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Studies of the Reduction of the Nickel(II) Complex of 5,10,15,20-Tetraphenyl-21-thiaporphyrin To Form Corresponding Nickel(I) Complexes

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The divalent nickel complex of 5,10,15,20-tetraphenyl-21-thiaporphyrin Ni^{II}(STPP)Cl undergoes one-electron reduction ($E_{1/2}^{\circ}$ = −0.23 V) to give Ni^{I}(STPP). The product of the chemical reduction was isolated and characterized. It reacts with sulfur dioxide to give a paramagnetic five-coordinate Ni^{I}–SO$_2$ adduct and coordinates nitrogenous bases (amines, pyridines, imidazoles) to form respective five- and six-coordinate complexes. The nature of the reduced species and its adducts was examined by EPR spectroscopy. The ESR parameters are unique for Ni^{I} located in a four-donor macrocyclic environment. Typical values of the **g**-tensor components are as follows: Ni^{I}(STPP), g_1 = 2.109, g_2 = 2.040, g_3 = 2.030; Ni^{I}(STPP)(SO$_2$), g_1 = 2.187, g_2 = 2.087, g_3 = 2.075; Ni^{I}(STPP)(1,2-Me$_2$Im), g_1 = 2.414, g_2 = 2.247, g_3 = 2.114; Ni^{I}(STPP)(MeIm)$_2$, g_1 = 2.237, g_2 = 2.198, g_3 = 2.136. From the EPR spectra of Ni^{I}(STPP) oriented in liquid-crystal nematic glasses, the out-of-plane **g**-tensor component was determined. Coordination of nitrogenous bases switched the direction of the principal axis from the normal to the thiaporphyrin plane to the in-plane location. EPR parameters can be used to determine the axial ligation of Ni(I) in synthetic and natural (F-430 protein-bound) systems.

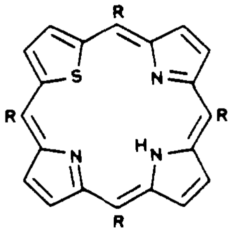
Introduction

A metal ion in the environment of a macrocyclic ligand is characterized by properties that are difficult to generate in simple coordination compounds. Particularly, kinetic and thermodynamic stability of the metal ion–macrocycle system lead to quite unexpected electrochemical and chemical properties. Often the macrocyclic ligand stabilizes metal ions in formal oxidation states that normally are not subject to isolation or study in other types of coordination compounds. This affords the opportunity to study the chemical reactivity and spectroscopic properties of uncommon oxidation states for series of structurally related ligands to establish systematically the influence of electronic and structural factors. A special effort was dedicated to the chemistry of Ni(I) in the tetraaza macrocyclic environment.[1] Mononuclear nickel(II) complexes of tetraaza macrocyclic ligands undergo one-electron reduction to give either nickel(I) species or species containing nickel(II) complexed to a ligand anion radical.[2–4]

Intramolecular electron transfer was also observed between metal and ligand.[1] Redox potentials are controlled by the cavity size and π conjugation within the ligand. Ni(I) tetraaza macrocycle species reduce alkyl halides to the respective alkanes and coordinate carbon monoxide.[4,5] The mechanism of alkyl halide reduction was studied electrochemically and by UV–vis spectroscopy.[5,6]

Stolzenberg and Stershic reported the formation and reactivity of nickel(I) octaethylisobacteriochlorin anion, [Ni^{I}(OEiBC)]$^{-}$.[7] Under similar conditions reduction of nickel(II) octaethylporphyrin leads to ligand reduction. The range of central cavity sizes readily accessible in these complexes and the reduction potentials of these macrocycles were proposed to determine the stabilization of Ni(I).

Recently, we have reported synthesis and characterization of a new macrocyclic ligand, 5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH), in which one of the pyrrole moieties of tetraphenylporphyrin is replaced by thiophene.[8]



This ligand coordinates a large variety of metal ions including nickel(II) to form five-coordinate Ni^{II}(STPP)Cl.[9] The most notable feature of the tetraphenyl-21-thiaporphyrin complexes is the nonplanarity of the thiaporphyrin ligand. The thiophene moiety is bent out of the plane of the thiaporphyrin. The bending opens up the center to accommodate the metal and allows the metal ion to interact with thiophene sulfur in a side-on fashion. Thus, thiophene is η^1-bonded to the metal through sulfur, which is pyramidal. The metal is situated out of the plane of three nitrogens in the direction of the apical chloro ligand.[7,8] The thiophene sulfur and chloro ligand are on different sides of the nitrogens' plane. The displacement from the N$_3$ plane depends directly on the ionic radius of the central atom. A tendency toward stabilization of lower oxidation states[10] including Ni(I) by thiaporphyrin could be expected.

In the present work we wish to present the results of our studies on chemical and electrochemical reduction of Ni^{II}(STPP)Cl. EPR spectroscopy is a definitive method for detecting products of one-electron reduction of nickel(II) macrocycles, and it allows determination of the electronic structure of the product.[1–4,7] The EPR spectra of Ni(I) species have been investigated far less than those of the isoelectronic d^9 copper(II),[11–15] since the Ni(I) complexes are much less common.[16–20] However, the relation between

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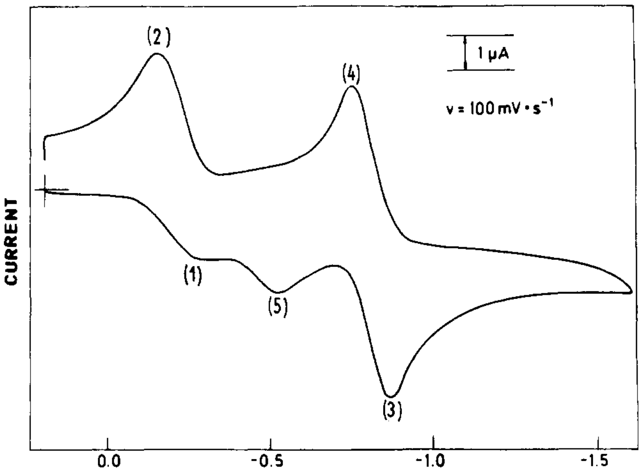
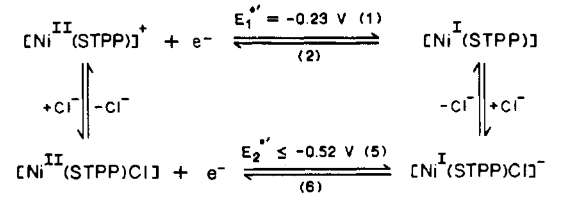


Figure 1. Voltammogram for 0.5 mM $Ni^{II}(STPP)Cl$ in 0.1 M TBAP/THF at 298 K. Potential scan rate is indicated. Numbers in parentheses refer to redox processes involved as described in equations.

Scheme I



the geometry and the EPR spectrum pattern seems to be clearly established.[12-20]

The recent interest in the chemistry of Ni(I) complexes is prompted by the fact that F-430,[21] a Ni(II) hydrocorphinoid complex,[22] is the prosthetic group of methyl coenzyme M reductase. This enzyme catalyses the reductive cleavage of *S*-methyl coenzyme M, 2-(methylthio)ethanesulfonate, to methane. On the basis of EPR data,[24] the importance of the Ni(I) form was proposed. It is likely that systematic studies of Ni(I) macrocyclic complexes, particularly of coordination by nitrogenous ligands, will shed light on the binding mode of F-430 by the apoprotein.

Results and Discussion

Electrochemical Reduction of $Ni^{II}(STPP)Cl$. In the potential range accessible in 0.1 M TBAP medium two anodic process occur on scan reversal after the three cathodic ones in the cyclic voltammogram of $Ni^{II}(STPP)Cl$ (Figure 1). The assignment of cathodic waves to a particular heterogeneous electron-transfer process was based on the analysis of peak current ratios vs potential scan rate and the initial concentration of the Ni(II) complex.

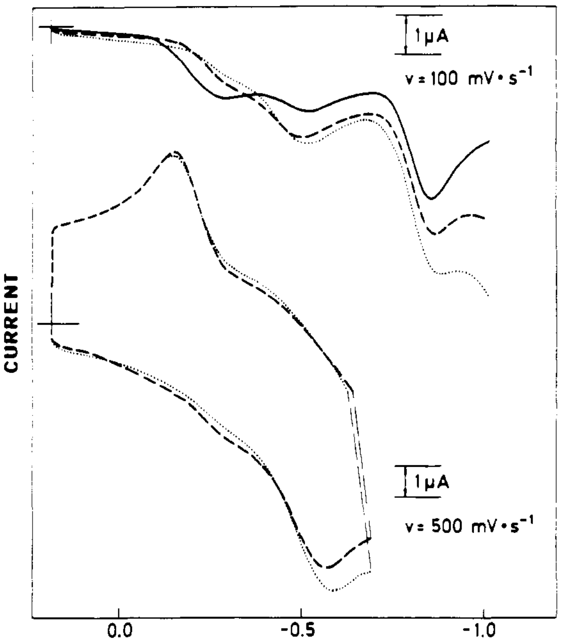


Figure 2. Effect of LiCl on voltammetric responses for $Ni^{II}(STPP)Cl$ in THF: —, no LiCl; - - -, $c_{LiCl}°/c_{Ni(STPP)Cl}° = 10$; ···, $c_{LiCl}°/c_{Ni(STPP)Cl}° = 40$. Potential scan rates are indicated. Other parameters are as in Figure 1.

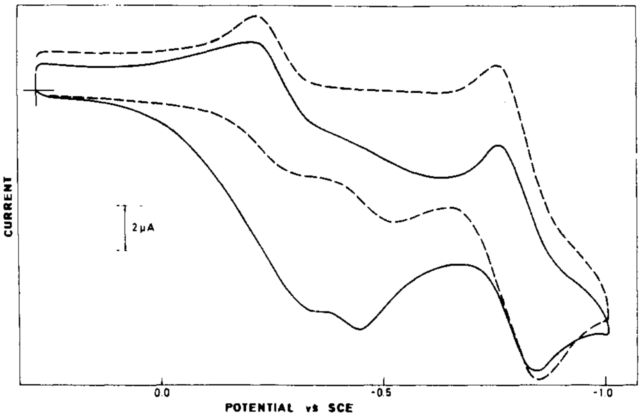


Figure 3. Effect of n-C_3H_7Cl on the voltammogram of $Ni^{II}(STPP)Cl$ in THF: - - -, no n-C_3H_7Cl added: —, after addition of n-C_3H_7Cl (1:5 molar ratio). The potential scan rate is 100 mV/s.

The reduction processes correspond to two succesive one-electron transfers. The voltammogram of $Ni^{II}(STPP)Cl$ in THF indicates the presence of two Ni(II) forms. The coupled chemical reactions are observed and the reduction–reoxidation sequence involves two separate oxidation–reduction pathways. Both one-electron-reduced species give rise to corresponding anodic scan current peaks although that at more negative potentials can be detected only at higher potential scan rate (500 mV/s), indicating a fast follow-up chemical reaction. On the basis of the potential values, the first electron addition of $Ni^{II}(STPP)Cl$ in THF is definitely localized on Ni(II) ion and corresponds to the Ni(II)/Ni(I) couple. The respective reduction potentials are located in the range not accessible for any thiaporphyrin-centered process (half-wave potentials for the first reduction and oxidation of the free-base STPPH in $C_2H_2Cl_2$ are equal, respectively −1.065 and 1.03 V[10]). The mechanism of the process is described as presented in Scheme I.

The reduction potential is located in the upper limit of half-wave potentials for a Ni^{II}/Ni^{I} couple in any macrocyclic[1-7] system in spite of the aromaticity of the $STPP^-$ ligand. Respective Ni^{II} porphyrins are not reduced on Ni^{II} but on porphyrin.[7,25] An

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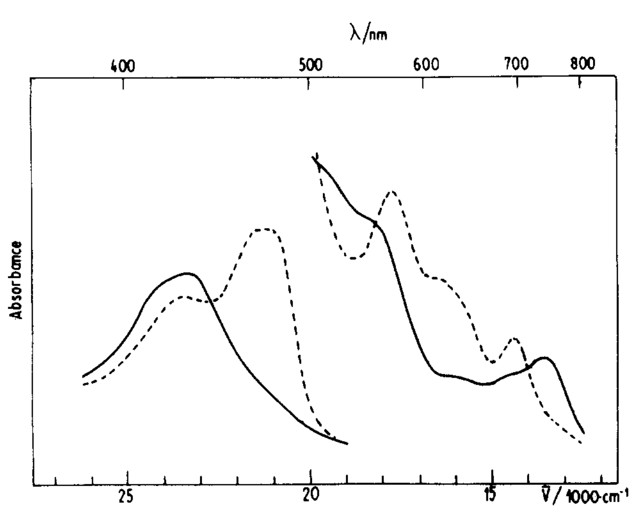

Figure 4. Electronic spectra of $Ni^{II}(STPP)Cl$ (---) and $Ni^{I}(STPP)$ (—) in toluene.

assignment of the waves to the particular species was obtained from a titration with lithium chloride in THF as a source of a chloride ligand (Figure 2). The dependence of the peak curents is consistent with the mechanism proposed.

The last cathodic wave (wave 3, Figure 1) can be considered as corresponding to a ligand-centered process according to the reaction

$$Ni^{I}(STPP) + e^- \underset{(4)}{\overset{E_3^{\circ\prime} = -0.82\ V\ (3)}{\rightleftharpoons}} [Ni^{I}(STPP^{\bullet -})]$$

The observed heterogeneous electron-transfer steps in the $Ni^{II}(STPP)Cl$ reduction exhibit quasi-reversible characteristics. The formal potential values reported here were determined as halfway between corresponding anodic and cathodic peak potentials at potential scan rates where coupled chemical reaction contributions could be neglected.

In view of the electrocatalytic activity of Ni(I) tetraaza macrocycles[5,6] and $[Ni^{I}(OEiBC)]^-$ species[7] toward alkyl halides we examined the reactivity of $Ni^{I}(STPP)$ toward alkyl halides. The changes in the voltammogram of $Ni^{II}(STPP)Cl$ resulting from the addition of n-C_3H_7Cl (PrCl) are presented at Figure 3. A significant current enhancement is observed at potentials characteristic for the Ni(II)/Ni(I) couple. The voltammogram characteristic could be accounted for by an ECE-type process.[26] This process involves the regeneration of the $Ni^{II}(STPP)Cl$ via the reduction of alkyl halide by electrogenerated Ni(I) species, which is similar to the reaction established for Ni^{I} tetraaza macrocyclic systems.[5,6]

The reactivity of chemically generated $Ni^{I}(STPP)$ toward propyl chloride, benzyl chloride, chloroform, and dichloromethane in benzene solutions were observed. The recovery of $Ni^{II}(STPP)$ was quantitative, as found by NMR and electronic spectra.

Chemical Reduction of $Ni^{II}(STPP)Cl$. Moderate reducing agents should be sufficient to generate nickel(I) tetraphenyl-21-thiaporphyrin species. Reduction by sodium anthracenide, sodium hyposulfite, sodium sulfite, ascorbic acid, zinc powder, or sodium thiosulfate produced $Ni^{I}(STPP)$. With sodium anthracenide the reduction can be carried out in homogeneous solution whereas with the other reductants the reaction was performed under heterogeneous conditions. The redox titration was conveniently followed by electronic spectroscopy (Figure 4) and isosbestic points were observed. $Ni^{II}(STPP)Cl$ underwent reversible, one-electron reduction to form $Ni^{I}(STPP)$. The spectrum of $Ni^{I}(STPP)$ is characterized by well-defined Soret and visible bands. The Soret band has a molar extinction slightly smaller than that of $Ni^{II}(STPP)Cl$ and is blue shifted. Similarly, the blue shift was observed on metal-based reduction of metalloporphyrins.[7] Identical electronic spectra were obtained when other reductants were used. Most of the reducing agents listed above are strong enough to put in the second electron. A stoichiometric amount (1:1) of reductant was employed and/or the reaction was stopped when one-electron reduction was accomplished as determined by UV-vis electronic spectra.

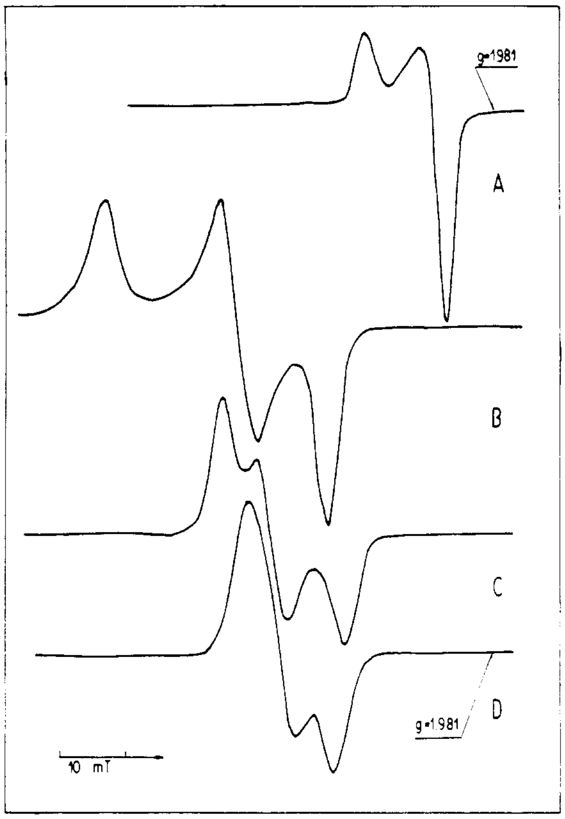

Figure 5. EPR spectra of $Ni^{I}(STPP)$–nitrogenous base systems in toluene (77 K, X-band): (A) $Ni^{I}(STPP)$; (B) $Ni^{I}(STPP)$–1,2-Me_2Im (1:10 molar ratio); (C) $Ni^{I}(STPP)$–piperidine (1:10 molar ratio); (D) $Ni^{I}(STPP)$–1-MeIm (1:10 molar ratio). No nitrogen hyperfine coupling was observed in the conditions of the experiment.

The EPR spectra of the reduction product unequivocally confirmed the $Ni^{I}(STPP)$ formulation. The frozen-solution ESR spectrum (Figure 5) corresponds to the nearly tetragonal symmetry ($g_z > g_x \simeq g_y$) that is considered typical for a d^9 electronic configuration, but the g values are less anisotropic then others reported for Ni(I) macrocyclic complexes. The magnetic moment of $Ni^{I}(STPP)$ as measured by the Evans technique in benzene solution at 300 K is 1.94 μ_B, as expected for d^9 electronic structure.

Reactivity of $Ni^{I}(STPP)$. Exposure of a toluene solution of $Ni^{I}(STPP)$ to sulfur dioxide results in the formation of $Ni^{I}(STPP)(SO_2)$. The characteristic EPR spectrum of the adduct is shown in Figure 6. The formation of this adduct is reversible. Exposure of the toluene solution of $Ni^{I}(STPP)(SO_2)$ to vacuum followed by repressurization with dinitrogen results in the loss of the adduct spectrum and the growth of the spectral features of $Ni^{I}(STPP)$. However, they do preserve nearly tetragonal symmetry. The anisotropy of the g tensor and the hyperfine coupling to three pyrrole nitrogens are consistent with the Ni(I) formulation. Attempts were made to quantitate the relative amounts of $Ni^{I}(STPP)$ and the SO_2 adduct under conditions where the signals from both species are observed. A toluene solution of $Ni^{I}(STPP)$ was titrated with toluene saturated with SO_2. A log–log plot of the ratio of the intensities of $Ni^{I}(STPP)$ and the SO_2 adduct (as measured by peak heights) vs SO_2 concentration resulted in the straight line with the slope 1.05 ∓ 0.06 (Figure 7). Accordingly, $Ni^{I}(STPP)$ coordinates one molecule of SO_2 to form $Ni^{I}(STPP)(SO_2)$ probably with a formation of a Ni^{I}–S bond:

$$Ni^{I}(STPP) + SO_2 \rightleftharpoons Ni^{I}(STPP)(SO_2)$$

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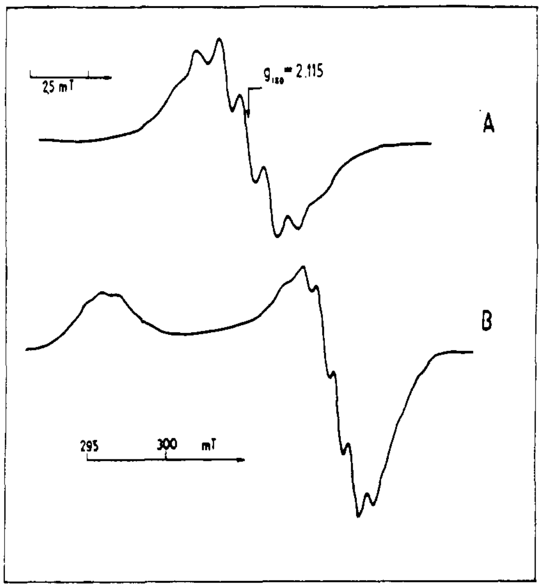

Figure 6. EPR spectra of $Ni^{I}(STPP)(SO_2)$ in toluene: (A) 298 K; (B) 77 K.

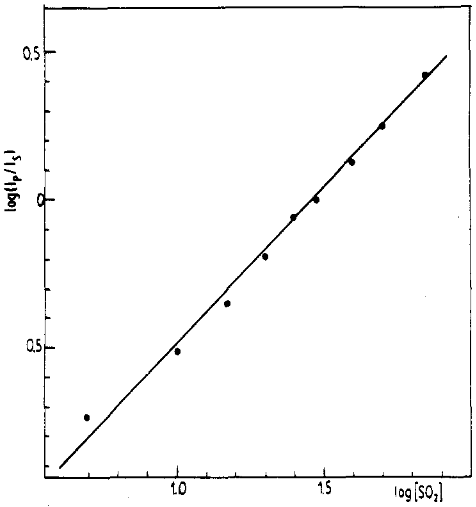

Figure 7. Log–log plot of the ratio of the intensity of the $Ni^{I}(STPP)$ signal vs the SO_2 concentration. The SO_2 concentration is given in arbitrary units related to the volume of the added, saturated toluene solution (298 K, in toluene).

To the best of our knowledge, this is the first experimentally confirmed case of SO_2 coordination to a Ni(I) center.[27] In contrast, $Ni^{I}(STPP)$ does not react with carbon monoxide or triphenylphosphine.

In toluene at 300 K, nitrogenous bases do not coordinate to $Ni^{I}(STPP)$, since the isotropic EPR spectrum is not altered. The measured g_{iso} value is that of $Ni^{I}(STPP)$ and is always smaller as compared to g_{av} calculated from anisotropic, low-temperature, frozen-solution spectra. However, at low temperatures in frozen-toluene glasses, evidence for coordination of amines has been obtained. Titration of the $Ni^{I}(STPP)$ toluene solution with 1-MeIm produces a growth of two sets of lines in frozen-solution spectra, while the spectrum of the starting species diminishes in intensity. The following process accounts for the spectroscopic experiment:

$$Ni^{I}(STPP) \xrightleftharpoons{\text{1-MeIm}} Ni^{I}(STPP)(1\text{-MeIm}) \xrightleftharpoons{\text{1-MeIm}} Ni^{I}(STPP)(1\text{-MeIm})_2$$

The five-coordinate $Ni^{I}(STPP)(1\text{-MeIm})$ form is characterized by a markedly large value of the **g**-tensor component ($g_1 = 2.421$).

Table I. ESR Parameters of $Ni^{I}(STPP)$ Complexes

compd	$g_{\text{in plane}}$	$g_{\text{in plane}}$	$g_{\text{out of plane}}$	g_{iso}
$Ni^{I}(STPP)$	2.030	2.040	2.109	2.062
$Ni^{I}(STPP)(SO_2)$	2.075	2.087	2.187	2.115
	9.84[a]	9.34[a]	11.51[a]	9.42[a]
$Ni^{I}(STPP)(1,2\text{-}Me_2Im)$	2.414	2.247	2.114	
$Ni^{I}(STPP)(Im)$	2.421	*b*	*b*	
$Ni^{I}(STPP)(MeIm)$	2.421	*b*	*b*	
$Ni^{I}(STPP)(2,4\text{-}Me_2py)_2$	2.417	*b*	*b*	
$Ni^{I}(STPP)(py)_2$	2.264	2.212	2.128	
$Ni^{I}(STPP)(4\text{-}CNpy)_2$	2.270	2.223	2.123	
$Ni^{I}(STPP)(4\text{-}CHOpy)_2$	2.269	2.224	2.127	
$Ni^{I}(STPP)(3\text{-}CNpy)_2$	2.269	2.219	2.127	
$Ni^{I}(STPP)(3\text{-}Clpy)_2$	2.268	2.219	2.127	
$Ni^{I}(STPP)(3,4\text{-}Me_2py)_2$	2.257	2.210	2.151	
$Ni^{I}(STPP)(2,4\text{-}Me_2py)_2$	2.262	2.233	2.131	
$Ni^{I}(STPP)(n\text{-}BuNH_2)_2$	2.241	2.183	2.136	
$Ni^{I}(StPP)(s\text{-}BuNH_2)_2$	2.244	2.193	2.138	
$Ni^{I}(STPP)(pip)_2$	2.267	2.207	2.129	
$Ni^{I}(STPP)(Im)_2$	2.237	2.207	2.143	
$Ni^{I}(StPP)(MeIm)_2$	2.238	2.198	2.136	

[a] Superhyperfine coupling constants in cm^{-1} 10^{-4}. [b] Overlapped with bisadduct lines.

The corresponding line is shown at lower concentration of 1-MeIm and vanishes at the larger ligand concentration. To confirm this assignment, we used 1,2-dimethylimidazole, i.e. the derivative which prefers five-coordination in metalloporphyrins. Because of the 2-methyl substitution, one can expect the lowered stability of the bisadduct. The five-corordinate $Ni^{I}(STPP)(1,2\text{-}Me_2Im)$ complexes produce EPR spectra with remarkable high rhombic distortion, as shown in Figure 5.

We can conclude that the number of nitrogenous bases coordinated determine the ESR spectral pattern. This conclusion is supported by the ESR spectra of a large variety of $Ni^{I}(STPP)(\text{nitrogenous base})_n$ (n = coordination number) complexes (Table I). Such factors as basicity, σ-donor and π-donor or π-acceptor properties, which are drastically different for these studied ligands, seem to play a minor role in determination of the electronic structure of Ni(I) in the system under discussion. The **g** tensor is determined mainly by the coordination geometry of Ni(I), which is defined by nitrogen and sulfur donors (vide infra).

ESR Spectral Analysis. The previous presentation clearly demonstrated the existence of three definitely different ESR spectral parameters for a $Ni^{I}(STPP)$ unit with a different axial ligand environment. Precise X-band ESR measurements of nickel(I) tetraphenyl-21-thiaporphyrin complexes in frozen glasses and in frozen ordered nematic phases provided some basis for the determination of the electronic ground state.

To provide a basis for the preliminary determination of the g-tensor orientation with respect to the molecular coordinate system, the ESR spectra were obtained in frozen oriented nematic phases. The basic principles of this technique were reported and applied for copper(II), vanadyl, cobalt(II), and silver(II) in planar or tetragonal-pyramid coordination geometry.[28-32] This technique is based on the property of nematic liquid crystals to be aligned in a magnetic field with the long axis of the liquid crystal molecules parallel to the applied field. A roughly planar solute molecule is aligned sympathetically with the long axis parallel to the nematic solvent long axis. This alignment is maintained as the sample is frozen. The shape of the molecule determines the alignment. For convenience the metalloporphyrin can be treated as a planar disk with a 20-Å o.d., as estimated from the HGV model.[33] The

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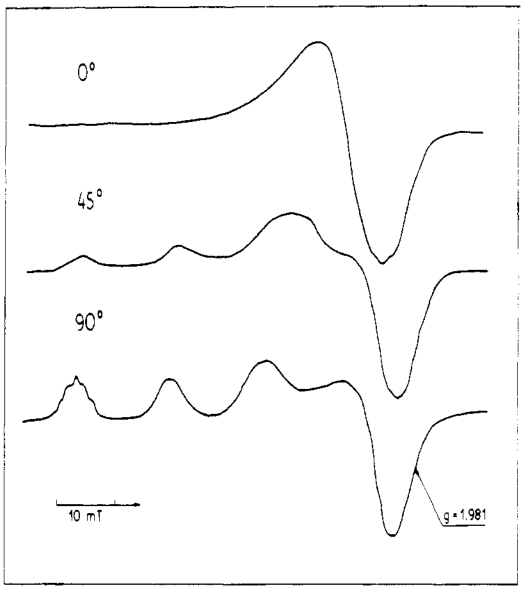

Figure 8. EPR spectra of $Cu^{II}(STPP)Cl$ in the frozen oriented nematic phase of the liquid crystal at 77 K. The orientation of the sample is indicated.

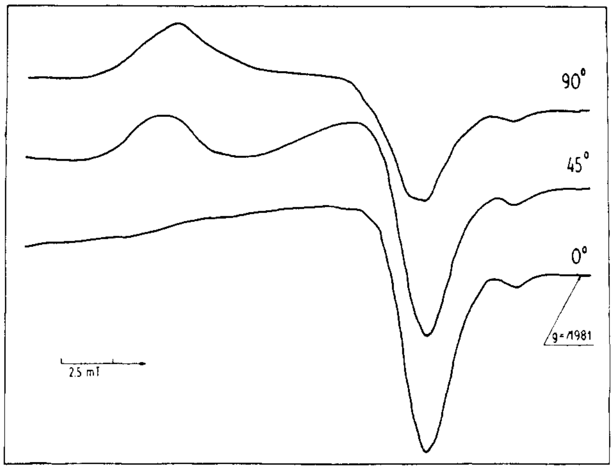

Figure 9. EPR spectra of $Ni^I(STPP)$ in the frozen oriented nematic phase of the liquid crystal at 77 K. The orientation of the sample is indicated.

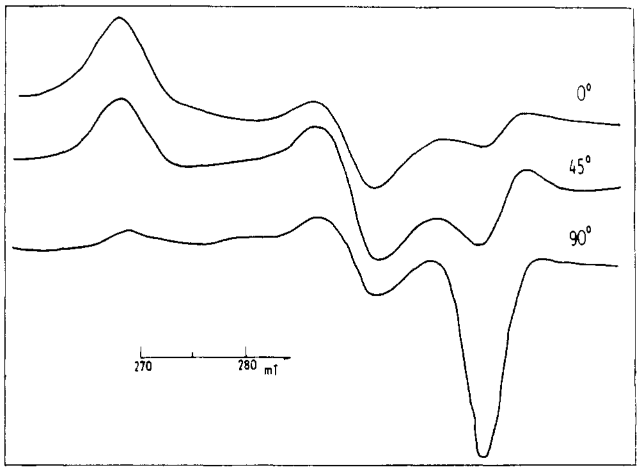

Figure 10. EPR spectra of $Ni^I(STPP)(1,2\text{-}Me_2Im)$ in frozen oriented nematic phase of the liquid crystal at 77 K. The orientation of the sample is indicated.

thickness of the disk is determined by the axial ligand dimensions. The ratio of the thickness to the diameter reflects the degree of planarity and can be used to predict qualitatively the expected orientation of the system in the nematic mesophase. The planarity coefficients are 0.150, 0.355, and 0.710 for $Ni^I(STPP)$, $Ni^I(STPP)(1.2\text{-}Me_2Im)$, and $Ni^I(STPP)(1\text{-}MeIm)_2$, respectively, and this suggests some orientation for each case under discussion.

In order to confirm the orientation of metalloporphyrins in the nematic mesophase, the EPR spectra of $Cu^{II}(STPP)Cl$ were reexamined.[10] The spectra in Figure 8 demonstrate the effect of metalloporphyrin orientation on the EPR spectra. Similar studies on Fe(TPP)Cl and $[Fe(TPP)(1\text{-}MeIm)_2]^-$ gave an assignment of the *g* out-of-plane component identical with that from single-crystal studies.[35] Representative examples of $Ni^I(STPP)$ complexes are presented in Figures 9 and 10.

The ordered sample of $Ni^I(STPP)$ (0°) exhibits an absorption that must arise from the in-plane **g**-tensor components (Figure 9). At 90° $Ni^I(STPP)$ exhibits the strong absorption for the *g* out-of-plane component. The spectral pattern is close to that expected for nearly tetragonal symmetry of the d^9 electronic state, where $g_z > g_x, g_y$ (a *z* axis perpendicular to the thiaporphyrin plane). Interesting orientation effects occur for $Ni^I(STPP)(1,2\text{-}Me_2Im)$. The spectrum is definitely of the rhombic symmetry (Figure 10). Two signals that must correspond to two in-plane **g**-tensor components are observed at 0° orientation, and the unique absorption of the *g* out-of-plane component becomes apparent at the 90° placement. The residual *g* in-plane signals are also visible. On the basis of these data, we cannot orient, even approximately, two-in-plane **g**-tensor components with respect to molecular axis coordinates, as one cannot expect on the grounds of the geometrical consideration any strongly preferred orientation ion the thiaporphyrin plane with respect to the liquid-crystal alignment axis.

Ordered samples of $Ni^I(STPP)(1\text{-}MeIm)_2$ exhibit a single strong absorption in the 0° orientation. The signal arises from one of the *g* in-plane components uniquely oriented for the system studied. In the 90° orientation the complex exhibits absorption for both *g* out-of-plane and one in-plane components. However, it is not possible to distinguish between them on the basis of nematic phase spectra. The respective assignment has been made by an analogy to five-coordinate $Ni^I(STPP)(1,2\text{-}Me_2Im)$ species.

Influence of geometry on Ni(I) electronic structure studied by ESR spectroscopy was widely examined for the d^9 electronic configuration both theoretically and experimentally.[12-20,36-38] The porphyrin core of $Ni^I(STPP)$ should be similar to that found for $Ni^{II}(STPP)Cl$ (five-coordinate)[9] or $Rh^{III}(STPP)Cl_2$ (six-coordinate).[39] Each core has idealized C_s symmetry. Moreover, the idealized Ni(I) coordination geometry can be described as planar in $Ni^I(STPP)$, tetragonal pyramidal in $Ni^I(STPP)(1,2\text{-}Me_2Im)$, and tetragonal bipyramidal in $Ni^I(STPP)(1\text{-}MeIm)_2$, each with strong rhombic distortion in the porphyrin plane due to the sulfur coordination.

In the case of $Ni^I(STPP)$ and $Ni^I(STPP)SO_2$ the ESR spectra reflect approximately tetragonal symmetry with some small rhombic distortion. The **g**-tensor values are similar or slightly smaller than these of related Ni(I) macrocyclic systems.[2,3,7] Clear nitrogen hyperfine structure was determined on the features of $Ni^I(STPP)(SO_2)$ spectrum. In spite of the presence of structurally unequivalent nitrogens, both isotropic and anisotropic spectra are described by a coupling to three effectively equivalent nitrogens. The strongly rhombic spectra of five-coordinate and six-coordinate nitrogenous base $Ni^I(STPP)$ complexes demonstrated the peculiar features that are typical of a very low symmetry environment with extensive mixing of different d orbitals in the electronic ground state.[12-16,36-38]

For the coordinate system with *z* axis perpendicular to the porphyrin plane and the *x*,*y* axes lying in the porphyrin plane,

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one can take as a ground state the linear combination of two orbitals: $(\sin \alpha)d_{x^2-y^2} - (\cos \alpha)d_{z^2}$, where sin α and cos α reflect the mixing. Since the procedure for evaluating these coefficients requires knowledge of metal-hyperfine coupling constants,[36] which are not available in this Ni^I system, we were unable to obtain these coefficients. However, knowledge of the orientation of the out-of-plane **g** tensor leads to the qualitative description of the electronic ground state for $Ni^I(STPP)$.

The EPR spectral pattern of $Ni^I(STPP)$ and $Ni^I(STPP)(SO_2)$ is that expected for a $d_{x^2-y^2}$ molecular orbital with some admixture of d_{z^2}. The electronic ground state in two remaining strongly rhombic cases is described in the identical way, but after interchanging the x (y) and z axes. These results are the direct consequence of the strong dissymmetry of the in-plane ligand field produced by tetraphenyl-21-thiaporphyrin.

The physical meaning is that upon axial coordination the direction of the principal axis can swich from the normal to the thiaporphyrin plane into the thiaporphyrin plane. A similar phenomenon was observed by Attanasio et al.[37] for copper(II) hemiporphyrazine complexes and Margerum et al. for nickel(III) bis(dipeptido) complexes.[38]

Concluding Remarks. An EPR signal was recently detected in whole cells of *Methanobacterium thermoautotrophicum*, which was attributed to the nickel ion of coenzyme F-430 in either the monovalent or trivalent state.[24] The same signal was found in purified methyl coenzyme M reductase. The in vivo spectra ($g_1 = 2.223$, $g_2 = 2.168$, $g_3 = 2.154$; $g_1 = 2.24$, $g_{2,3} = 2.025$; $g_1 = 2.284$, $g_2 = 2.231$, $g_3 = 2.175$) are of a type different from that of isolated nickel(I) containing F-430M (coenzyme F-430 is the hydrocorphinoid nickel(II) complex) ($g_1 = 2.250$, $g_2 = 2.074$, $g_3 = 2.065$), the latter shows much more pronounced axial anisotropy.[24,40] As a matter of fact the g_3 value of protein-bound F-430 is larger than any g_3 values established previously for isolated F-430, nickel(I) tetraaza macrocycle, or recently reported $[Ni^I(OEiBC)]^-$ systems.[2-4,7,40] The similar set of g_i values was demonstrated for Ni^I complexes with phosphines of relatively low symmetry,[16,19] for a Ni^I complex of a quinquedentate macrocycle,[41] and for Ni^I(catenate).[42] The EPR spectra of $Ni^I(STPP)$ complexes in a large variety of coordination environments seem to be unique in this feature for any Ni(I) complex of a four-donor macrocyclic system.

We demonstrated that a selective choice of axial ligands is sufficient to provide a set of ESR parameters that closely resemble those found for the enzyme-bound F-430 with Ni^I oxidation state. Two nitrogenous bases coordinated axially are required to convert an axial symmetry ESR spectrum into that which mimics the enzyme-bound nickel(I)-containing F-430 one. In the native enzyme environment F-430 exists as a hydrocorphinoid nickel(II) complex with axial ligation possibly to protein residues as established by means of X-ray absorption edge, EXAFS,[43] and Raman spectroscopy data.[44,45]

The EPR studies presented in this paper evidently relate the EPR spectrum pattern to the Ni^I axial coordination in the macrocyclic environment, Jaun and Pfaltz[40] suggested that striking differences between ESR spectra of isolated and protein bound F-430 (Ni^I) result from the axial coordination of Ni^I protein in the second case. Our results strongly support this hypothesis. The EPR spectral pattern for Ni^I macrocyclic systems including thiaporphyrins presents a useful probe for detecting the characterizing Ni^I species, particularly intermediates in enzyme environments. The structural differences between $Ni^I(STPP)$ and F-430 suggest, however, that such comparisons must be carefully evaluated.

The reduction potential of the $Ni^{II}(STPP)^+/Ni^I(STPP)$ couple is considerably positive of that of F-430,[40] nickel(II) tetraaza macrocyclic complexes,[1-6] nickel(II) octaisobacteriochlorin,[7] or nickel(II) porphyrins.[25] As suggested previously,[1,2,7] the range of available core sizes of these macrocycles should be one of the major factors that stabilizes the Ni(I) oxidation state. The structural aspects of the $Ni^I(STPP)$ coordination are presently under investigation.

Experimental Section

Chemicals. All common solvents were thoroughly dried and distilled under argon prior to use. Sodium anthracenite was synthesized as previously described.[46] Nitrogenous bases 2,4-lutidine (2,4-Me_2py)(Riedel Dekaen AG), 3,4-lutidine (3,4-diMepy)(Fluka), 2-chloropyridine (2-Clpy), 3-chloropyridine (3-Clpy), pyridine (py), 4-cyanopyridine (4-CNpy), 3-cyanopyridine (3-CNpy), piperidine (pip), pyridine-4-carbaldehyde (4-CHOpy), 1,2-dimethylimidazole (1,2-Me_2Im), *N*-methylimidazole (1-MeIm), imidazole (Im) (all Merck), *n*-butylamine (*n*-$BuNH_2$), *sec*-butylamine (*s*-$BuNH_2$) (International Enzymes) were used as received. Sulfur dioxide was generated from sodium sulfite with sulfuric acid by a standard procedure. Tetra-*n*-butylammonium perchlorate was synthesized from tetrabutylammonium hydroxide (Fluka) and perchloric acid and recrystallized from pentane/ethyl acetate.

Synthesis of Tetraphenyl-21-thiaporphyrin. STPPH was synthesized according to strategy established by Lindsey et al.[47] for tetraphenylporphyrin. Benzaldehyde (10 mM), pyrrole (15 mM), 2,5-bis(phenylhydroxymethyl)thiophene[46] (5 mM) were added to deoxygenated dichloromethane (1000 cm^3). After addition of boron trifluoride etherate (0.4 cm^3 of a 2.5 M solution in dichloromethane) the reaction mixture was stirred in the dark. *p*-Chloranil (Fluka) (15 mM) was added and the solution was refluxed (1 h) and then taken to dryness under reduced pressure by rotatory evaporation. The product was dissolved in tetrachloromethane and chromatographed on a basic alumina column. STPPH was eluted with CCl_4 as the second (orange) fraction, evaporated to dryness, and recrystallized from chloroform/hexane. Yield: 19%. The electronic and ^1H NMR spectra match with those previously reported.[8] 5,20-Diphenyl-10,15-di-*p*-tolyl-21-thiaporphyrin (SDPDTPH) was synthesized in an analogous manner. In this case benzaldehyde was replaced by *p*-tolylaldehyde.

Synthesis of Ni^I(STPP). $Ni^{II}(STPP)Cl$ was synthesized as previously described.[9] $Ni^{II}(STPP)Cl$ (0.1 mM) was dissolved in hot ethyl acetate (60 cm^3). Sodium hyposulfite (500 mg) was dissolved in water (20 cm^3) and added to the $Ni^{II}(STPP)Cl$ solution. This mixture was energetically stirred (1 h). In the course of the reaction the green solution turned orange. The solid product was filtered off, washed five times with water, dried in vacuo for 8 h, and recrystallized from benzene/acetonitrile. All experiments were done under argon by use of Schlenk techniques. The yield was 72%.

Electronic spectra [λ, nm (log ϵ_{max})]: 419 (4.85) sh, 430 (4.87), 547 (3.98) sh, 625 (3.49) sh, 689 (3.50) sh, 740 (3.59). Ni^I(SDPDTP) was synthesized according to the above described procedure. Anal. Calcd for Ni^I(SDPDTP), $C_{46}H_{32}N_3SNi$: C, 77.05; H, 4.49; S, 4.47; N, 5.86. Found: C, 76.49; H, 4.51; S, 4.28; N, 5.78.

Instrumentation. Electronic spectra were recorded on Cary 14 and Specord UV–vis spectrophotometers. ESR spectra were obtained with a Radiopan SE/X spectrometer. Magnetic fields were calibrated with a proton magnetometer and ESR standards. The following conditions were routinely used to record the EPR spectra: microwave power 2–20 mV, modulation amplitude 1–5 G, frequency 9.17 GHz. The ESR spectra were simulated by assuming orthorhombic symmetry. The program summed spectra due to all possible orientation, weighted by the solid angle element, $-^1/_2[\Delta(\cos\theta)](\Delta\phi)$, and the orientation-dependent transition probability, which was calculated according to Aäsa and Vaängard[49] for each particular transition. The fitting procedure was based on Marquardt's method,[50] i.e. using the minimalization procedure with respect to square deviations of the theoretical and experimental signal intensities calculated for 150 or 250 field values.

The MBBA liquid crystal (MBBA = *N*-(4-methoxybenzylidene)-4′-butylaniline) was used as a solvent for Ni^I(STPP) complexes. The or-

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iented nematic glasses were obtained according to the method described by Fackler et al.[28] Samples were heated to obtain the isotropic phase and oriented in a magnetic field of 8000 G during the cooling to the nematic phase temperature range. In the next step the temperature was lowered to 77 K. Samples were rotated with respect to the perpendicular to the magnetic field axis to obtain an angular dependence of line intensities. The concentration of the samples used was 0.2 mg/cm^3.

Samples were deoxygenated directly in the ESR tube by bubbling with N_2 through Teflon tubing immersed in the sample and sealed with a septum cap. Solutions used for titration were deoxygenated as described by the syringe technique. Gastight syringes were used for titration. Positive pressure of N_2 was kept during addition of reagents. Toluene saturated with sulfur dioxide was used for titration to determine the stiochiometry of the adduct. Nitrogenous bases were added in toluene solutions.

Electrochemical measurements were performed in tetrahydrofurn with tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte. Cyclic voltammograms were recorded for the potential scan rate (v) ranging from 0.02 to 0.5 V s^{-1} by using apparatus described previously.[10] The Pt-disk working electrode, Pt-foil axiliary electrode, and SCE (NaCl ‖ 0.1 M TBAP/solvent) reference electrodes were applied. The system was thermostated at 298 K, and the inert-gas atmosphere (Ar, N_2) was kept during the experiments. A Jeol-PS-100 NMR spectrometer was used for magnetic susceptibility measurements by the Evans technique[51] with C_6D_6 solution, with the peak of tetramethylsilane used as a standard. Diamagnetic correction was obtained by using the published values for the constitutive corrections for $TPPH_2$[52] and Pascal's constants.

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Spectrophotometric Study of the Equilibria between Nickel(II) Schiff Base Complexes and Ammonium-like Cations or Sodium Tetraphenylborate[1]

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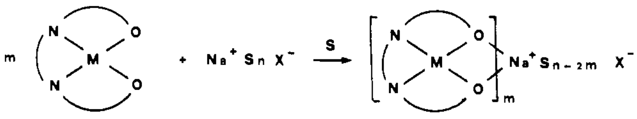
The formation constants of the chelate adducts originated from the interactions between [*N*,*N*′-ethylenebis(salicylideneaminato)]nickel(II) (Ni(salen)) and a series of ammonium-like cations and between bis(*N*-alkylsalicylaldiminato)nickel(II) (Ni(SB–R)$_2$; R = methyl, ethyl, isopropyl) and the sodium cation in acetonitrile were determined and compared. The general order of increasing stability of these adducts was correlated for the quadridentate Schiff base with the ability of the cations to form pairs of hydrogen bonding, while for the bidentate Schiff base it resulted dependent on the steric hindrance of the alkyl group. Two nonlinear least-squares programs were tested to determine the number of species in the solution and to estimate the stability constants.

Introduction

Quadridentate Schiff base metal complexes (M(SB)) with an N_2O_2 set of donor atoms can act as bidentate chelating ligands for inorganic and organic cations M'^{+} to generate polynuclear systems.[2] This can be exemplified by Scheme I, where O⌒N⌒N⌒O = salen and S = solvent.

We were attracted by the use of these "inorganic ligands" for complexing various cationic species,[2] by the change of the reactivity of the transition metal as a consequence of such complexation,[3] by the reactivity of the resulting polymetallic systems,[4] and by the use of cationic organic species as complex carriers in organic solvents. For this purpose we have recently started a study[5] of the equilibria between M(SB) and M'^{+} in different organic solvents. The stability and selectivity for cations acting like positively charged spheres were found to depend on the nature of the solvent and of the M(SB) complexes, on the charge of the cation, and on the balance of the electrostatic and steric factors, both conditioned by the O- - -O bite of the chelating ligand. The behavior of the NH_4^+ ion seems anomalous, and it is reasonable to assume that the anchoring of NH_4^+ to M(salen) is mainly regulated by the hydrogen-bond formation, in which the directional properties play an important role. This assumption is indirectly supported by the structural study of similar adducts in the solid state,[6,7] but nothing is known in solution. The aim of this paper is to evaluate the role of hydrogen bonding in the formation of these adducts and the different sequestering abilities of the quadridentate and bidentate Schiff bases. These chelate adducts with ammonium-like cations help to understand the biological processes involving organic molecules with the $\gtrdot NH^+$ functional group when hydrogen bonding plays an important role.

Scheme I



Experimental Section

Ni(salen) and Ni(SB–R)$_2$ (R = methyl, ethyl, isopropyl) complexes were prepared and purified according to the methods described in liter-

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