distinguished, that the protein has only a small overall negative charge on the 1–250 section of the protein relevant to this study. Examination of the sequence reveals pairs of positively charged residues at five places in the chain, and Willey et al.[11] speculate that these may well be brought together in the tertiary structure to form a positive patch that can interact with the negative patch on plastocyanin. Our quite independent evidence for a positive patch on cytochrome *f* first indicated in ref 14, is consistent with these observations.

Table V contains a summary of rate constants for the reaction of cyt *f*(II) with plastocyanin PCu^{II},[21,24,25] with proteins isolated from different sources. Assuming $\Delta H^* = 10$ kcal mol^{-1}, a rate constant of 2.1×10^7 M^{-1} s^{-1} at 10 °C increases to 5.1×10^7 M^{-1} s^{-1} at 25 °C. The rate constants listed will also show some variation with ionic strength as has been demonstrated in this study and elsewhere. The observation that PCu^{II} is some 30× more reactive with cytochrome *f* than with other (nonphysiological) cytochromes[25] is consistent with the high specificity of the two reactants for each other. The diffusion-controlled rate constants for such large molecules can be estimated as 10^9–10^{10} M^{-1} s^{-1},[24,25] which however ignores the need for the two proteins to be correctly oriented at the time of encounter. The rate constant observed is probably close to (or at) the limit possible for such a protein–protein reaction.

Structural features of plastocyanin indicated by Freeman[8,28] with the upper (north) surface of the protein hydrophobic may result in association of the protein at the thylakoid membrane surface. This could help in the orientation of the two proteins prior to electron transfer or, alternatively, could be relevant to the subsequent plastocyanin reduction of P700.

Adoption of a "dead-end" type of mechanism as an alternative to eq 9–11 is dependent on association (at the "east" site) completely inactivating the protein. Conformational change(s) that are close to 100% effective rather than an actual physical blocking of the binding site are required for this interpretation to hold. We keep an open mind on such possibilities (e.g., ref 2, p 183) but at present see no compelling evidence[8] for such an interpretation. Certainly we do not exclude small (possibly ~10%) contributions to reaction currently assigned to the Tyr-83 site as occurring at the "north" site. Reaction at the "north" site has the advantage of involving electron transfer to and from the Cu active site over a shorter distance. Reaction at the "east" site benefits from the extensive association due to more favorable electrostatic interactions that outweight the longer (approximately 2×) distance for electron transfer.

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Proton Nuclear Magnetic Resonance Characterization of Chloro(*N*-methyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) and Chloro(*N*-methyloctaethylporphyrinato)nickel(II) Complexes

LECHOSŁAW LATOS-GRAŻYŃSKI

Proton NMR studies of chloro(*N*-methyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) and chloro(*N*-methyloctaethyl-porphyrinato)nickel(II) complexes have been carried out. The full assignment of resonances has been achieved on the basis of selective deuteration and subsequent chloro and methyl substitution of phenyl rings. The characteristic pattern of pyrrole resonances (three downfield and one upfield) has been found. The temperature dependence of isotropic shifts demonstrated the essential deviation from the Curie law due to dipolar shift contribution arising from zfs. The isotropic shifts of pyrrole and *N*-methyl resonances are dominated by the σ-contact shift mechanism. The direct σ–π overlap mechanism has been proposed to account for the upfield shift of N-methylated pyrrole protons. The delocalization of spin density on phenyl rings via the π mechanism has been determined.

Introduction

N-Alkylporphyrins are formed as products of the interaction of cytochrome P-450 with a variety of substances.[1] This fact has drawn increasing interest toward the chemistry of N-substituted porphyrins and corresponding metal ion complexes. The nitrogen substitution influences to a large extent the structural and electronic properties of these complexes. Structural analysis undertaken via X-ray diffraction has clearly demonstrated a pronounced deviation from planarity, resulting from the nitrogen atom

substitution.[2] The *N*-methylporphyrin may serve as a model for the distorted porphyrins that incorporate the metal ion.[3–6] A coordination of some metal ions to *N*-methylporphyrins promotes the demethylation of the pyrrolic nitrogen and transfer of the CH$_3$$^+$ fragment to another nitrogen base present in solution.[7–10] This process should be essential in understanding alkyl fragment transfer within the porphyrin molecule.[11] Some complexes are

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strong alkylating agents that may show selective cytoxicity in case of leukemia diseases.[12]

In this report we present the result of ¹H nuclear magnetic resonance studies of chloro(N-methyl-5,10,15,20-tetraphenyl-porphyrinato)nickel(II) and chloro(N-methyloctaethyl-porphyrinato)nickel(II) complexes (Ni(N-CH₃(TPP))Cl and Ni(N-CH₃(OEP))Cl, respectively).

Valuable insight into magnetic and electronic properties of paramagnetic metalloporphyrins can be achieved by ¹H NMR spectroscopy.[14,15] The relation between the spectrum pattern, ligation, and electronic states has been well established in several paramagnetic metalloporphyrins.

The interest in high-spin Ni(N-CH₃(Por))Cl (Por = porphy-rinato) does not arise from their occurence in natural systems, which has not been reported, but rather from spectroscopic and theoretical considerations regarding the electronic properties of five-coordinate N-methylporphyrin complexes. This aspect of the studies has some relevance to iron N-alkylporphyrin systems. Particularly, the effect of N-methylation on the spin density distribution in the porphyrin skeleton has been a subject of interest. One has to note the characteristic patterns of ¹H NMR spectra observed for (vinylidenecarbene)(Por)Fe^{III}Cl and (N-CH₃-(Por))Fe^{II}Cl complexes.[13,16] The unusual downfield and upfield shifts of pyrrole resonances have been found for both systems mentioned above, but the mechanism of spin density delocalization has not been reported yet.

High-spin five-coordinate square-pyramidal Ni(II) porphyrin complexes are in a $d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{z^2}^1 d_{x^2-y^2}^1$ configuration. The Ni(II) complexes should yield information on the role of $d_{x^2-y^2}$ and d_{z^2} orbitals in the mechanism of spin density transfer in N-methylporphyrins. This mechanism is expected to be more complex as compared to that for metalloporphyrins with four equivalent nitrogens.

Experimental Section

1. Ligand Synthesis. Tetraphenylporphyrin derivatives (R)TPPH₂ were prepared by a literature method[17] based on a pyrrole–benzaldehyde condensation in propionic acid reflux (R = o-Cl, m-Cl, p-Cl, o-CH₃, m-CH₃, p-CH₃, and p-OCH₃). Octaethylporphyrin (OEPH₂, Aldrich) was used as obtained. Dimethyl sulfate was used as a powerful methylating agent. In a typical procedure 250 mg of (R)TPPH₂ was dissolved in 250 cm³ of 1,2-dichlorobenzene (EGA Chemie). The solution was refluxed and 1 cm³ of (CH₃)₂SO₄ (International Enzymes Ltd.) was added. The reaction mixture was refluxed for 1 h. The progress of the reaction was followed by the visible spectra. The solution was cooled down and neutralized with solid sodium carbonate. The solid residue was filtered off. The dichlorobenzene solution was chromatographed on acidic aluminia (I grade, POCh). The first band eluted with 10:1 v/v toluene–AcOEt correspond to unreacted (R)TPPH₂. N-CH₃(R)TPPH was eluted with CHCl₃ and crystallized from 1:1 v/v chloroform–ethanol. The yield of the procedure varies from 15 to 35% depending on porphyrin and on dimethyl sulfate concentrations. N-CH₃(OEPH) was synthesized in a similar manner. The identities of products were confirmed by their characteristic electronic and ¹H NMR spectra. Particularly, the N-CH₃ resonance of the neutral form at -4.1 ppm vs. Me₄Si (intensity of three protons) was observed for each derivative.[6]

2. Deuterated Derivatives.[18,19] TPP-d_8-H₂ (deuterated on β position) was prepared by refluxing of pyrrole in propionic-d acid (0.5 h) and the addition of benzaldehyde.[18] The product of the reaction was methylated by using the procedure described above. meso-tetradeuterated N-CH₃-
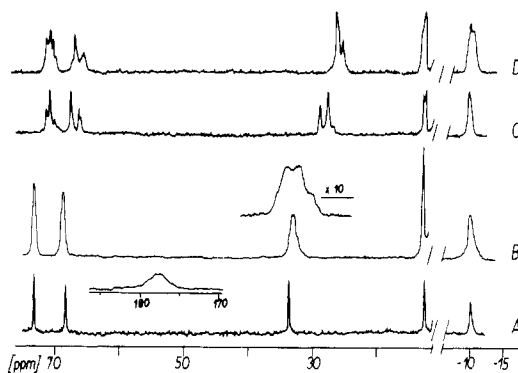
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Figure 1. ¹H NMR spectra of Ni(N-CH₃(R)TPP)Cl complexes (CDCl₃, -60 °C): (A) R = H; (B) R = m-Cl; (C) R = o-Cl; (D) o-CH₃. Only the pyrrole part is shown; the inset corresponds to the N-CH₃ resonance.
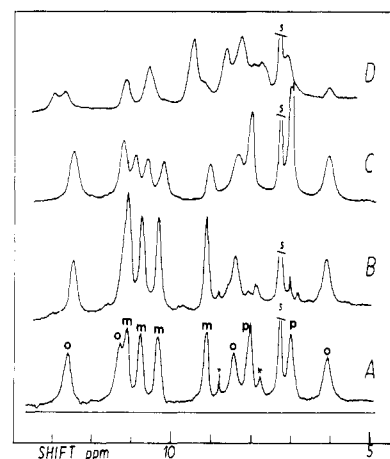

Figure 2. ¹H NMR spectra of Ni(N-CH₃(R)TPP)Cl complexes (CDCl₃, -60 °C): (A) R = H; (B) R = p-Cl; (C) R = m-Cl; (D) R = o-Cl. Only phenyl part is shown; s = solvent; * = impurities.

(OEP-d_4-H) was obtained as follows: N-CH₃(OEPH) (10 mg) was dissolved in 0.5 cm³ of D₂SO₄–D₂O (9:1 v/v) and the resultant mixture kept for 24 h. The solution was poured into ice water, extracted with chloroform, neutralized with K₂CO₃, and dried. The crude product was chromatographed on silica gel. The meso resonances disappeared in the ¹H NMR spectrum of N-CH₃(OEP-d_4-H).

3. Synthesis of Nickel(II) Complexes. The syntheses of Ni(N-CH₃-(R)TPP)Cl and Ni(N-CH₃(OEP))Cl complexes were carried out as described previously.[20] The product of the metalation was chromatographed on silica gel (250–400 mesh, Merck). The demethylation product (NiTPP) formed during the synthesis was eluted first by CHCl₃. A methanol–chloroform mixture (1:10 v/v) was used to elute quickly the unstable[9] Ni(N-CH₃(Por))Cl complex. The solution was evaporated under vacuum. Visible electronic spectra matched these reported previously.[6,9] ¹H NMR spectra have shown only small amount of diamagnetic NiTPP(R) in samples of Ni(N-CH₃(R)TPP)Cl.

4. Equipment and Sample Preparation. ¹H NMR spectra were measured on a JEOL PS 100 spectrometer operating in the pulse mode. A total of 300–1000 scans were taken, usually depending on concentration. The probe temperature was calibrated by Van Geet's method.[21] NMR samples were prepared by dissolving 1–3 mg of the complex to be studied in 0.5 cm³ of CDCl₃ (99.8%, IBJ). The respective amount of the complex was chromatographed directly before NMR measurements on the short column on silica gel as described above, evaporated to dryness, and dissolved in CDCl₃. The NMR samples were kept in a dry ice-acetone bath (-80 °C) to prevent demethylation, which is fast for N-methylporphyrin complexes of Ni(II).[9] All assignments have been made at -60 °C to avoid decomposition during spectrum acumulation.

Results and Discussion

Resonance Assignment. Ni(N-CH₃(R)TPP)Cl. ¹H NMR spectra of the Ni(N-CH₃(R)TPP)Cl complexes are essentially different from the metalloporphyrin spectra in any spin and ligation

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Table I. Proton NMR Resonances for Ni(N-CH$_3$(R)TPP)Cl

assgnt	$(\Delta H/H)^a$	$(\Delta H/H)_{iso}$	$(\Delta H/H)_{dip}$	$(\Delta H/H)_{con}$
pyrrole H12	−9.84	−18.12	7.72	−25.84
pyrrole H22	33.67	24.72	6.74	17.98
pyrrole H23	72.64	63.69	6.74	56.95
pyrrole H42	68.19	59.32	7.24	52.08
o-H16	8.44	−0.16	2.30	−2.46
o-H12	11.40	2.80	4.76	−1.96
o-H26	5.91	−2.57	1.70	−4.27
o-H22	12.74	4.14	5.80	−1.66
m-H15	10.39	2.39	1.41	0.98
m-H13	10.84	2.85	1.96	0.89
m-H23	11.23	3.23	2.21	1.02
m-H25	9.14	1.14	1.34	−0.20
p-H14,24	8.01	0.13	1.52	−1.67
p-H14,24	6.92	−1.85	1.60	−3.34
N-CH$_3$	177.8	182.0	−31.8	213.8
p-CH$_3$(Ph1,2)	6.00	3.30	1.12	2.18
p-CH$_3$(Ph1,2)	4.69	1.99	1.12	0.87
m-CH$_3$,23	4.35	1.65	1.56	0.09
m-CH$_3$,25	2.78	0.08	0.81	−0.73
m-CH$_3$,13	3.61	0.91	1.34	−0.43
m-CH$_3$,15	2.39	−0.31	0.87	−1.18
p-OCH$_3$	5.19	1.09	1.09	0
p-OCH$_3$	5.02	0.93	0.93	0

^{a} Zn(N-CH$_3$(R)TPP)Cl and N-CH$_3$(R)TPPH$_2$$^+$ have been used as diamagnetic reference (shift in ppm, −60 °C).
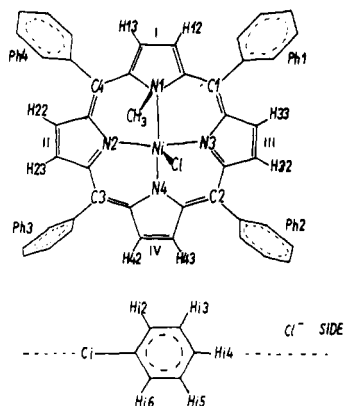

Figure 3. Molecular geometry and proton notation for Ni(N-CH$_3$(TPP))Cl.

state,[14,15,22] including Ni(TPP)(nitrogen base) systems as well[23] (Figures 1 and 2; Table I). The Ni(N-CH$_3$(R)TPP)Cl resonances are easily combined in three groups corresponding to the different parts of the ligand: i.e., pyrrole, N-methyl, and phenyl resonances.

The pyrrole resonances have been assigned by selective deuteration at the β-pyrrole position. Three of them are shifted downfield, and one unexpectedly is shifted upfield. The broadest resonance (line width 300 Hz) shifted strongly downfield with relative intensity corresponding to three protons could be unambiguously assigned to the N-CH$_3$ group. A more detailed assignment of the phenyl resonances has been achieved by selective chloro or methyl substitution of the phenyls (Figure 2). Thus, para proton resonances have been removed in the case of para substitution, and intensities of meta (ortho) resonances have been cut in half due to the respective meta (ortho) substitution. Simultaneously, methyl resonances could be identified (Table I).

The X-ray structure of Ni(N-CH$_3$(TPP))Cl has not been determined. However, one can safely assume a large similarity to the structure of Co(N-CH$_3$(TPP)) reported in the literature.[2] The schematic diagram of the molecular geometry is presented in Figure 3. The complex has a mirror plane passing through the N1, N4, and Cl atoms. Ph1, Ph4 and Ph3, Ph2 rings are respectively equivalent by symmetry. In every case when a metal

Table II. Axial Geometric Factors and r^{-6} Values Calculated for Ni(N-CH$_3$(R)TPP)Cl

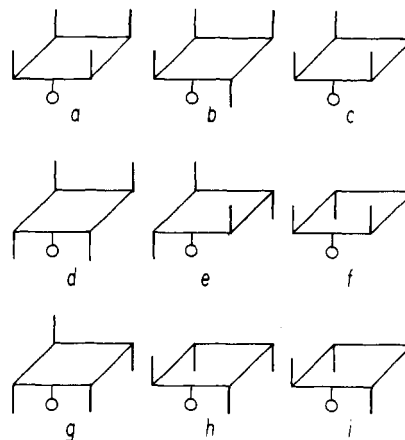| proton posn	GF, 10^3 Å^{-3}	r^{-6}, 10^5 Å^{-6}	proton posn	GF, 10^3 Å^{-3}	r^{-6}, 10^5 Å^{-6}
H12	−7.19	6.19	Ph25	−1.26	0.41
H22	−6.30	4.92	Ph24	−1.50	0.24
H23	−6.44	5.33	N-CH$_3$	29.8	117.5
H42	−6.77	5.53	p-CH$_3$(Ph1)	−1.06	0.12
Ph12	−4.44	3.52	p-CH$_3$(Ph2)	−1.11	0.13
Ph16	−2.15	2.69	m-CH$_3$,13	−1.26	0.29
Ph13	−1.84	0.43	m-CH$_3$,15	−0.82	0.23
Ph15	−1.33	0.37	m-CH$_3$,23	−1.47	0.35
Ph14	−1.43	0.21	m-CH$_3$,25	−0.76	0.27
Ph22	−5.45	4.75	p-OCH$_3$(Ph1)	−0.895	0.11
Ph26	−1.60	2.87	p-OCH$_3$(Ph2)	−0.959	0.11
Ph23	−2.07	0.52			

Figure 4. Schematic presentation of Ni(N-CH$_3$(TPP))Cl atropisomers.

ion undergoes a displacement from the porphyrin plane, the two ortho and two meta positions of each phenyl are nonequivalent in a limit of a slow phenyl rotation.[24] Hence, two ortho and two meta resonances should be observed for each symmetry-equivalent phenyl rings. The presence of 10 phenyl resonances is completely consistent with the expected structure of the complex.

The relative line width of the porphyrin resonances should vary as the relative values of r^{-6} (r = proton-to-Ni(II) distance) due to the dipolar mechanism of relaxation.[14] The r^{-6} values have been calculated from the Co(N-CH$_3$(TPP))Cl data[2] (Table II). The small differences in r^{-6} precluded the more detailed assignment of phenyl resonances based on the analysis of r^{-6}. An attempt has been made to differentiate pyrrole resonances. The structural data available for several N-alkylated complexes[2,25,26] clearly demonstrate a specific character of the N-alkylated pyrrole ring as the bond lengths, hybridization of nitrogens, and position of the pyrrole plane are different from the corresponding parameters for three other pyrrole rings. The only upfield pyrrole resonance could be assigned to the N-methylated pyrrole ring (H12), which should have a different mechanism of contact shift. The line width analysis confirmed that tentative assignment of the theoretical line width ratio as $r_{12}:r_{22}^{-6}:r_{42}^{-6}$ = 1.258:1:1.083:1.128 remains in good agreement with experimental one of 1.44:1:0.98:1.16. Substitution of the phenyl ring in the meta or ortho positions caused noticeable and specific changes of the pyrrole resonances (Figure 1). As the rotation of the phenyl groups is slow in the temperature range studied (vide infra), the meta (ortho) substitution leads to formation of atropisomers.[27–29]

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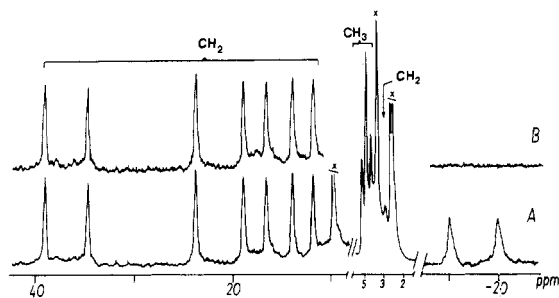
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Figure 5. ^1H NMR spectra of Ni(N-CH$_3$(OEP))Cl (A) and Ni(N-CH$_3$(OEP-d_4))Cl (B) complexes (–60 °C). A and B respectively.

Because of nonequivalence of two N-methylporphyrin planes eight atropisomers can be formed (optical isomers not included; Figure 4). Isotropic shift of pyrrole resonances should be slightly dependent on the isomer structure. This effect is usually neglected in the analysis of spectral parameters. However, 360-MHz spectra of (m-CH$_3$(TPP))Fe^{II} have demonstrated well-defined structure of all resonances due to the formation of atropisomers with slightly different NMR spectra.[30] It is noteworthy that the effect was observed even for the nearly planar structure characteristic for (Por)Fe^{II} complexes.[31]

The presence of the N-CH$_3$ group increases the extent of the steric interactions reinforcing the pyrrole shift differentiation for atropisomers. The recent extensive studies of Walker et al.[32-34] demonstrated the distinct dependence of pyrrole proton shifts on phenyl substitution. The meta substitution (Cl, CH$_3$) caused the multiplet structure of two pyrrole resonances (33.7 and –9.8 ppm at –60 °C). The shape of two downfield resonances remained almost unchanged (Figure 2). The noticeable steric interaction should be expected only for Ph1 and Ph4 phenyls located in the most crowded part of the complex. The multiplet structure of resonances should be observed for H12,13 and H22,33 with much smaller ones for H23,32 protons. As the H12,13 resonance has been assigned on the basis of line width analysis, the 33.7 ppm resonance can be assigned to H22,33 protons.

Ni(N-CH$_3$(o-Cl)TPP)Cl and Ni(N-CH$_3$(o-CH$_3$)TPP)Cl have demonstrated an opposite pattern to the one discussed above with the largest differentiation of two downfield resonances. The syntheses of N-CH$_3$(o-Cl)TPPH and N-CH$_3$(o-CH$_3$)TPPH have to be at least partially stereospecific as the steric hindrance might prevent the formation of atropisomers with o-CH$_3$ groups of Ph1 and Ph4 located on the same side of the porphyrin plane as the N-CH$_3$ one. Such atropisomers are strongly disfavored due to the very short methyl–N-methyl distance estimated to be equal 2–3 Å for protons.[35]

As a result, three atropisomers, i.e. $\alpha^1,\alpha^2,\alpha^3,\alpha^4$, $\alpha^1,\beta^2,\alpha^3,\alpha^4$, and $\alpha^1,\beta^2,\beta^3,\alpha^4$, should dominate in solution.

As the orientation of Ph1 and Ph4 phenyls is well-defined and fixed, the largest spread of pyrrole resonances should be shown by the protons sensitive to the orientation of Ph2 and Ph3 rings, i.e. H23,32 and H42,43, and a smaller spread for H22,33, which is in agreement with the proposed assignment.

Resonance Assignment. Ni(N-CH$_3$(OEP))Cl. All resonances of the Ni(N-CH$_3$(OEP))Cl complex have been assigned on the basis of areas and line width analysis (Figure 5; Table III). The presence of eight methylene resonances is consistent with the expected structure of complexes. Four α-CH$_2$ resonances are expected as the complex possesses a symmetry plane. The out-

Table III. Proton NMR Resonances for Ni(N-CH$_3$(OEP))Cl

assgnt	$(\Delta H/H)^a$	$(\Delta H/H)_{iso}{}^b$	$(\Delta H/H)_{con}{}^c$
	38.95	34.95	30.35
	34.55	30.55	25.95
	23.57	19.57	14.97
α-CH$_2$	18.75	14.75	10.15
	16.43	12.43	7.83
	13.90	9.90	5.30
	11.73	7.73	3.13
	2.95	–1.05	–5.65
	5.37	3.52	0.12
β-CH$_3$	5.02	3.17	–0.23
	4.53	2.68	–0.72
	3.89	2.04	–1.36
meso 1,4	–15.18	–25.40	–35.48
meso 2,3	–20.06	–30.36	–41.82
N-CH$_3$	190.2	194.8	228.6

^{a} In ppm vs. Me$_4$Si at –60 °C. ^{b} Zn(N-CH$_3$(OEP))Cl was used as a diamagnetic reference.[48] ^{c} Dipolar shift contributions were estimated as for Ni(N-CH$_3$(TPP))Cl. Geometric factors were calculated for each α-CH$_2$ and β-CH$_3$ position, and averaged values were considered.

of-plane displacement of the Ni(II) ion renders the α-CH$_2$ protons diastereotopic,[36] which has been demonstrated by the doubling of the α-CH$_2$ resonances to eight. The identity of two meso resonances has been confirmed by the selective deuteration in this position. The line width ratio of meso resonances 1:1.25 is in the very good agreement with the theoretical value 1:1.21. The meso resonances at –15.2 and –20.1 ppm (–60 °C) have been assigned to H1,4 and H2,3 protons.

Variable-Temperature Studies. ^1H NMR spectra of Ni(N-C-H$_3$(TPP))Cl and Ni(N-CH$_3$(OEP))Cl in CDCl$_3$ have been recorded over the accesible temperature range. The complicated temperature dependencies have been observed in both cases. The simple Curie plots gave unrealistic diamagnetic intercepts particularly for pyrrole resonances (0.15, 6.1, and 6.6 and 7.7 vs. 9.0 ppm found for diamagnetic reference). The observed curvature may result from dipolar shift arising from the zfs (vide infra). The instability of complexes precluded the more detailed observation of the phenyl-ring rotation. Some broadening of the respective resonances has been noted at 40 °C.

Analysis of Isotropic Shift. The *meso*-phenyl resonances of paramagnetic TPP complexes have been shown to yield characteristic shift patterns depending on whether the contact shift or dipolar shift dominates.[37] Shift direction alternation of the phenyl ring is characteristic if π-contact shift dominates; the ring proton and methyl protons exhibit shifts of opposite sign for any position. On the other hand, dominant dipolar shifts are characterized by the shifts, the sign and magnitude of which are determined by geometric factor and magnetic susceptibility tensor symmetry and orientation with respect to the molecule.[14,38] The widely used axial symmetry approach in the interpretation of the pseudocontact contribution of TPP complexes[15,16] has to be used with caution in the analysis of Ni(N-CH$_3$(TPP))Cl.

The analysis of isotropic shift and evaluation of dipolar contribution is possible only in an approximate manner. The main magnetic axis was located in the symmetry plane passing through the N1–Ni–N4 atoms and was assumed to be perpendicular to the N2–N3–N4 plane. The atomic coordinates of Co(N-C-H$_3$(TPP))Cl[2] were used. The phenyl rings were rotated to achieve perpendicular position with respect to the N2–N3–N4 plane. The values of calculated geometric factors (GF) and r^{-6} values are collected in Table II.

The observed changes of the direction of phenyl shifts are not compatible with only contact or only dipolar contributions. The contribution of both mechanisms is of comparable size.

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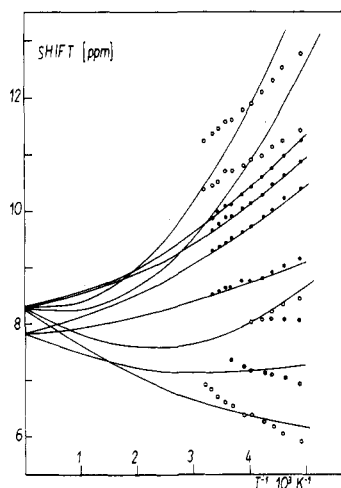(38) Beher, D. V.; Birdy, R.; Mitra, S. *Inorg. Chem.* **1982**, *21*, 386.

Figure 6. Plot of the temperature dependence of the shifts of Ni(N-C-H₃(TPP))Cl (see text): O, ortho; ●, meta; ◐, para.

As a methoxy group is well isolated from the phenyl ring, its isotropic shift has to be dominated by the dipolar mechanism. As the geometric factors were determined for each proton in the complex one can apply the method of spin-isolated nuclei to evaluate the dipolar contribution to isotropic shifts (Table I). The geometric factor of the methoxy group was calculated as an average of geometric factors for six possible rotamers with respect to the $C_4(Ph)$–O bond. Since a full assignment of ortho, meta, and para resonances is not possible, an attempt has been made to obtain a contact shift pattern consistent with the π-delocalization mechanism, i.e. to put the isotropic and dipolar shifts in pairs that would result in comparable values of contact shift for ortho, meta, and para positions, and the sign alternation would be achieved. The alternation of contact shifts after methyl substitution has been shown in this way as well. Only in two cases the deviation from the π-delocalization scheme has been found (*m*-H and *m*-CH₃). It probably results from the sensitivity of these particular positions on the assumptions built in the GF calculations. (The small changes of the susceptibility tensor or phenyl orientations caused the large changes of GF values for *m*-H and *m*-CH₃ under discussion.)

For a high-spin d^8 ion such as Ni(II) the **g** tensor is highly isotropic, which would normally be expected to lead to negligible dipolar shifts.[39] Sizable dipolar shifts can arise as a result of the anisotropy of zero-field splitting (zfs).[40,41] The detailed theory indicates that dipolar shifts arising from zfs have a characteristic T^{-2} dependence for high-spin d^8 ions in contrast to the T^{-1} dependence of the contact contribution to the paramagnetic shift.

Thus, the shift for high-spin Ni(II) can be written in the form

$$(\Delta H/H)_{iso} = \alpha/T + \beta/T^2 \qquad (1)$$

where $\alpha = 2g\mu_B A/(3\hbar\gamma_n k)$, $\beta = (2\mu_B^2(g_\parallel^2 + 0.5g_\perp^2)D/(27k^2))$GF, D = zfs parameter, GF = geometric factor, μ_B = Bohr magneton, g = average value of **g** tensor, A = hyperfine coupling constant, and other terms have their usual meanings.

The equation involves only two parameters and allows determination of them by fitting the temperature-dependent shift data. The procedure allowing α_i and β_i (i.e., A and D) to vary freely gave unacceptable values of these parameters; particularly β_i/β_j ratios were different from the expected values calculated as GF_i/GF_j ratios. In order to reduce the number of variable parameters the β_i values have been calculated for each proton with the dipolar shift of the methoxy (m) group as a standard, $\beta_i = \beta_m GF_i/GF_m$, and the data were fitted only with the α_i parameter.

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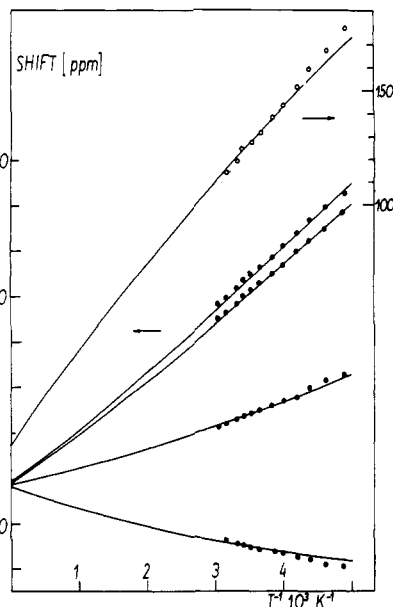(42) Tovrog, B. S.; Drago, R. S. *J. Am. Chem. Soc.* **1977,** *99,* 1203.

Figure 7. Plot of the temperature dependence of the shifts of Ni(N-C-H₃(TPP))Cl (see text): O, N-CH₃; ●, pyrrole.

Even in this model the results were not completely satisfactory with the largest deviations for ortho resonances. However, a very good fit was observed for all meta and H22,33 protons and reasonable one for the rest of pyrroles and N-CH₃ (Figure 6 and 7).

The detailed analysis of temperature dependence of isotropic shift requires the knowledge of the susceptibility tensor as was shown by Mitra et al. for d^5 (TPP)FeCl.[38] Even in the analysis of the (TPP)FeCl data large systematic deviations for ortho resonances from the calculated plot were found, up to 0.5 ppm in the extreme temperatures, i.e. identical with that for Ni(N-CH₃(TPP))Cl discussed in this paper. The choice of a suitable diamagnetic reference especially for the ortho position is usually difficult.[37] Zn(N-CH₃(TPP))Cl shifts used in this work could also be a source of the fitting problems.

Mechanism of Spin Density Delocalization (Porphyrin Ring). The N-alkylated porphyrin ligand forms usually three strong bonds to the metal ion together with one weaker bond between the methylated nitrogen atom and the metal ion. The change toward sp^3 character of N1 has been noted.[2,25,26] The nonplanarity of the macrocycle does not block delocalization of the π bonding.[2] The structural and bond character changes should produce a pronounced influence on the mechanism of the spin density delocalization. The pattern of downfield pyrrole (rings II–IV) and α-CH₂ (attached to these rings) shifts is indicative of the σ delocalization to the H22, H23, and H42 pyrrole protons. This is consistent with the ground state of high-spin Ni(II), which should have two unpaired electrons in the σ symmetry orbitals $d_{x^2-y^2}$ and d_{z^2}.

The large upfield shifts at meso positions indicate the presence of the π spin density due to the M–L π delocalization. This suggest that d_{xz} and d_{yz} orbitals are engaged in extensive M–L back-bonding and that net electron spin density in these orbitals is polarized by the unpaired electrons in $d_{x^2-y^2}$ and d_{z^2}. Both orbitals are connected to d_{xz} and d_{yz} by spin–orbit coupling, which may be a mechanism by which π positive spin density appears at meso-carbon positions. A similar model was discussed in the case of high-spin (TPP)Ni(nitrogen base)₂ complexes.[23]

The isotropic shift of N-methylated pyrrole ring I requires a separate analysis. The downfield N-CH₃ shift results from the direct σ delocalization via three bonds. The direction and magnitude of the shift are close to those reported for a variety of *n*-alkylamine high-spin Ni(II) complexes.[43] The N-methylation changes hybridization of the N1 atom. This fact and the tilt of the N-methyl ring change the geometry of the spin density de-

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localization path as compared to pyrrole rings II–IV. It reduces the σ effect at H12 position to the negligible amount as the mechanism is strongly geometry dependent.[44]

The unpaired spin density is localized on a σ-hybridized N1 orbital, which is not orthogonal to π orbitals of pyrrole ring I. A σ–π overlap within pyrrole ring I will permit the direct transfer of unpaired spin density of the N1 σ pair into the π system without any π M–L bonding.[45]

The 30 ppm difference in the shifts of the H22 and H23 resonances may result from the positive π-spin density delocalized by the porphyrin framework to the C22 carbon but none or relatively small one to the C23 atom. The σ contribution should be similar in both positions. The more detailed theoretical background is lacking in the literature so the semiquantitative analysis of this difference is difficult. A similar shift pattern as this shown by the N-methylated pyrrole ring was proposed for N-methylimidazole ligand coordinated by the amine nitrogen (NCH₃), i.e. large downfield shift of NCH₃ and upfield shift of the H4 proton situated in the position corresponding to the pyrrole proton in NCH₃(TPPH).[42] The contribution of the mechanism proposed in the case of meso protons may also be marked in the π delocalization contribution to isotropic shift of pyrrole protons.

The shifts of α-CH₂ of Ni(N-CH₃(OEP))Cl are slightly confusing. After the separation of the contact shift, it was found that seven of eight resonances have downfield shifts, which is consistent with both proposed spin delocalization mechanisms. The magnitude of the α-CH₂ shift depends on the pyrrole proton shift in the same position.[15] The group of strongly downfield shifted resonances could be assigned to α-CH₂ of pyrrole rings II–IV. The shifts of α-CH₂ (ring I) are smaller as usually observed in the case when the π-delocalization mechanism is only acting.[14,15] The upfield shift for only one component of the diastereotopic pair

(Table III) is probably due to the specific orientation of the ethyl group (preferred in the temperature range studied) as coupling from the α-CH₂ group and pyrrole p_z electron could be accounted by an angular dependence

$$A_{CH_2} = B + B_2 \cos^2 \theta \qquad (2)$$

where θ = angle between the p_z orbital and proton, $B < 0$, and $B_2 > 0$.[46,47] Under the condition $\theta \simeq 0$, the B part would dominate the shift, leading to the upfield contact contribution, but only for one proton as a second one has to be shifted downfield (θ = 120°).

Conclusion

The spectroscopic properties of Ni(N-CH₃(TPP))Cl and Ni-(N-CH₃(OEP))Cl complexes are different in many respects from those observed for their nonmethylated counterparts, i.e. Ni-(TPP)(nitrogen base)₂ and Ni(OEP)(nitrogen base)₂.[23] However, in both systems the σ-delocalization mechanism dominates the isotropic shifts. The N-methylation imposes the large asymmetry that results in the characteristic pattern of pyrrole resonances. Such a pattern can be used as a "fingerprint" of N-methyl substitution in paramagnetic metalloporphyrins. The isotropic shift in Ni(N-CH₃(TPP))Cl is caused by the unpaired electrons on $d_{x^2-y^2}$ and d_{z^2} orbitals, which are responsible mainly for the σ delocalization. Understanding of the spin density distribution mechanism in complexes of N-alkylporphyrins will require further studies with metal ions possessing unpaired electrons on orbitals interacting directly via π bonds.

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Potentiometric and Raman Spectroscopic Study of the Complex Formation of Gallium(III) in KCl–AlCl₃ Melts at 300 °C

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Potentiometric measurements with chlorine–chloride concentration cells and Raman spectroscopic measurements on dilute solutions of GaCl₃ in KCl–AlCl₃ melts at 300 °C give evidence for the formation of GaCl₄⁻ in the basic melts (0.26 < pCl < 3.01). In the acidic melts (pCl > 3.01) the measurements are best explained by assuming the formation of the mixed Ga(III)–Al(III) chloride complex GaAlCl₇⁻ and Ga₂Cl₇⁻. The pK values at 300 °C (based on molar concentrations) for the equilibria (i) GaCl₄⁻ + AlCl₄⁻ ⇌ GaAlCl₇⁻ + Cl⁻ and (ii) 2GaCl₄⁻ ⇌ Ga₂Cl₇⁻ + Cl⁻ were found to be 6.78 ± 0.04 and 6.56 ± 0.11, respectively.

Introduction

In many respects GaCl₃ behaves like AlCl₃. They are both Lewis acids having a strong affinity for chloride ions. Phase diagrams[1] of the MCl–GaCl₃ systems (M = Li, Na, K, Cs) show the existence of the compounds MGaCl₄ and MGa₂Cl₇ (except in the LiCl–GaCl₃ system). Raman spectral[2] and crystal structure[3] studies indicate that solid KGa₂Cl₇ has the constitution K⁺Ga₂Cl₇⁻. Raman spectroscopic measurements by Øye and Bues[4,5] on

CsCl–GaCl₃ melts and by Mascherpa-Corral and Potier[6] on KCl–GaCl₃ melts were explained in terms of GaCl₄⁻, Ga₂Cl₇⁻, and higher polymers of the type Ga$_n$Cl$_{3n+1}$⁻.

Recently Dioum, Vedel, and Trémillon[7] interpreted voltammetric measurements on the KCl–GaCl₃ molten system by the equilibrium

$$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^- \qquad (1)$$
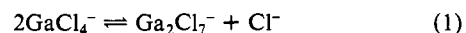
with an autodissociation constant (Ga₂Cl₇⁻)(Cl⁻) of 4.25 mol² kg⁻² at 300 °C.

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