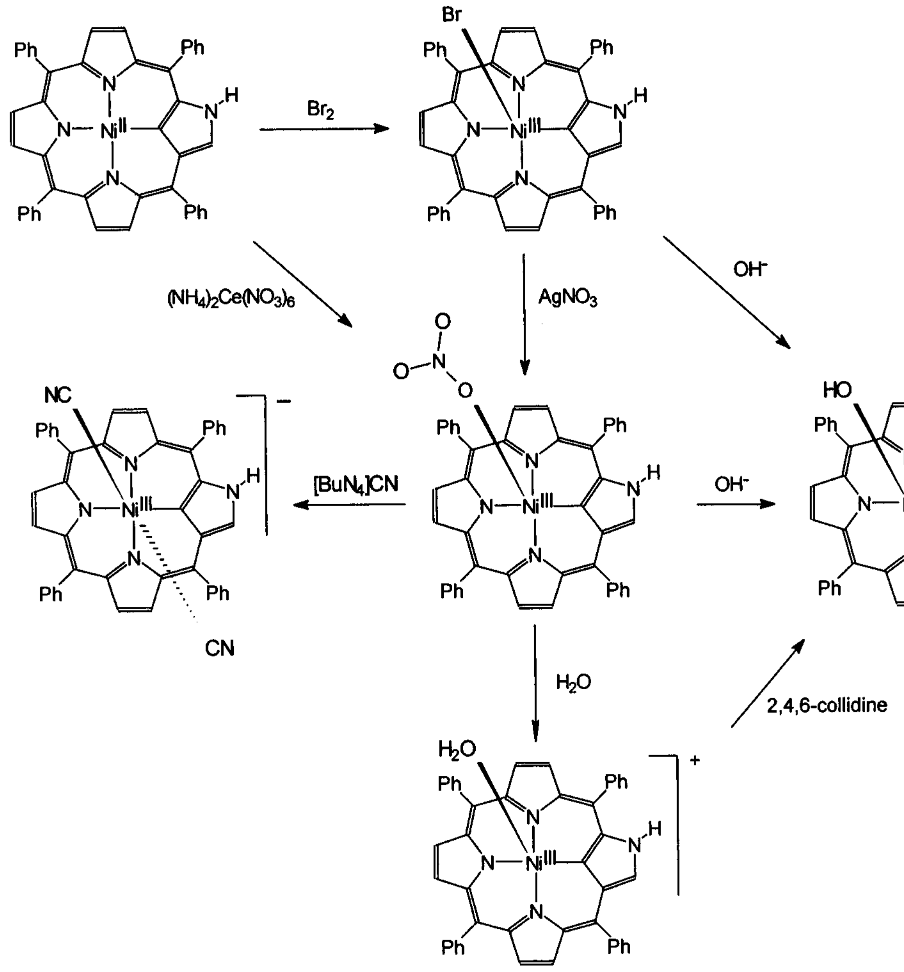
Scheme 1



scavengers, e.g. sterically hindered 2,4,6-collidine, to solutions of (CTPP)Ni^{III}NO$_3$ or (MeCTPP)Ni^{III}NO$_3$ in dichloromethane resulted in their conversion to the hydroxy (presumably five-coordinate) Ni^{III} complexes: (CTPP)Ni^{III}OH or (MeCTPP)Ni^{III}-OH. The hydroxy ligand can be generated in the reaction of proton scavengers with the residual water. Analogous species have been formed directly by addition of sodium hydroxide in methanol to the dichloromethane solution of (CTPP)Ni^{II}NO$_3$ or (MeCTPP)Ni^{III}NO$_3$. The hydroxy complexes produce the EPR spectra with the remarkable high rhombic distortion (trace C in Figure 2). The similarity of the EPR spectra of (CTPP)-Ni^{III}OH and (MeCTPP)Ni^{III}OH suggests that even in the presence of OH$^-$ in excess both macrocycles act as dianionic ligands. The hypothetical dissociation of 2-NH proton of (CTPP)Ni^{III} would create a trianionic equatorial ligand (structure **B** in Chart 2) and hence a complex of approximately square planar structure. In consequence modification of the EPR spectrum in comparison to that of (MeCTPP)Ni^{III}OH, where such a ligand transformation is not accessible, would be rationally expected.

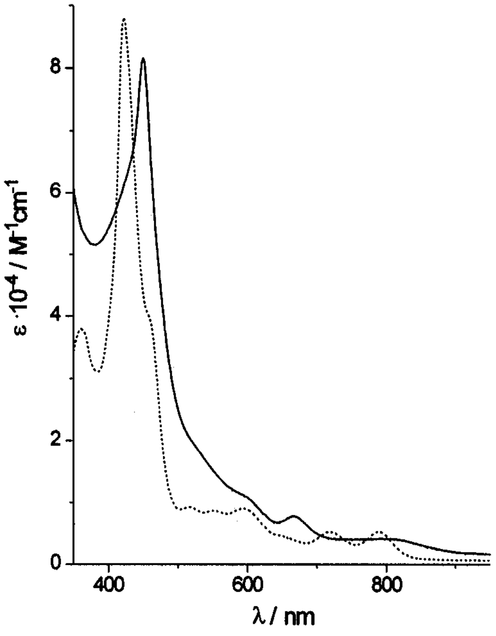


Figure 1. UV/vis absorption spectra (293 K, dichloromethane) of (CTPP)Ni^{III}Br (solid line) and (CTPP)Ni^{II} (dashed line).

Titration of (CTPP)Ni^{III}X with tetrabutylammonium cyanide ((TBA)CN) or bis(triphenylphosphine)nitrogen(1+) cyanide ((PPN)CN) in dichloromethane generates ([(CTPP)Ni^{III}(CN)$_n$]$^{1-n}$ species ($n = 1$ or 2) . The stoichiometry of the product could not be defined based on the EPR data. However, we have noticed that the EPR parameters are dependent on the choice of a countercation of cyanide applied. This observation is consistent with the ionic pair formation [(CTPP)Ni^{III}(CN)$_2$]TBA or [(CTPP)Ni^{III}(CN)$_2$]PPN. Consequently, it requires an axial coordination of two cyanides to obtain an anionic [(CTPP)-Ni^{III}(CN)$_2$]$^-$ fragment.

The EPR spectral patterns of the one-electron oxidized species differentiated by ligation have been determined at 293 and 77 K. In both temperatures the spectral parameters markedly depend on the axial ligand introduced by oxidants or in methathesis. In each case (Tables 1 and 2) the spin-Hamiltonian

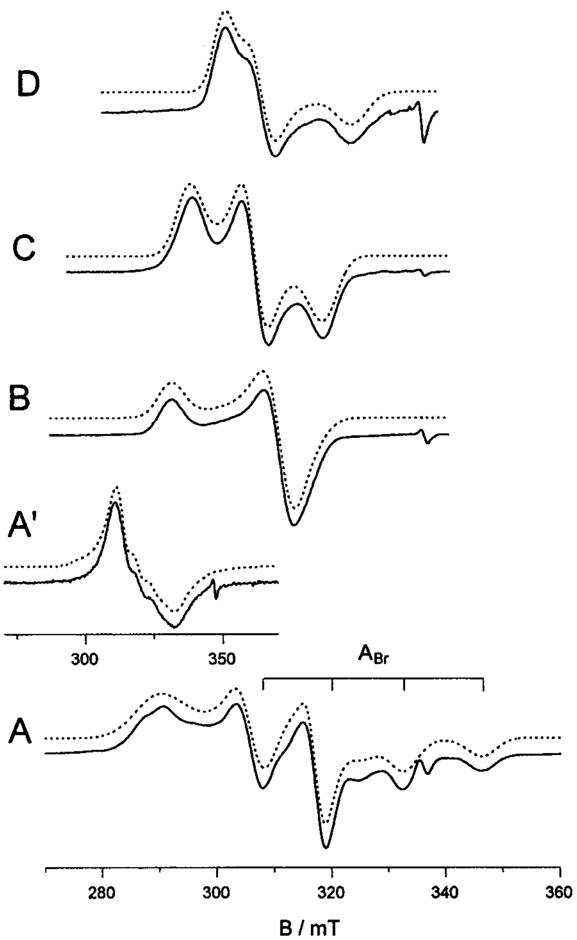


Figure 2. EPR spectra (X-band, 77 K, dichloromethane): (A) (CTPP)$Ni^{III}Br$; (B) (CTPP)$Ni^{III}(NO_3)$; (C) (CTPP)$Ni^{III}(OH)$; (D) [(CTPP)$Ni^{III}(CN)_2$]TBA. Inset in trace A presents the isotropic spectrum of (CTPP)$Ni^{III}Br$ at 293 K. The superhyperfine splitting with $^{79,81}Br$ is presented schematically. The solid lines correspond to the experimental spectra. The simulated spectra are shown as dashed lines. Conditions: microwave frequency, $\nu = 9.4175$ GHz for the anisotropic spectra and 9.7288 GHz for the isotropic spectrum; microwave power, 10 mW; modulation amplitude, 0.6 mT; modulation frequency, 100 kHz.

parameters ($g_{av} > 2.1$ (77 K) or $g_{iso} > 2.1$ (293 K)) reveal a metal-centered oxidation rather than a cation radical formation ($g_{iso} \approx 2.002$).[16,17] The localization of the one-electron oxidation on the nickel ion has been supported by analysis of ^{61}Ni hyperfine coupling. Enrichment of the representative species (CTPP)$Ni^{III}(OH)$, (CTPP)$Ni^{III}Br$, (CTPP)$Ni^{III}NO_3$, and [(CTPP)$Ni^{III}(CN)_2$]$^-$ into 90.4% ^{61}Ni ($I = {}^3/_2$) affords hyperfine splitting (Figure 3). The direct comparisons of (CTPP)$^{58}Ni^{III}X$ and (CTPP)$^{61}Ni^{III}X$ spectra illustrate an impact of the isotope replacement on the EPR spectral patterns although demonstrated only by noticeable broadening of EPR lines. The ^{61}Ni hyperfine coupling constants have been evaluated by simulation (Table 2). The measured values are rather small but in the range of those detected for the quite rare cases of $^{61}Ni^{III}$ compounds investigated till now by EPR.[18] On the other hand, the previously reported (TPP)$^{61}Ni^{III}$ did not present hyperfine splitting related features.[19]

Considering the low symmetry of the system under investigation the determination of the ground states in the observed nickel(III) d^7 complexes on the basis of g values and ^{61}Ni hyperfine splitting alone may be infeasible unless **g** and **A** tensors are unambiguously oriented with respect to a specific molecular axis system. In the extreme case of the axial symmetry for the low-spin d^7 nickel(III) the following electronic structures can be expected (in parentheses is given the order of **g** tensor values): planar $(d_{xz})^2(d_{yz})^2(d_{z^2})^2(d_{xy})^1d_{x^2-y^2}$ ($g_\perp < g_\parallel$), tet-

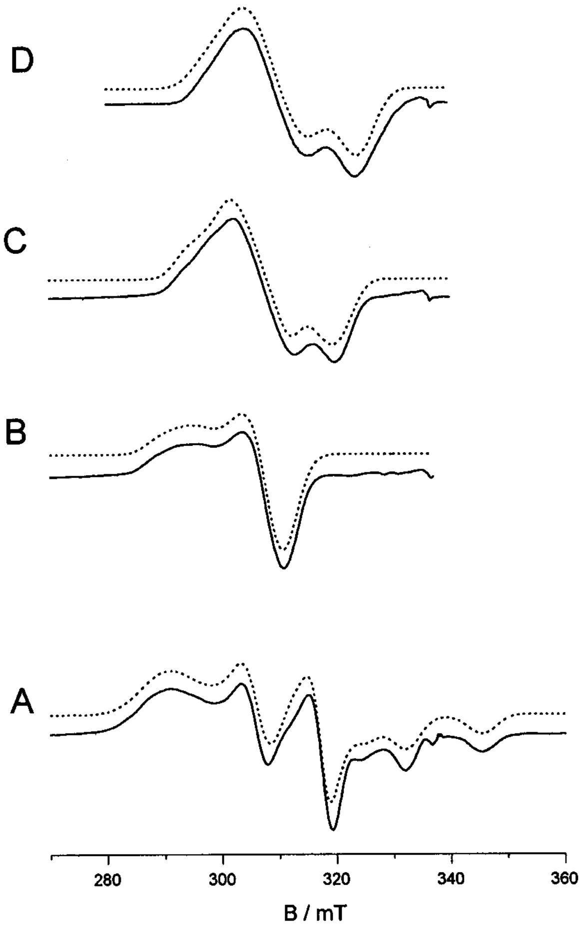


Figure 3. EPR spectra (X-band, 77 K, dichloromethane): (A) (CTPP)$^{61}Ni^{III}Br$; (B) (CTPP)$^{61}Ni^{III}(NO_3)$; (C) (CTPP)$^{61}Ni^{III}(OH)$; (D) [(CTPP)$^{61}Ni^{III}(CN)_2$]TBA. The solid lines correspond to the experimental spectra. The simulated spectra are shown as dashed lines. Conditions: microwave frequency, $\nu = 9.4344$ GHz; microwave power, 10 mW; modulation amplitude, 0.6 mT; modulation frequency, 100 kHz.

Table 1. EPR Parameters[a] of (CTPP)Ni^{II} and (MeCTPP)Ni^{II} Oxidation Products in Dichloromethane

L	g_1	g_2	g_3	g_{iso}
		(CTPP)Ni^{III}L		
Cl^-	2.386	2.146	2.088	2.187
Br^- [b]	2.344	2.128	2.068	2.160
I^- [c]	2.275	2.115	2.035	2.138
NO_3^-	2.307	2.163	2.145	2.233
H_2O	2.258	2.185	2.136	2.198
CH_3COO^-	2.296	2.192	2.048	2.147
OH^-	2.274	2.190	2.109	2.193
$CN^-[TBA]^+$	2.233	2.185	2.078	2.170
$CN^-[PPN]^+$	2.227	2.185	2.076	2.162
		(MeCTPP)Ni^{III}L		
Br^- [d]	2.334	2.128	2.068	2.158
NO_3^-	2.315	2.189	2.187	2.230
CH_3COO^-	2.293	2.193	2.046	2.145
OH^-	2.258	2.201	2.132	2.197

[a] Frozen solution spectra taken at 77 K; isotropic parameters measured at 293 K. [b] $^{79,81}Br$ hyperfine constants ($\times 10^4$ cm^{-1}): $A_1 \approx 23$, $A_2 \approx 3$, $A_3 = 126$, $A_{iso} = 54.6$. [c] ^{127}I hyperfine constants ($\times 10^4$ cm^{-1}): $A_1, A_2 \approx 10$, $A_3 = 165$, $A_{iso} = 60$. [d] $^{79,81}Br$ hyperfine constants ($\times 10^4$ cm^{-1}): $A_1 \approx 20$, $A_2 \approx 0$, $A_3 = 125$, $A_{iso} = 50.0$.

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Table 2. ^{61}Ni Hyperfine Constants ($\times 10^4$ cm^{-1}) of (CTPP)^{61}Ni^{III}L[a]

L	A_1	A_2	A_3	A_{iso}
Br^-	13.4	16.7	3.2	10.0
NO_3^-	28.3	5.2	13.3	7.5
OH^-	37.6	25.0	14.0	28.0
$CN^-[TBA]^+$	33.3	25.9	10.7	22.1

[a] Frozen dichloromethane solution spectra taken at 77 K; isotropic spectra taken at 293 K.

ragonally elongated octahedral symmetry $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^1d_{x^2-y^2}$ ($g_\perp > g_\| = 2.0020$), tetragonally compressed octahedral symmetry $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{x^2-y^2})^1d_{z^2}$ ($g_\perp < g_\|$).[16,17,20−22] If the rhombic field is involved, the observed large anisotropy of **g** and **A** may result from the extensive mixing of d_{z^2}, d_{xy}, $d_{x^2-y^2}$ orbitals and the g_z values reflects components of the extreme, e.g. $(d_{x^2-y^2})^1$ and $(d_{z^2})^1$, configurations.[17,20] The cases of such low symmetry systems that cannot be readily assigned to either of above ground states are well exemplified by (CTPP)Ni^{III}OH and [(CTPP)Ni^{III}(CN)$_2$]$^-$.

Coordination of bromide and iodide give orthorhombic EPR spectra which resemble those for roughly square pyramidal d^7 complexes[2] where both Zeeman parameter values and hyperfine splitting due to one apical Br$^-$ or I$^-$ ligand indicate the essential d_{z^2} orbital contribution to the SOMO.[2,16] On the other hand, EPR spectra of (CTPP)Ni^{III}NO$_3$ ((MeCTPP)Ni^{III}NO$_3$) and (CTPP)Ni^{III}H$_2$O reveal the $g_1 > g_2 \sim g_3 > 2.002$ relation. These observations may be accounted for by the presence of an unpaired electron on the molecular orbital which includes nickel d_{xy} and $d_{x^2-y^2}$ orbitals.[20−22] On this ground, the weaker axial ligation in relation to bromide (iodide) may be inferred, leading to a reverse order of d_{z^2} and d_{xy}.

Altogether the EPR results on nickel(III) carbaporphyrins are in contrast to the isomeric one-electron oxidation product of nickel(II) tetraphenylporphyrin,[19,23] which demonstrates the temperature dependent valence tautomerism in the presence of ClO$_4^-$ and PF$_6^-$:

$$\pi\text{-cation radical (TPP)Ni}^{II}\text{ (293 K)} \rightleftharpoons \text{low spin } (S = {}^1/_2)\text{ (TPP)Ni}^{III}\text{ (77 K)}$$

This equilibrium was shifted toward the radical in the presence of water or Br$^-$ or to nickel(III) when pyridine, THF, or CH$_3$CN were added.[23] In the case of investigated one-electron oxidized nickel carbaporphyrins the nickel(III) electronic structure exclusively prevails even in the presence of the identical potential ligands.

The ^{2}H NMR spectroscopy has been used as an independent probe to determine the nickel(III) carbaporphyrin electronic structure. The resonances of pyrrole protons of paramagnetic metalloporphyrins have been shown to be specially diagnostic in determination of their electronic states.[11,12,24] In particular, this can be very useful methodology in cases of the complex electronic structure in which metal ion and/or ligand orbitals are mixed in a fashion that is not easily categorized by conventional oxidation and electronic state assignments. The essential narrowing of analytically important resonances renders ^{2}H NMR spectroscopy particularly useful in detecting those paramagnetically broadened spectra which are not accessible in ^{1}H NMR. Such an approach can be complementary to the EPR studies.[12] Particular, it allows one to observe directly the spin density delocalization on the macrocycle. Considering EPR analysis three representative species, i.e. (CTPP-d_7)Ni^{III}Br, (CTPP-d_7)Ni^{III}NO$_3$, where all but 2-NH pyrrole protons are substituted with deuterium, and (Me-d_3-CTPP)Ni^{III}OH with a CD$_3$ group attached to the external nitrogen atom of the inverted pyrrole, have been selected for presentation (Figure 4). In the case of (CTPP-d_7)Ni^{III}Br all resonances assigned to the pyrrole deuterons are located within a region of 2−8 ppm that is consistent with the $(d_{z^2})^1$ formulation of the electronic ground state.[24] No spin density in the β-pyrrole positions is present since there is no overlap of the metal out-of-plane orbital with the ligand orbitals. All but one pyrrole peaks of (CTPP-d_7)Ni^{III}NO$_3$ are shifted downfield. They are widely spread covering a 0−50 ppm region. The similar, although definitely broader features have been found for (CTPP-d_7)Ni^{III}OH. The downfield shifts of the pyrrole resonances is indicative of σ-delocalization spin density and requires the considerable $d_{x^2-y^2}$ metal orbital contribution to the SOMO as determined already by EPR.

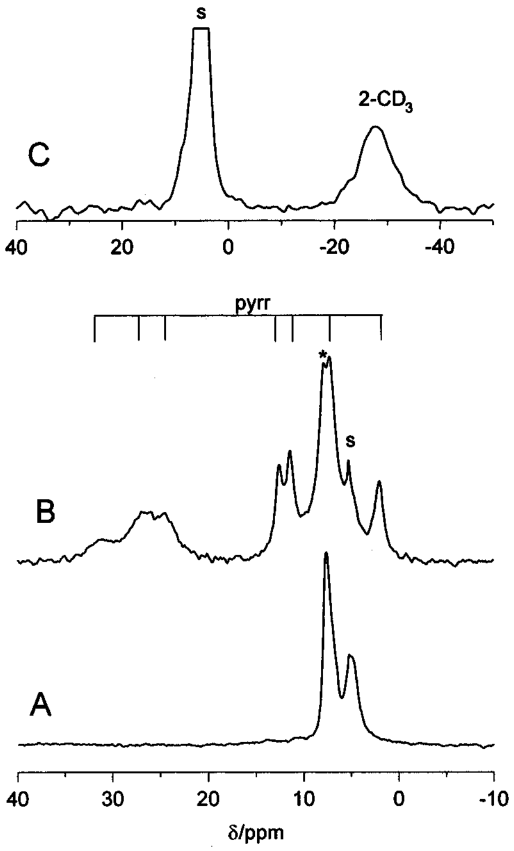

Figure 4. 46 MHz ^{2}H NMR spectra (298 K, dichloromethane): (A) (CTPP-d_7)Ni^{III}Br; (B) (CTPP-d_7)Ni^{III}NO$_3$; (C) (Me-d_3-CTPP)Ni^{III}OH. The labelling of seven pyrrole resonances of (CTPP-d_7)Ni^{III}NO$_3$ is marked schematically. An asterist denotes signal due to residual unoxidized nickel(II) species; s denotes a solvent peak.

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Considering the geometry imposed by the strict requirement of coordination by the inverted porphyrin and the established structures of the C-methylated derivatives, it seems unlikely that after the reversible one-electron oxidation the 21-C binding center may escape from the coordination to Ni^{III}. In the search for independent experimental evidence of coordination of the inverted pyrrole ring *via* 21-carbon we have resorted to ^2H NMR as well. We have assumed that the coordination may result in the noticeable paramagnetic shift of inverted pyrrole resonances but for these species where the essential contribution of $d_{x^2-y^2}$ orbital in the ground electronic state has been already determined, providing however that the Ni−C bond remains intact. Although we could identify all pyrrole resonances of (CTPP-d_7)Ni^{III}(NO_3) or (CTPP-d_7)Ni^{III}(OH) the necessary specific assignment of the analytically crucial 3-CD resonance remains at present beyond experimental reach. Conveniently we could probe the paramagnetic shift at the inverted pyrrole ring using the easily accessible (Me-d_3-CTPP)Ni^{II} as a substrate for oxidation. The representative ^2H NMR spectrum of (Me-d_3-CTPP)Ni^{III}OH is shown in trace C of Figure 4. The spectrum contains the single paramagnetically shifted 2-NCD_3 resonance at −28 ppm (293 K) with the line width equal to 330 Hz. The position of the 2-NCD_3 resonance is strongly dependent on the axial ligand. The 2-NCD_3 upfield shifted line of (Me-d_3-CTPP)-Ni^{III}(NO_3) has been found at −11 ppm (293 K) and is characterized by a smaller line width equal 110 Hz. The determined paramagnetic shift of the methyl group attached to the nitrogen of the inverted pyrrole ring is accountable for by the significant delocalization of the spin density onto this fragment of the macrocycle using the Ni^{III}−(21-C) bond as a vital element of the pathway.

In conclusion, the inverted porphyrins do stabilize the novel nickel(III) organometallic complexes, where the usually unstable Ni^{III}−carbon fragment is efficiently protected in the macrocyclic environment.

Acknowledgment. The financial support of the State Committee for Scientific Research KBN (Grant 3 T09A 14309) is gratefully acknowledged.

IC9608760