trap via attractive ion/dipole interactions. This is entirely consistent with other complexation properties of this macrocyclic ligand, which forms very stable complexes with sodium and potassium salts in Me_2SO.[17] Despite the fact that nitrogen ligands are generally considered to be relatively soft, this and other hexaaza[18]annulene derivatives form stronger alkali metal complexes than their oxygen analogues. Therefore, Cd^{2+} complexes of other sexipyridine-derived torands[18] would be expected to show similar chemical shifts. This explanation accounts for the chemical shift of the cadmium and the essential absence of nitrogen ligand effect on that shift. Moreover, the nitrogen-cadmium distance differentiation has analogy in tin complexes where the metal-ligand atom distances are determined by the ionic Coulombic terms rather than by formal bonding distances.[36]

The cadmium shielding tensor of **1** is necessarily nonaxial since the metal ion site symmetry is lower than that of the macrocycle which at best could have a 2-fold rotation axis.[37,38] Based upon detailed studies involving single crystals of cadmium complexes coordinated exclusively by oxo ligands[5,6] and also mixed N-O and S-O complexes,[7] it has been found that the most shielded tensor element is oriented orthogonal to the longest Cd-ligand bond. From the X-ray structure of **1**, the longest Cd-ligand bonds occur within the pseudoplane containing the six nitrogen atoms. Hence the most shielded tensor element in **1** should be oriented most nearly orthogonal to the pseudoplane containing the metal ion and six nitrogens. The two remaining shielding tensor elements are found, experimentally, to have similar magnitudes, and, therefore, are expected to have similar orthogonal environments.[6] We, therefore, assign the perpendicular tensor elements to lie in the pseudoplane of the ligand. This assignment is consistent with the ^{113}Cd powder pattern depicted in Figure 2a. The fact that all the tensor elements are more shielded than those of cadmium perchlorate confirm the necessarily weak in-plane and axial covalent interactions for this complex.

The unusual ^{113}Cd NMR spectral properties of this cadmium complex and the stability data have led to an unusual situation. The cadmium ion is weakly covalently ligated and yet strongly bound. We propose an interpretation based upon inefficient covalent Cd-N bonding, manifested by the long Cd-N bonds in **1**, that arises because of the nonoptimal size of the macrocycle cavity. This interpretation is derived from observations of the ^{113}Cd NMR spectra but it can be applied to other systems where such spectral data are not available. In this vein these data and conclusions offer an attractive rationale for the equally strong binding of Ca^{2+} ions in related torands. The data clearly contrast with the expectation that Ca^{2+} would not bind in such systems, in view of the absence of known covalent bonding between Ca^{2+} and N donors. Finally, this kind of bonding avoids the inconsistencies of models based on hard/soft acid base theory and may prove useful for finding other examples.

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Bimodal Inclusion of Nitroxide Radicals by β-Cyclodextrin in Water As Studied by Electron Spin Resonance and Electron Nuclear Double Resonance[1]

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Abstract: Bimodal inclusion of some nitroxide radicals in aqueous solutions of β-cyclodextrin has been detected by electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectroscopy. Inclusion complexes in which nitroxide radicals reside in the cavity of β-cyclodextrin in two different ways are observed. The assignments are based on differences in hyperfine splittings (hfs's). Three nitroxide radicals, diphenylmethyl *tert*-butyl nitroxide (**1**), α-methylbenzyl *tert*-butyl nitroxide (**2**), and α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide (**3**), have been used as spin probes. In each case, both the nitrogen and β-hydrogen hfs's change in magnitude upon inclusion. On the basis of the characteristic change of hfs upon inclusion, the direction of incorporation is assigned. The association constants, $\Delta H°$, and $\Delta S°$ are determined from the concentration and temperature dependences of the ESR intensity of each species. The nature of the interaction between β-cyclodextrin and the functional group in the probe is discussed.

Inclusion phenomena by various kinds of molecular receptors have attracted a great deal of attention as a step toward the understanding of the mechanism of molecular recognition.[2] Cyclodextrin (CD) is at the origin of the study of water-soluble molecular receptors since it has a relatively hydrophobic cavity that can include various organic molecules.[3,4] In CD inclusion complexes the structure and the site of inclusion has been studied by using various spectroscopic techniques.[2] X-ray diffraction studies have shown a definitive structure for the CD inclusion complex. Although some indication of statistical disorder of small

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substrates in the cavity is recognized in some cases,[3] the crystal structure is the ultimate result of the balance of many inter- and intramolecular interactions. Thus, it is sometimes difficult to correlate the crystal structure to that of a solution structure of the same complex since the interactions with solvent molecules cannot be taken into account.

Although the possibility of CD including substrates from two different directions (i.e., bimodal inclusion) has been suggested or implied by many investigators,[5] no appropriate method has been available to detect this possibility. A study of the driving forces controlling bimodal inclusion could give helpful clues for the understanding of the recognition of the whole substrate as well as a given group in the same molecule. Since it is not likely that the crystals of inclusion complexes that include the same substrate in two different directions can be isolated, the detection of bimodal inclusion is probably limited to the solution phase.[6]

NMR has been a major tool for the study of CD inclusion complexes in solution.[2,5,7] The structure of the complex in solution and the role of charge and the direction of penetration have been extensively studied for substituted aromatic molecules. However, NMR has not been able to explicitly distinguish included species from free species because the lifetimes of both the free and included states are too short to be observed as individual signals. Therefore, the structure deduced of the inclusion complex is that of the most probable possibility resulting from dynamic averaging of many possible dispositions of the guests. ESR has a faster time scale than NMR, and thus it is not surprising that spin probes in CD solutions show two different ESR spectra corresponding to the included and the free species.[8]

Recently, by using new spin probes we have reported the observation of *two* included species in addition to the free species in β-CD aqueous solution, and bimodal inclusion was suggested.[1] A nitroxide (aminoxyl) radical bearing a β-hydrogen is a suitable probe for the detection of differences in microscopic environments, because the β-H hfs functions as a detector of the distortion of the probe upon inclusion while the hfs of nitrogen acts as a detector of the polarity of the cavity of CD. In this report, bimodal inclusion as illustrated below has been studied in detail by using three different nitroxides as probes. These three probes have substituents of different sizes and thus show characteristic behavior upon inclusion. More evident proof of the presence of two kinds of complexes is provided and the association constants and standard enthalpy and entropy of the formation of the complex are given.

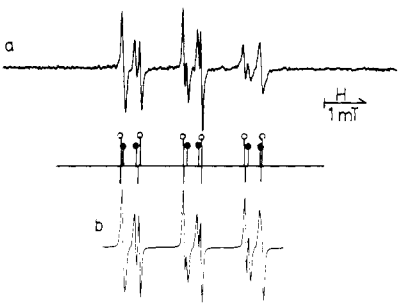
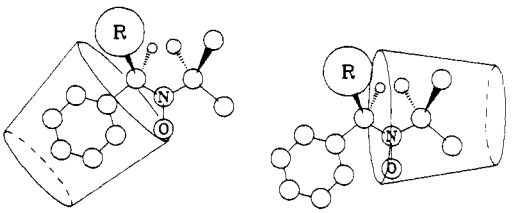
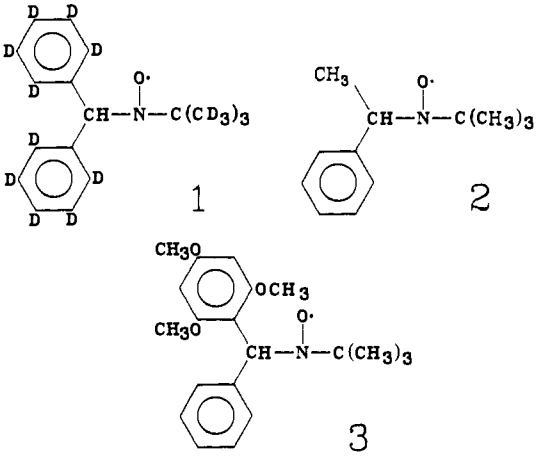


Figure 1. (a) ESR spectrum of **1** in water in the presence of 1×10^{-2} M β-CD at 290 K. Stick spectrum shows ESR line positions for *tert*-butyl-in complex (○), phenyl-in complex (●), and free species. (b) Computer-simulated spectrum of a. Parameters used for the simulation are listed in Table I.



Results and Discussion

Three different nitroxide probes were synthesized, and the ESR spectra were obtained in the presence of various concentrations of β-CD in water. Diphenylmethyl *tert*-butyl nitroxide (**1**), α-methylbenzyl *tert*-butyl nitroxide (**2**), and α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide (**3**) have characteristic behavior upon inclusion, depending on the size of the substituents. A common change in the ESR spectral features upon addition of β-CD is the appearance of two new spectral species in addition to the free species. The dependence of the ESR intensity on the β-CD concentration and on the temperature strongly suggests that the two newly produced species are both inclusion complexes.



The probes have three ESR spectral parameters which are sensitive to the change of environment, i.e., β-H hfs, N hfs, and *g* value. The N hfs and *g* value can detect the polarity around the nitroxide group. In apolar media the N hfs becomes smaller and the *g* value simultaneously becomes larger; thus the center

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Table I. hfs Constants of β-CD Inclusion Complexes of Nitroxides **1–3** in Water at 290 K[a]

nitroxide		$A_{\beta\text{-H}}$/mT	A_N/mT	Δg/mT[d]
1	free	0.422	1.599	0
	phenyl-in	0.288	1.565	0
	tert-butyl-in	0.422	1.541	−0.012
2	free	0.361	1.651	0
	phenyl-in	0.408	1.643[b]	0
	tert-butyl-in	0.466	1.607[b]	−0.012
3[c]	free	0.952	1.632	0
	phenyl-in	0.581	1.588	0
	tert-butyl-in	1.189	1.580	−0.012

[a] Error is ±0.005 mT. [b] By ENDOR at 300 K. [c] In 2.5 vol % ethanol aqueous solution. [d] Relative *g*-value shift from center of spectrum of free probe at X-band. Δg = 0.01 mT corresponds to the *g*-value shift of 1.4×10^{-4}.

Table II. Association Constants, $\Delta H°$, and $\Delta S°$ of β-CD Inclusion Complexes of Nitroxides **1–3**

nitroxide		K_a(290 K)	$\Delta H°$/ kcal M^{-1}	$\Delta S°$/ cal K^{-1} M^{-1}
1	phenyl-in	$(1.2 \pm 0.1) \times 10^3$	−6.7 ± 0.8	−5 ± 4
	tert-butyl-in	$(1.8 \pm 0.2) \times 10^3$	−8.7 ± 1.0	−8 ± 4
2	phenyl-in	$(1.0 \pm 0.1) \times 10^3$	*a*	*a*
	tert-butyl-in	$(1.6 \pm 0.2) \times 10^3$	*a*	*a*
3[b]	phenyl-in	$(0.7 \pm 0.1) \times 10^2$	−6.6 ± 0.7	−14 ± 5
	tert-butyl-in	$(5.7 \pm 0.6) \times 10^2$	−8.9 ± 1.0	−7 ± 6

[a] Accurate determination of the relative intensity is difficult due to the overlap of ESR lines. [b] In 2.5 vol % ethanol aqueous solution.

of the spectrum shifts to lower field from that observed in polar media. A change in the environment indirectly affects the conformation of the probe. The β-H hfs is a sensitive function of the dihedral angle between the C–β-H and the unpaired electron orbital. The magnitude is expressed by the Heller–McConnell equation:[10]

$$A_{\beta\text{-H}} = (B_0 + B_2 \cos^2 \theta)\rho \qquad (1)$$

where B_0 and B_2 are constants, θ is the dihedral angle, and ρ is the spin density on the nitrogen atom. It should be stressed that the sensitivity to a small change in θ is proportional to $d(A_{\beta\text{-H}})/d\theta = B_2 \sin(2\theta)$, which has a maximum at $\theta = 45°$. By using these spectral and equilibrium parameters, inclusion complexes in which the probe resides in the cavity in two different ways, i.e., phenyl-in complex and *tert*-butyl-in complex, are identified.

Diphenylmethyl *tert*-Butyl Nitroxide (1). In order to get clearer ESR spectral separation of the two included species, deuterated **1** (**1**-d_{19}) was synthesized. The ESR spectrum of the inclusion complex of β-CD with **1** and **1**-d_{19} has been described elsewhere.[1] The detailed analysis is presented here. The ESR spectrum of **1**-d_{19} in water in the presence of 1×10^{-2} M β-CD is shown in Figure 1a. This spectrum shows the presence of two radical species each having six lines due to one nitrogen and one hydrogen nucleus. These components are assigned to two included probes, and the ESR spectrum can be reproduced by computer spectral simulation using hfs constants listed in Table I. The simulated spectrum is shown in Figure 1b. Upon decrease of the β-CD concentration, the free (nonincluded) species appears in the spectrum. By using the area intensity of the ESR spectrum of each species the association constants are determined and listed in Table II. The standard enthalpy and entropy ($\Delta H°$ and $\Delta S°$) of the formation of the complexes are calculated on the basis of the temperature dependence of the association constants. These are also listed in Table II.

α-Methylbenzyl *tert*-Butyl Nitroxide (2). The ESR spectrum of this radical in the presence of β-CD shows an asymmetric line shape (Figure 2a). The spectrum was computer simulated with the superposition of two spectra of slightly different N and β-H hfs's. When the concentration of β-CD is decreased, the ESR lines from the free species appear. The dependence of these spectral features on the concentration of β-CD is shown in Figure 2.

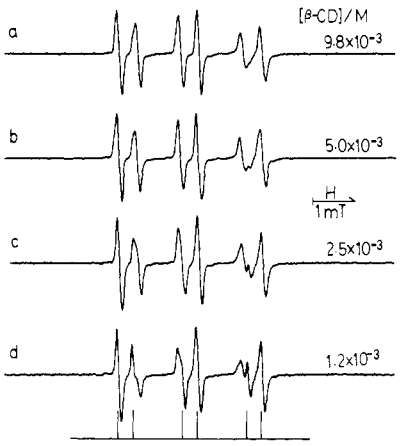

Figure 2. ESR spectra of **2** in water in the presence of various concentrations of β-CD at 290 K. Concentrations of β-CD are (a) 9.8×10^{-3} M, (b) 5×10^{-3} M, (c) 2.5×10^{-3} M, (d) 1.2×10^{-3} M.

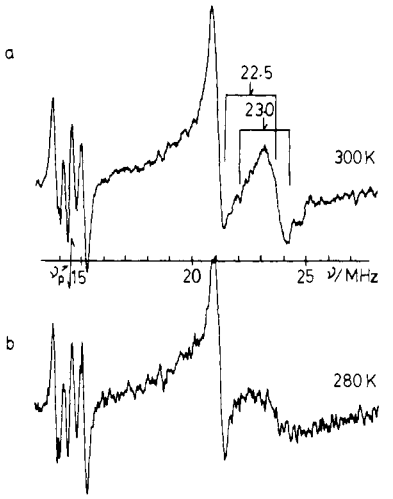

Figure 3. ENDOR spectra of **2** in water in the presence of 9.8×10^{-3} M β-CD. The external field was fixed at the third ESR line from the low field. Incident microwave power and rf power are 100 mW and 150 W, respectively. Signals are accumulated for 200 times. (a) At 300 K. The two pairs of lines centered at 22.5 and 23.0 MHz are the N ENDOR lines, and the single line at 21.0 MHz is the high-frequency line of the β-H ENDOR doublet. Both resolution and the signal-to-noise ratio become worse at higher temperatures. (b) At 280 K.

The solubility of the inclusion complex of **2** is higher than that of **1** and **3** and the ENDOR spectrum could be obtained. The ENDOR spectra obtained at two different temperatures are shown in Figure 3. The β-H ENDOR peak was not resolved into two lines; however, the N ENDOR line shows the presence of two species as shown in Figure 3a. Additional ENDOR peaks from methyl and other groups are also detected. Analysis of the ENDOR spectrum provides support for the conclusions reached from the ESR spectrum simulation. The ENDOR hfs constants are listed in Table I. The association constant is calculated from the dependence of the ESR spectrum on the β-CD concentration and is given in Table II.

There is a reason for the small differences in hfs found in the complexes of **2**. Molecular models show that the β-CD cavity is large enough to contain the α-methylbenzyl group. Thus, the depths of inclusion from two directions may not be different enough for clear separation of the two species.

α-(2,4,6-Trimethoxyphenyl)benzyl *tert*-Butyl Nitroxide (3). This probe shows well-separated ESR spectra for the two included species in addition to the free species (Figure 4a). There are two reasons for the good spectral separation of the two included species: (a) the large volume of the trimethoxyphenyl group helps to

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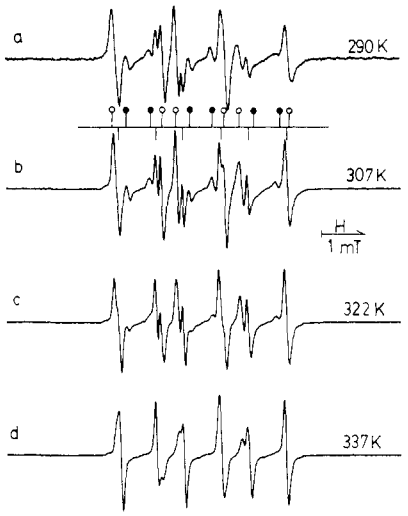

Figure 4. ESR spectra of **3** in water in the presence of 9.8×10^{-3} M β-CD. (a) At 290 K. (b) At 307 K. (c) At 322 K. (d) At 337 K. Stick spectrum shows the line positions for *tert*-butyl-in complex (○), phenyl-in complex (●), and free species.

intensify the distortion of the conformation upon inclusion of the phenyl group and (b) the differential sensitivity of the β-H hfs to unit change in dihedral angle is larger than in **1** and **2** (i.e., the dihedral angle θ is closer to 45°).

The association constants, $\Delta H°$, and $\Delta S°$ were determined based on the dependence of the ESR signal intensity on the temperature and the concentration of β-CD. The temperature dependence of the ESR spectra of the complex of **3** is shown in Figure 4 and values are listed in Table II.

Assignment of the Direction of Inclusion. There are supporting reasons for the conclusion that the two species appearing in the ESR spectra in the presence of CD are both included ones: The slowing down of the tumbling motion, which is revealed by the weaker intensity of the high-field ($M_1 = 1$) line, happens to the same degree for both species. It is thus not likely that association of the probe with *two* β-CD molecules occurs in one of these cases. In addition, the association constant determined at one concentration with the assumption of a one-to-one complex at certain CD concentrations can reproduce ESR spectra at other CD concentrations.

Since β-CD has a torus shape, there are four possible ways of inclusion of a nonsymmetric molecule, i.e., head first and tail first from either the wider or the narrower ends. However, the average inside diameter of the narrower end of the β-CD is estimated to be approximately 5 Å by space-filling models.[11] Thus, the inclusion of the *tert*-butyl or the phenyl group from the narrower end is not likely to occur.

The characteristic difference in the hfs of the two included species is that one mainly decreases its N hfs from that in water while the other changes its β-H hfs. The inside diameter of the wider end of the β-CD cavity is known to be 6.4 Å and is not large enough to include the probe from the phenyl side as far as the NO group if another substituent attached to the α-carbon is large. As is deduced from the result of the inclusion of di-*tert*-butyl nitroxide,[8j] the penetration of **1**, **2**, and **3** from the *tert*-butyl side can occur until the substituents on the α-carbon hinder further insertion. Consequently, the NO group enters the cavity and shows a smaller N hfs and a larger g value than in water due to the nonpolar environment of the inside of the cavity. The inclusion from the phenyl side is blocked by the other bulky group on the α-carbon, resulting in a change mainly in β-H hfs. On this basis the species shown in Table I are assigned. However, the β-H hfs of the phenyl-in complex is smaller than that of *tert*-butyl-in complex. A possible reason is that **2** is the only case in which both substituents on the α-carbon, i.e., phenyl and methyl, are included so that the steric hindrance occurs in a different way from **1** and **3**. Also the diffference of N hfs in **3** does not seem to help the assignment. Support for this assignment can be obtained by introducing a different functional group instead of the phenyl group in **3**.[12] Then the larger β-H hfs assigned to the *tert*-butyl-in complex stays relatively unchanged (1.1–1.2 mT), while the smaller β-H hfs is a sensitive function of the volume of the adding group.

Association Constants, $\Delta H°$, and $\Delta S°$. For all three probes the association constants of the *tert*-butyl-in complexes are larger than those of the phenyl-in complexes. As is clear from the change of hfs's upon inclusion, the *tert*-butyl-in complex penetrates more than the phenyl-in complex. This leads to an increase in the contact area between the cavity interior and the probe. The association constant is a sensitive function of the relative size of the cavity and the probe. The association constants of the α-CD complexes of **1** are smaller than those of β-CD complexes by 2 orders of magnitude.[1] The outside diameter of the *tert*-butyl group is smaller and more flexible than that of the phenyl group. This appears to be one of the reasons for the larger association constant of the *tert*-butyl-in complex. A bulky group on the α-carbon decreases the association constant, as revealed in the case of **3**.

There have been a large number of reports dealing with the nature of the interaction between the probe and the CD cavity;[13] however, here the differences in $\Delta H°$ and $\Delta S°$ are examined to see whether there is an effect on the distortion of the probe during inclusion. Although the thermodynamic constants for the equilibrium in the present system do not show any anomalies compared to those reported for other β-CD complexes,[3] the $\Delta H°$s of both complexes are negative and the absolute value is larger for the *tert*-butyl-in complex. This means that the enthalpic driving force for the *tert*-butyl-in complex is larger than that for the phenyl-in complex. If one assumes that the enthalpy of removal of the inner water and the stabilizing energy upon incorporation of the probe are the same, then the difference in $\Delta H°$ between *tert*-butyl-in and phenyl-in complexes must come from the difference in the degree of distortion of the probe. It is reasonable that the phenyl-in complex has more hindrance, resulting in the loss of some enthalpic driving force for the inclusion. The difference of the internal energy between rotational isomers is known to be a few kilocalories per mole; thus the difference in the two complexes is reasonable as caused by the distortion of the probe.

Experimental Section

Preparation of Spin Probes. Nitroxides **1**-d_{19}, **2**, and **3** were synthesized by using the following nitrone spin traps available in these laboratories: phenyl-*N*-*tert*-butylnitrone (PBN), perdeuterated PBN except for the β-H (PBN-d_{14}),[14] and (2,4,6-trimethoxyphenyl)-*N*-*tert*-butylnitrone (MO_3PBN).[15] A typical procedure for the preparation of the spin probe is as follows: to 1 mL of a 10^{-2} M benzene solution of a spin trap was added the equivalent amount of an ether solution of phenyllithium or methyllithium under nitrogen atmosphere. The same volume of water was added slowly, and the organic layer was washed by 1 mL of water twice. The organic portion was separated and was bubbled with oxygen gas. The solvent was purged by nitrogen gas to obtain a dry residue. Water was added to make up a 2-mL stock solution of the spin probe. The concentration of the probe was estimated by the ESR intensity. In the case of probe **3**, ethanol was used for the solvent of a stock solution. Phenylmagnesium bromide-d_5 was synthesized from bromobenzene-d_5 of 99% isotopic purity and used to obtain **1**-d_{19}.

A stock solution of 1.0×10^{-2} M β-CD was used to make up the solutions of desired concentration.

Materials. β-CD, phenyllithium, methyllithium, and bromobenzene-d_5 were obtained from Aldrich and were used as received. Water was distilled and Millipore treated.

Measurements. A Bruker ER 200D SRC ESR spectrometer equipped with an ENDOR accessory was used for the ESR and ENDOR measurements. Sample solutions were prepared in a Pyrex tube of 1-mm i.d. and 2-mm o.d. The field modulation width was less than 0.032 mT, and

(11) The entrance diameter of the narrower end may change due to the conformation of six CH_2OH groups on the rim.

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the incident microwave power was kept less than 10 mW (-13 dB) for the ESR measurement. The temperature was controlled by a Bruker VT4211 variable-temperature unit.

Determination of Association Constants, $\Delta H°$, and $\Delta S°$. Association constants were determined by assuming the following equilibrium:

$$R + CD \rightleftharpoons R\text{-}CD$$

where R, CD, and R-CD denote the probe, the cyclodextrin, and the inclusion complex, respectively. Thus the association constant is

$$K_a = [R\text{-}CD]/[R][CD] = (r_1/r_2)(C - R_0 r_1/(r_1 + r_2))^{-1}$$

whwere R_0 and C denote the initial concentrations of R and CD, and r_1 and r_2 show the relative concentrations of included and nonincluded species, respectively. R_0 was estimated to be less than 10^{-4} M from ESR intensity, which is much smaller than C. Thus, K_a is calculated by using $K_a = (r_1/r_2)/C$. The relative concentrations were determined by the area intensity measured from the spectrum simulation. Due to the difficulty in exact fitting of the simulated spectrum to that of observed, the maximum error estimated for r_1/r_2 is ±10%.

The temperature dependence of the association constants was observed from 290 to 340 K at every 10 K. $\Delta H°$ and $\Delta S°$ were determined by using a Van't Hoff plot of K_a at these temperatures.

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Ruffling of Nickel(II) Octaethylporphyrin in Solution

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Abstract: Nickel(II) octaethylporphyrin (NiOEP) plays a central role in studies of the molecular properties of tetrapyrroles and tetrapyrrole-containing enzymes. NiOEP in noncoordinating solvents is found to be a mixture of planar and nonplanar, ruffled species. At 77 K in frozen solutions, the S_4 ruffled form is more prominent than at room temperature. The ruffled form is most prominent for laser excitation to the red of the Soret absorption maximum, suggesting that the ruffled form has a red-shifted Soret band. The presence of multiple forms coexisting in solution requires that normal coordinate analyses based on NiOEP spectra be reexamined.

Nickel(II) octaethylporphyrin (NiOEP) plays a central role in studies of the molecular properties of porphyrins and porphyrin-containing enzymes. NiOEP's importance stems from its use in isotopic substitution work for vibrational analysis of porphyrins[1-3] molecular orbital calculations,[4] X-ray crystallographic structural studies,[5-7] and many structural studies using a variety of spectroscopic techniques.[8] These fundamental studies have had a significant influence on the development of our understanding of metalloporphyrin structure and bonding. The work with the nickel derivative has taken on added significance with the recent discovery of an enzyme (methylreductase) that contains a nickel tetrapyrrole as a prosthetic group.[9]

One aspect of porphyrin structure that is of current interest is the propensity for forming nonplanar structures. These nonplanar ruffled, domed, or flexed conformations may influence many chemical and photochemical properties of porphyrins in biological reactions. Specifically, nonplanar conformations have been proposed to play a role in reactions catalyzed by vitamin B_{12},[10] in the function of cofactor F_{430} in methylreductase,[11] and in the photophysics of tetrapyrrole pigments of photosynthetic reaction centers.[12]

Nickel octaethylporphyrin is known to crystallize in three dramatically different structures, one of which is nonplanar.[5-7] Consequently, NiOEP again provides an interesting test case for studies of nonplanar porphyrin macrocycles. Two of the NiOEP structures are planar triclinic forms (here designated A and B),[7] and the third is a ruffled tetragonal form. The most striking difference between the triclinic and tetragonal forms is the pronounced nonplanarity of the macrocycle in the tetragonal form. The methine bridge carbons are 0.5 Å out of the mean macrocycle plane. There is a marked S_4 symmetry ruffling of the macrocycle wherein adjacent pyrrole rings are tilted in opposite directions with respect to the mean plane of the pyrrole nitrogens. The ruffling effectively reduces the molecular symmetry from D_{4h} to D_{2d}. The angle between adjacent pyrrole planes is 32.8° for the tetragonal structure, but only 2.1° for the triclinic A structure.[5]

Single-crystal resonance Raman spectra clearly distinguish among the three crystalline forms.[7,13] In particular, differences in the frequencies of the Raman core-size (center-to-nitrogen-(pyrrole) distance) marker lines are observed.[13] Further, previous resonance Raman results have shown that the frequencies of the Raman core-size marker lines of NiOEP in noncoordinating solvents are closest to those of the Raman spectrum of the triclinic forms, indicating that NiOEP is planar in solution.[13]

We present new resonance Raman spectra of NiOEP obtained in noncoordinating solvents at 295 K and at 77 K, using a variety of excitation wavelengths near resonance with the Soret absorption

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